The Pennsylvania State University

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FABRICATION OF WEARABLE MULTIFUNCTIONAL SENSORS ON BIODEGRADABLE, STRETCHABLE, AND 3D COMPLICATED SURFACES

A Dissertation in

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by

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ABSTRACT

Skin-integrated, wearable electronics have attracted significant attention because of their unique role from preventative monitoring and diagnostic confirmation to convenient therapeutic options. The ultimate application of these bio-integrated devices for practical and convenient applications hinges on the seamless integration of on-body sensors. Multifunctional on-body sensors can precisely and continuously monitor the health conditions of the human body, whereas the wireless transmission modules can wirelessly power up the sensors and transmit the data generated from them to the cloud for the healthcare professionals. Conventional electronics are mainly fabricated on rigid and planar substrate, which is incompatible with the soft and complicated topography of human skin. To achieve successful application of electronics on human skins, this thesis demonstrates various strategies that can be used to build wearable multifunctional circuits.

Biodegradable substrates from natural sources have gained broad interest due to the advantages of being biodegradable, recyclable, sustainable, and cost-efficient. More importantly, a strong adhesion between the biodegradable substrates and human skin can be achieved through a partial dissolution and softening of the substrates with the presence of water. As an alternative biodegradable material, galactomannan has direct relevance to the emerging biodegradable or transient electronics. Temperature sensor, electromyogram (EMG) sensor, and electrocardiogram (ECG) sensor have been fabricated on a thin biodegradable galactomannan film to fabricate a skin-attachable health monitoring device. Such a biodegradable multifunctional sensor pad is able to monitor body temperature, muscle activity, and heart beat rate in a real time manner.

Soft and stretchable silicone elastomers such as polydimethylsiloxane (PDMS), Ecoflex, and Silbione, are also widely used as substrates for wearable electronics. Non-stretchable Electronic components can be integrated onto silicone elastomers substrate with properly designed structure or layout to achieve stretchability. The commonly used stretchable structures in wearable electronics include wrinkled structures from a pre-strain strategy, island-bridge layouts or serpentine interconnects, strain isolation layer, and their combinations. The stretchable multifunctional sensor pad is then able to accommodate the strain of human skin induced by body motions. Two types of stretchable gas sensor based on molybdenum disulfide@reduced graphene oxide (MoS₂@rGO) and laser-induced graphene (LIG) are built for on-skin detection of NO₂ as a demonstration. The good stretchability of the gas sensors enables accurate reading of the ambient NO₂ level, even the sensors are stretched.

Finally, the thesis presents a new fabrication method for constructing electronics on a 3D complicated surface. Deployment of functional circuits on a 3D freeform surface is of significant interest to wearable devices on curvilinear skin/tissue surfaces or smart Internet-of-Things with sensors on 3D objects. A new fabrication strategy that can directly print functional circuits either transient or long-lasting onto freeform surfaces by intense pulsed light-induced mass transfer of zinc nanoparticles (Zn NPs) is proposed. The intense pulsed light can locally raise the temperature of Zn NPs to induce evaporation. Laminating a soft semi-transparent polymer film with Zn NPs conforming to a 3D surface and expose the assembly to intense pulsed light can be obtained with the placement of shadow mask between the Zn NPs and the 3D surface. Immersing the Zn patterns into a copper sulfate or silver nitrate solution can further convert the transient device into a long-lasting device with copper or silver.

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Chapter 1

Statement of Purpose and Thesis Organization

1.1 Statement of Purpose

Traditional sensors are mainly fabricated through vacuum-based technologies such as chemical vapor deposition or physical vapor deposition with the help of either shadow mask or photolithography. Most of the traditional sensors are bulky, rigid, and imcompatible with the soft human tissues. How to build multifunctional sensors onto human skin to achieve wearable sensors is a hot topic in recent decade due to the promising outlook of werable sensors in various applications, such as health condition monitoring, motion detection, and early diagnosis of diseases. Many methods have been proposed to make sensors stretchable to accommodate the deformation from human motion. Notable examples includes: buckling structure induced by prestrain, island-bridge layout, and strain isolation layer. However, many fabrication methods are complicated and not cost effective. As a materials scientist, I start to think: how to build the wearable electronics with new fabrication methods that have commercialization potential with low cost and maintain their high performance at the same time. Especially for wearable sensors that are able to detect either important biological signals from human body or biomarkers that may be related to the health of human.

Another thought comes from the concern of the constantly accumulating of electronics wastes and medical wastes. Building wearable electronics that can be degraded into nonhazadous products can effectively solve the problem. The utilization of water soluble metals such as zinc, tungsten, or molybdenum as conductors and the utilization of water soluble substrates such as polyvinylalchohol, poly (lactic-co-glycolic acid), or carboxymethyl cellulose have been successfully demonstrated to build transient electronics including resistors, capacitors, and antennas. The use of transient wearble sensors can achieve goals that can't be achieved by traditional electronics. For example, implantable medical devices or skin attachable devices that remain functional for an engineered time span with out the concern of retrieval.

Finally, directly building electrics onto a complicated surface remains challenging yet may bring exceptional opportunites for wearable electronics. Though several methods have been proposed to address this challenge such as omnidirectional printing, aerosol jet printing, and adaptive printing, the fabrication requires complicated programming and time consuming. Inspired by the evaporation and condensation of zinc from zinc nanoparticles induced by laser scanning, we believe intense pulsed light with proper parameter setting can achieve similar phenomenon. With the help of soft shadow mask attachable to non-flat surface, such phenomenon can therefore be utilized to construct transient electronics on 3D complicated surface. Such method enables direct circuit printing on arbitrary objects and holds promising outlooks for the applications of Internet-of-Things.

1.2 Thesis Organization

The thesis was constructed with four main topics focusing on the design, fabrication, and characterization of transient on various types of target substrates.

Chapter 2 discusses the building of a tranent multifunctional sensor pad capable of onskin monitoring of vital biological signals. The synthesis of a new type of water soluble substrates, the fabrication of transient temperature sensor, biopotential sensor, the performance analysis of the multifunctional transient sensors, and the water dissolution behavior of the transient electronics are presented.

Chapter 3 presents the development of a stretchable gas sensor capable of sensing NO2 at room temperature with a fast response/recovery rate. The synthesis of the molybdenum@reduced graphene oxide sensing materials, the characterization of the sensing material, the low-cost fabrication method of the stretchable gas sensor, and the evaluation of the sensor performance are discussed in details.

Chapter 4 further describes the construction of a stretchable gas sensing platform with self-heating capabilities. The design and fabrication of the gas sensing platform, the examination

of the self-heating function, and the analysis of the gas sensing performance are presented.

Chapter 5 discusses the method of directly building electronics on a 3D complicated surface. The effect of various process parameters, the characterization of the resulted circuits, and demonstrations of potential application of the fabricated sensors are discussed.

Finally, Chapter 6 summarizes the thesis, provides on-going research, and proposes future research directions.

Chapter 2

Fully Water-soluble, High-performance Transient Sensors on a Versatile Galacomannan Substrate Derived from the Endosperm

* The contents in this section have been pulished as Yi, N., Cheng, Z., Yang, L., Edelman, G., Xue, C., Ma, Y., Zhu, H. and Cheng, H., 2018. ACS applied materials & interfaces, 10(43), pp.36664-36674.

2.1 Introduction

As rapid technological advances have led to a significant decrease in the lifetime of consumer electronics, an ever-growing number of electronic items are ending up in landfills (a total electronic waste of \sim 3.2 M/year in the US ¹⁻²). To address such long-standing challenge, it is of increasing interest to explore biodegradable materials for device fabrication, where the electronic systems disappear at controlled rates with environmental-benign end products when exposed to water. For instance, one can use an electronic component as a temporary monitor in the environment and allow it to safely dissolve on its own without the need for recollection.³⁻⁵ This ability opens a wide range of applications from diagnostic/therapeutic implants ⁶⁻¹³ to permanent destruction of hardware for data security.¹⁴⁻¹⁵

Certain applications could, however, benefit from the utilization of natural renewable biomaterials as the substrate, in which the disposed devices could be recycled and further used in the environment (or even in the human body). Representative examples of materials with natural origin include gelatin,¹⁶ shellac,¹⁷ silk,¹⁸ rice paper, and biodegradable cellulose nanofibril.¹⁹ In comparison to the protein-based material such as gelatin and fibroin that consist repeating units of amino acids, the galactomannan is a polysaccharide-based biomaterial associated with a simpler, greener, and more energy efficient extraction process.^{5, 17} In addition, the galactomannan film exhibits a relatively good mechanical property and a certain degree of flexibility, whereas the gelatin and fibroin films are usually brittle, due to the rigid partial double bond in the peptide chain resulted from the polar groups (i.e. C-N bond in the protein macromolecular).²⁰⁻²¹ Although biodegradable wood-derived polymers enable paper-based

electronics, the large surface roughness of regular paper at micrometer scale often triggers device failure.²² As an alternative, nanopaper made from nanocellulose (nanofiber or nanocrystal) has been explored for electronics fabrication.²²⁻²⁸ However, nanocellulose extraction process is typically associated with high energy and water consumption. The energy input to produce cellulose nanofiber is between 20000-30000 kWh/t.²⁹ Meanwhile, the chemicals used to prepare nanocellulose, such as (2,2,6,6-tetramethylpiperidine-1-yl) oxidant (TEMPO) for cellulose nanofiber preparation and 98 % H2SO4 for cellulose nanocrystal preparation, are toxic, corrosive, and costly. In addition, the cellulose nanopaper is not shape-stable in organic solvents, which is a big challenge for the device fabrication in organic solvents and indeed impedes its widescale industrial applications. The aforementioned challenges also hold true for other resorbable biomaterials that have been explored in the initial demonstration of transient electronics.

The central focus of transient electronics has been on the exploration of various materials toward a functional device. Similar to conventional circuits, critical components of transient electronics also include semiconductors, conductors, and insulators. Rapid developments of transient electronics have nucleated on a recent discovery ³⁰ that single-crystal silicon can undergo hydrolysis to dissolve in biologically relevant conditions, i.e., body temperature and near neutral pH levels. Additional inorganic semiconductors, a variety of transient metals have been studied,³² including Mg, Zn, Fe, Mo, and W. Biodegradable insulators that serve as passivation and encapsulation in microelectronics are also critical for the operation of the device.¹¹ In addition, they can serve as the substrate for the entire transient device to reside. Many early demonstrations ³³⁻³⁴ relied on synthetic biodegradable polymers or materials with a natural origin. Due to tunable properties, a wide range of synthetic biodegradable polymers ³⁵⁻³⁷ have been developed, including polyfluorene (PF),³⁸ poly(vinyl alcohol) (PVA),³³ polycaprolactone (PCL), and poly(lactic-co-glycolic acid) (PLGA), a copolymer of polylactic acid (PLA) and polyglycolic acid (PGA).³⁹ However, to the best of our knowledge, no prior

study has reported the use of galactomannan derived from the seeds of Leucaena leucocephala as a water-soluble and biodegradable substrate for transient electric sensors.



Figure 2-1: (a) Galactomannan composed with Mannose and Galactose structure. (b) Leucaena leucocephala seed is comprised of cotyledon, endosperm, and testa. (c) Digital image of the seeds of Leucaena leucocephala. (d) Digital image of Leucaena leucocephala.

Widely used in the food and biomedical industry, galactomannan, an earth-abundant reproducible polysaccharide, represents a promising alternative. The chemical structure (**Figure 2-1a**) of galactomannan consists of mannose backbone by β -1,4-glucosidic bonds and galactose side chains by α -1,6-glucosidic bonds, and the mannose/galactose (M/G) ratios differ depending on botanic source.⁴⁰ Compared with other degradable materials, the galactomannan film has several unique features: 1) The extraction method is facile and scalable, where the galactomannan is extracted from the endosperm (**Figure 2-1b**) of the dicotyledonous seeds (**Figure 2-1c**) from Leucaena leucocephala (**Figure 2-1d**),⁴¹ Cyamopsis tetragonoloba,⁴² and Sesbania cannabina⁴³ with low cost; 2) The aqueous extraction and ethanol purification method to obtain galactomannan is also more environmentally friendly and energy efficient when compared with that used for nanocellulose; 3) The water-soluble galactomannan substrate is shape-stable in organic solvent, providing a good shape stability in organic solvent-based fabrication method. To demonstrate the application of galactomannan film to form functional components in this study. Capable of temperature mapping and electrophysiological signal

detection, the resulting device can enable potential diagnosing arrhythmogenic disease states of the heart. As a proof-of-concept demonstration toward low-cost, fully biodegradable transient electronics, for the first time, we have fabricated high-performance zinc-based four by four temperature sensor array and electrodes endowed on galactomannan substrates for continuous monitoring of temperature variation and electrophysiological signals, respectively. This work paves the way to develop next-generation sustainable, biodegradable, and economical substrates, which are capable of superseding plastic to create greener electronics. Though the demonstrations as disposable environmental sensors or cardiac monitors are not carried out in this study, the literature and our previous studies on device integration⁴⁴⁻⁴⁶ and cytotoxicity^{47,49} have indicated the possibility toward the in vivo applications. Stable in the organic solvent, the biodegradable galactomannan also promises solvent-based fabrication processes that may be combined with recent advances in additive manufacturing techniques for a novel manufacturing method.

2.2 Results and Discussion

2.2.1 Fabrication of Galactomannan film

The Leucaena leucocephala's seed endosperm was first grounded to 100 fine mesh powders. Next, the endosperm powder was dispersed in the water under mechanical stirring. After 24 h, the mixture was centrifuged at 10000 rpm for 20 min, followed by sufficient wash in ethanol. By using the freeze dryer, the galactomannan powder with a purity of 99.0 % was obtained in the resulting precipitate. Weight analysis of the seed structure indicates the endosperm contains 58.65 % of galactomannan in weight. The ratio of mannose/galactose (M/G) is ca. 1.3:1, and the average molecular weight Mw is 1.26×106 Da. Dissolving 10 mg/ml of galactomannan in deionized (DI) water under mechanical stirring, the dispersion was then degassed for 20 min in a bath sonicator until no bubbles were observed. Slowly pouring different volumes of the galactomannan suspension (10 mg/ml) into a polystyrene petri dish and drying at ambient temperature resulted in the galactomannan films of various thicknesses. The

aqueous extraction method can prepare galactomannan films with size in a wide range. Taken together with the fact that Leucaena leucocephala is a fast-growing mimosoid tree with abundant volume in nature, the galactomannan films are suitable for potential large-scale production.

2.2.2 Characterization of Galactomannan film

Galactomannan forms highly viscous colloidal aqueous solutions when hydrated in water, leading to easy fabrication of the film with an excellent optical transparency. The resulting galactomannan films are optically transparent (Figure 2-2a) and the transmittance property has been further investigated by UV-Vis spectrometer. The result, shown in Figure 2-2b indicates that the film has a total optical transmittance of >85% in the wavelength range of 400 nm to 800 nm. The high transparency enables direct visualization of the tissues under the transparent film integrated with sensing devices. The excellent optical transmittance property could also find potential applications in optoelectronic devices, such as to increase the power output of light-emitting diodes (LEDs). As revealed by a root mean square (RMS) value between 0.86 nm and 1.77 nm from atomic force microscopy (AFM) (Figure 2-2c), the transparent substrate possesses a super smooth surface, beneficial for the device fabrication. When used as a dielectric material in transistors, the property may also provide enhanced device performance. Most importantly, the galactomannan films display a completely different stability in water and organic solvents (e.g., ethanol). While the film is stable and maintains its structural integrity in ethanol after 24 h (Figure 2-2d), it completely disintegrates after immersion in water for only 5 min (Figure 2-2e).



Figure 2-2: (a) Digital image of the galactomannan film with high optical transparency. (b) Light transmittance of the galactomannan film in the wavelength range of 400 nm to 800 nm. (c) AFM image of the galactomannan film with a super smooth surface. (d) Galactomannan film maintains its shape after immersion in ethanol for 24 h. (e) Partially dissolved galactomannan film collapsed after immersion in water for 5 min.

The mechanical property of the galactomannan film plays an essential role in the integration of sensing devices. To quantify the mechanical property of the galactomannan film, the stress-strain curve of the film was measured in Figure 2-3a. From the stress-strain curve, the tensile strength and elastic modulus of galactomannan film are obtained as 47.9 MPa and 48.1 MPa, respectively. The thermal stability of the galactomannan film in the air was also studied. The corresponding thermogravimetric analysis (TGA) curve (Figure 2-3b) indicates that the initial weight loss appears from 80 to 150 °C, due to the evaporation of free and bound water. The thermal decomposition of the galactomannan film happens from 300 to 400 °C, and the weight loss is approximately 80 %. The thermal decomposition rate of the galactomannan film was calculated from the derivative thermogravimetric analysis (DTA), indicating the maximum degradation rate occurs at 302 °C (Figure 2-3b). This thermal analysis provides critical insight



Figure 2-3: (a) Stress-strain curve of the galactomannan film, with an elastic modulus of 48.13 MPa calculated from the linear range. (b) Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG, dW/dT) curves show the thermal stability of galactomannan film. Maximum degradation rate occurs at 302 °C. (c) Fourier transfer infrared (FTIR) spectra curve of the galactomannan. (d) ¹³C NMR curve of the galactomannan.

The chemical groups of the galactomannan measured with Fourier transfer infrared (FTIR) spectra (Figure 2-4a) exhibit a principle absorption peak at 3400 cm-1 that corresponds to the stretching vibrations of the -OH group. This -OH group could enable us to program the properties of the galactomannan further. The weak peak at 2900 cm-1 is attributed to -CH stretching vibration. The representative spectrum shows a strong peak at 1600 cm-1, corresponding to the -OH bending vibration. The representative peaks at 815 cm-1 and 870 cm-1 are related with the anomeric glycosidic linkages, which are ascribed to α -D-galactopyranose and β -D-mannopyranose, respectively.⁵⁰⁻⁵¹ The strong absorption peaks of 1190 cm-1 and 980 cm-1 corresponded to the stretching vibrations of C-O groups.



Figure 2-4: (a) Fourier transfer infrared (FTIR) spectra curve of the galactomannan. (b) 13 C NMR curve of the galactomannan.

Nuclear magnetic resonance (NMR) spectroscopy is an effective characterization tool indispensable for analysis of chemical structure. The galactomannan extracted from Leucaena leucocephala seeds was analyzed by 13C NMR spectroscopy. As plant-derived heterogeneous polysaccharide, galactomannan consists of a mannose backbone with galactose side groups. As observed in Figure 2-3b, 13C NMR analyses of polysaccharides have revealed specific carbohydrate signals that are characteristic of the galactomannan with low molecular weights. It can be seen that the 13C NMR spectrum reveals well-resolved signals in the anomeric region, corresponding to the C1 of an α -D-galactopyranose at 106 ppm.⁵² In addition, the signal at 85 ppm is associated with C4 of an unbranched β-D-mannopyranose at the O6 position.⁵³ Moreover, the 70-78 ppm region gives important information about the structure due to the specific strong signal at 73 ppm attributed to C2, C3 and C5 of β -D-mannopyranose branched at the O6 position. The signal at 66 ppm is assigned to C6 of the main chain mannopyranose with galactose branches.⁵⁴ Attempts have been made to draw the possible molecular structural formula based on the FTIR and NMR results that show the majority of functional groups. But the other functional groups as well as the specific connection in between bonds (e.g., the C-C bond), are still needed before the molecular structural formula can be inferred.

Figure 2-5 demonstrates the deposition of biodegradable metals on a 50 um thick galactomannan film to yield passive sensing devices that include temperature sensors and electrodes for biomedicine. With increasing interest in applying tattoo-like sensors in internetof-things devices for human health, the potential exponential proliferation could lead to adverse environmental effects. In this context, the completely biodegradable sensors can uniquely address such a challenge by disintegrating in water with environmentally benign end products to eliminate waste streams. The temperature sensor for precision thermometry of the skin can provide clinically relevant information for many important aspects of the human physiology. The fabrication process started with cutting a single-sided adhesive Kapton film on thermal release tape (TRT) to form a shadow mask for water-dissolvable metal deposition. The purpose of employing the TRT is to ensure a flat surface when applying the shadow mask to the Galactomannan film. In this proof-of-concept demonstration, we focused on water-soluble, biodegradable metals such as zinc, which is important for its essential biological function and biodegradability.^{32, 55-56} Zn films deposited by magnetron sputtering (Kurt J Lesker CMS-18) formed patterned traces in the temperature sensor. The adhesive on the Kapton shadow mask helped ensure good contact between the shadow mask and the water-soluble substrate, leading to improved pattern precision in the temperature sensor. Removal of the Kapton shadow mask left the temperature sensor on the galactomannan substrate.



Figure 2-5. Fabrication process of a zinc sensor through a laser-cut shadow mask.

The resulting temperature sensor (Figure 2-6a) was connected to a digital multimeter

(DMM) (HEWLETT PACKARD, 34401A Multimeter) in a probe station (Cascade Microtech 11000) for calibration. Placing the temperature sensor on the stage of the probe station allowed accurate control of the temperature by the Cascade thermal system (Abbess's Snow River, -60 to 200 °C). During calibration, the temperature was ramped up from 35 °C to 60 °C with a step of 1 °C. At each step, the temperature was held constant for 25 seconds to ensure thermal equilibrium. A metal shield that enclosed the stage minimized the effect of airflow for enhanced accuracy. Resistances of the sensor at different temperatures were measured and recorded by the DMM. The resistance of a material scales linearly with the temperature by following the

equation of $R = R_{ref} \left[1 + \alpha \left(T - T_{ref} \right) \right]$, where Rref is the measured resistance of the material at a reference temperature Tref, and α is the temperature coefficient of resistance (TCR). Linear regression between resistance R and temperature T results in a TCR of 1.48×10-3 and a reference resistance of 3.42×103 Ohm at the reference temperature of 0 °C, with a coefficient of determination R2 of 0.998 (**Figure 2-6b**). The TCR in the thin film Zn temperature sensor is ~ 38.4 % of that in bulk zinc (i.e. $3.85 \times 10-3$) ⁵⁷. The decrease of the TCR in the thin film can be explained by the Fuchs-Sondheimer model, which indicates that reduction of the bulk metal material in one dimension is associated with increased surface scattering that is temperature independent.⁵⁸ The increased contribution from surface scattering leads to increased resistance, thereby decreasing the TCR.



Figure 2-6: (a) Temperature sensor on the galactomannan substrate. (b) Calibration curve of the zinc temperature sensor where its resistance is shown as a function of temperature (symbol: experimental measurements; red line: fitted calibration curve). (c) On-skin temperature measurement setup. The commercial thermistor is fixed above the Zn sensor by the Tegaderm medical dressing. (d) Real-time temperature measurement from the Zn temperature sensor.

To demonstrate the high-fidelity temperature sensing, both the water-soluble, biodegradable Zn temperature sensor and a commercial thermistor were placed on the skin of the subject with a Tegaderm medical dressing (3M) for temperature measurement (**Figure 2-6c**). The subject was asked to sit still during the temperature measurement. An air blower was then used to blow at room temperature (cold air) at the sensors' location for 30 s. Then the air blower was turned off for 30 s before blowing warm air at the sensor location for another 30 s. The real-time monitoring of the temperature from the biodegradable temperature sensor demonstrates the utility (**Figure 2-6d**). The sharp changes (i.e. decrease induced from the cold air and increase induced from the warm air) of the captured signal indicate the fast response of the water-soluble, biodegradable sensor for real-time body temperature sensing.

2.2.4 Performance analysis of temperature sensor and biopotential sensor

Integrating a single sensor in an array (Figure 2-7a) can also enable non-invasive spatial

mapping of skin temperature, as well as simultaneous quantification of the thermal conductivity

of the underlying tissues. As a first step towards this goal, a temperature sensor array of four by four was created by electron beam (e-beam) evaporation (Semicore evaporator) of Zn through a patterned shadow mask (Figure A-1a). The resulting temperature sensor array was flexible and capable of bending over a small radius (e.g., 1 cm) of curvature without damage (Figure A-1b). SEM images (Nova NanoSEM630, FEI) were taken to show the pattern of one single temperature sensor. The surface of the deposited zinc by both e-beam evaporation and sputtering were also characterized by the SEM (Figure A-1cd).



Figure 2-7. (a) Temperature sensor array on a heater, with the location indicated by the red arrow. (b) Reference resistance of 16 temperature sensors at the temperature of 0 °C. The position of the temperature sensor in figure 5a is indicated by numbers (x-axis: 1 to 4 indicates from left to right; y-axis: 1 to 4 indicates from bottom to top). (c) TCR of 16 temperature sensors obtained from the calibration curve. (d) Temperature mapping result before the heater was turned on. (e) Temperature mapping result after the heater was turned on for 5 mins. The color map was depicted by OriginPro 8.5.

When taken together with a multiplexing scheme, the temperature sensor array could be used for applications ranging from non-invasive spatial mapping to revelation of the timedynamic influence of blood flow and perfusion, as demonstrated in our previous work on ultrathin conformal temperature array.⁵⁹ To demonstrate the temperature mapping capability, a custom-built control circuit (Figure A-2a) was used to accomplish the multiplexing among temperature sensors in the array. The four by four temperature sensors were connected to the measuring unit (Keithley 2401 source meter) through anisotropic conductive films (ACF), a SOIC-32 to DIP-32 SMT adapter board, a 16 channels relay (Sainsmart), and an Arduino Mega 2560 microcontroller (Figure A-2b). The microcontroller enabled customizable multiplexing of the sensors and manual control of the relay, which facilitate the temperature mapping and the calibration of each sensor in the array. The reference resistance and the TCR of each temperature sensor were obtained through the same calibration procedure as aforementioned. The reference resistance from each temperature sensor at the reference temperature of 0 °C falls in the range from 3.01×103 Ω to 4.06×103 Ω (Figure 2-7b), where the variation in resistance is attributed to the different lengths in the interconnect region of each sensor. The TCR of the temperature sensors ranges from $1.21 \times 10-3$ to $1.53 \times 10-3$ (Figure 2-7c). A simple patterned design of titanium with a thickness of 100 nm from e-beam evaporation on a glass slide yields a heater used in the demonstration of the temperature mapping. The heater can raise up the temperature by 21.6 °C (digital thermometer, DIGI-SENSE) when a 1.5 V voltage is applied. The heating unit was placed below the transient temperature sensor array at the lower center of the array indicated by the red arrow in Figure 5a. Temperature mapping was performed before (Figure 2-7d) and 5mins after (Figure 2-7e) the heater was turned on, demonstrating the successful capture of the spatial mapping of the temperature.

Through the use of shadow mask deposition, patterned electrodes can also be obtained through either sputtering or e-beam evaporation. As a proof-of-concept demonstration, electrodes for measurement of ECG and EMG signals in a rectangular (10 mm by 2 mm) geometry were obtained through sputtering. In order to improve the contact quality and avoid the influence of the surface native oxide, small contact pads (4 mm by 8 mm) consisting a thin layer of chromium (5 nm) and gold (50 nm) were evaporated through Kapton shadow mask deposition on the galactomannan film prior to the deposition of the Zn electrode. A quarter of the Au contact pad overlapped with the sputtered Zn electrode (thickness of 100 nm) to provide electrical connection. Such a simple testing setup minimizes the effect of the Zn oxidation in an ambient environment on the contact impedance between the Zn electrode and flexible cables. The resulting electrodes were mechanically robust to deformations. To demonstrate such idea, a rectangular (10 mm by 2 mm) Zn electrode with a thickness of 100 nm connected to two Au contact pads (50 nm) was fabricated on the galactomannan film through the Kapton shadow mask following the deposition method described earlier. The two contact pads of the electrode and a digital multimeter was accomplished by silver epoxy paste (Silver Epoxy Adhesive 8331, MG Chemicals) and copper ribbons (Pyralux AC091200EV, DuPont). The resistance of the electrode only changed by less than 2% when a compressive strain up to 30 % was applied to induce the bending of the electrode (**Figure A-3**). The negligible change in the resistance is attributed to the small bending strain in the Zn electrode predicted by the theoretical analysis. Upon compression, the Zn electrode on the galactomannan substrate bends out-of-plane to take a

sinusoidal shape $y = A \sin \frac{\pi x}{L_0(1-\varepsilon)}$, where y is the out-of-plane displacement of the film from its initial position, x is the coordinate along the initial film direction, A is the maximum displacement occurred at the midpoint of the film, L0 = 12 mm is the initial distance between two clamps, and is the applied compressive strain. Upon a compressive strain of 30 %, the maximum displacement A is determined to be 2.5 mm. The maximum bending strain in the Zn electrode is given as $\varepsilon_{peak} = y''|_{max} \cdot d$, where d is the distance from the top surface of the Zn layer to the neutral mechanical plane of the Zn-Galactomannan double-layered composite.⁶⁰ The

distance d is calculated from
$$d = \sum_{i=1}^{N} \overline{E_i} h_i \left(\sum_{j=1}^{i} h_j - \frac{1}{2} h_i \right) / \sum_{i=1}^{N} \overline{E_i} h_i \int_{0}^{0} \frac{1}{N} e^{i t} h_i e^{i t} h_i$$

total number of layers in the composite, and $\overline{E_1} = \overline{E_{Zn}} = 115.2 \text{ GPa}$ and $h_1 = h_{Zn} = 100 \text{ nm}$ ($\overline{E_2} = \overline{E}_{galactomannan} = 64.17 \text{ MPa}$, $h_2 = h_{galactomannan} = 50 \ \mu\text{m}$) are the plane-strain Young's modulus and thickness of the zinc electrode (galactomannan film), respectively. The maximum bending strain in the Zn electrode is therefore calculated as 0.19 %, which helps explain the small resistance variation.

Although simple in the device design, the electrodes are capable of monitoring electrophysiological processes related to the activity of the heart (ECG), muscle tissues (EMG), and the brain (electroencephalogram, EEG). The EEG signal monitoring can be quite challenging, partially due to poor signal-to-noise ratio without proper signal amplification. Therefore, we focused on the monitoring of ECG and EMG signals in this study. PowerLab (16/35, ADInstruments) with BioAmp modules (Octal BioAmp, ADInstruments) served as the hardware for data acquisition and analysis for both ECG and EMG signals. A copper/polyimide laminate film (Pyralux AC091200EV, DuPont) was cut into thin ribbons to connect the sensor with the data acquisition system. One end of the copper ribbons was bonded to the gold contact pad via a small amount of silver epoxy paste and the other end was connected to the BioAmp through microhooks. Commercially available silver/silver chloride (Ag/AgCl) gel electrodes were also placed in the vicinity of disposable sensors on the skin for direct comparison. Slightly different from the measurement setup that uses commercial Ag/AgCl gel electrodes, the Zn electrodes were placed on the surface of the forearm with a Tegaderm medical dressing to ensure good adhesion and comfort.

EMG signals were collected with the Zn electrodes placed along the direction of the flexor muscle (**Figure 2-8a, left**). Measurements were recorded with the subject clinching the hand every 7 s. Passing the output of the electrode to a digital 500 Hz low pass filter followed by an analog-to-digital converter in the PowerLab system yielded data at a sampling rate of 1 kHz. A 60 Hz analog notch filter was applied in the BioAmp to filter out the powerline noise. A 500 Hz low pass filter was also chosen to filter out high-frequency noise in the EMG signal. The EMG signal collected from the Zn electrodes was compared with those from the commercial gel electrodes of the similar size (**Figure 2-8b**). The excellent level of agreement in EMG signals captured by the biodegradable zinc electrodes and Ag/AgCl gel electrodes establishes the

precision of EMG signal measurement. The signal-to-noise ratio (SNR) of captured EMG signal was calculated by the SNR function in MATLAB using 2 seconds of signal and 2 seconds of the noise. The SNR value of the signal collected from the Zn electrodes is only slightly larger than that of the commercial gel electrodes, indicating a high-fidelity sensing capability from the Zn electrodes. The measurement repeated 15 days later still showed a relatively high signal-to-noise ratio. A slight decrease in signal-to-noise ratio from 15.57 ± 0.76 to 11.28 ± 0.49 for EMG and from 25.76 ± 1.15 to 23.06 ± 1.75 for ECG indicates the minimum effect of the surface oxidation on the measurement (**Figure A-4**). The contact impedance between the electrode and the skin surface was also measured by an LCR meter, after 15 days of the sensor fabrication (**Figure A-5**).



Figure 2-8. (a) Photographs showing the sensor locations for the measurement of electromyogram (EMG, left) and electrocardiogram (ECG, right) signals. (b) EMG signals collected from the Zn electrode and gel electrode. (c) ECG signals collected from the Zn electrode. Baseline drift is observed in the ECG signal collected from the Zn electrode. A magnified view of the ECG signal in the inset shows PQRST waves.

A three-lead setup enabled real-time recording of ECG using the Zn electrode on the

water-soluble substrate. The measurement and reference electrodes were placed on the left and

right front wrists, and the ground electrode was placed on the left ankle. A digital 55 Hz lowpass filter was applied to eliminate high-frequency noise. **Figure 2-8c** presents a direct comparison between the ECG signals collected from the Zn electrodes and commercial gel electrodes. The SNR value of the ECG signal was also calculated following the definition of $SNR = 20 \log(V_s/V_n)$, where Vs is the peak-to-peak value (between the R peak and S peak) of the signal and Vn is the peak-to-peak value of the noise.⁶² In such definition, the signal refers to the PQRST waves, and the noise refers to all the other portions of the data that are not PQRST waves. Due to the high SNR value in the ECG signals collected from the Zn electrodes (slightly higher than that from the commercial gel electrode), characteristic features such as PQRST waves can be identified. The EMG and ECG signals collected from non-biodegradable Cu electrodes are also compared to those from commercial gel electrodes (**Figure A-6**). Given the comparison to the common commercial gel electrode, the biodegradable Zn electrodes have demonstrated performance comparable to the non- biodegradable electrodes. It should be noted that the baseline drift of ECG signals collected from both Cu and Zn electrodes is likely attributed to respiration or body movement.⁶³

2.2.5 Dissolution test of the transient sensors

Dissolution behavior of the disposable sensors (e.g., electrodes or temperature sensors) was studied by placing them in ethanol and distilled water for 24 h, respectively. It can be observed that the disposable sensors disintegrated and most of the device components were dissolved in water (**Figure 2-9a**) but remained stable in ethanol (**Figure 2-9b**). Due to the patterned geometry, the temperature sensor dissolved slightly quicker than that of the electrode. It should also be noted that dissolution of the Zn electrode leads to visible bubbles of hydrogen trapped between the Zn electrode and the petri dish when the Zn electrode was taped.



Figure 2-9. (a) A sequence of images shows the dissolution of the Zn electrode in water, where sensor rolled up at the beginning of the dissolution process. (b) A sequence of images shows that the Zn electrode is stable in ethanol. Photo credit: H. Cheng, Penn State University® and Northeastern University®.

2.3 Experimental procedures

2.3.1 Materials

Leucaena leucocephala seeds were obtained from Hebei baiwei biotechnology co. LTD.

Ethanol (99.5 wt %) was purchased from Fisher Scientific. All other chemicals were of analytical reagent grade and were used directly without further purification.

2.3.2 Atomic Force Microscopy (AFM) Test

Galactomannan film was characterized using the fast scan dimension Atomic Force Microscope (Bruker, USA). A mica substrate was used for the sample preparation, and AFM was performed in the tapping mode of operation with a scan rate of 1.85 Hz using silicon cantilevers (force constant 18 N/m, resonance frequency 1400 kHz).

2.3.3 Mechanical Test

The mechanical properties of the film were investigated using an electronic universal testing machine (SHIMADZU, AG-Xplus). The 60 μ m thickness of the galactomannan film was cut to a 0.5 × 6 cm rectangle, and the stretch rate was set at 1.0 mm/min. The Young's modulus was calculated according to the stress versus strain curve in the linear range.

2.3.4 UV-vis Spectrum

Light transmittance spectra of the galactomannan films were measured from 400 to 800

nm with a TFProbe spectroscopic reflectometer (Agilent 8453, USA).

2.3.5 Fourier Transform Infrared Spectroscopy (FTIR) Test

The galactomannan powder was completely mixed with KBr and crushed into a superfine powder using a mortar and a pestle. The mixture was then pressed into a KBr pellet then moved into a desiccator for 24 h at a temperature of 100 °C. The FTIR spectra recorded ranged from 4000 cm-1 to 400 cm-1 on an FTIR instrument (Nicolet, USA).

2.3.6Thermogravimetric Analysis (TGA) Test

PC (TGA instrument, Germany). The sample was heated in air at a rate of 10 °C/min. The test temperature was set at a range of 40 to 800 °C.

The degradation property of galactomannan film was measured by the Netzsch STA 409

2.3.7 Nuclear Magnetic Resonance (NMR) Test

The 13C NMR spectra were recorded from 10 mg of purified galactomannan in 1 mL of D2O on a Bruker AVANCE 600 MHz spectrometer equipped with a 5 mm BBO probe using an inverse gated proton decoupling sequence. Then the solution was transferred to the Shigemi microtube and characterized at 25 °C. The detailed acquisition parameters were: 90 pulse width, a relaxation delay of 1.7 s, and an acquisition time of 1.2 s. A total of 20,000 scans were collected. The 2D data set was processed with 1000 and 91,000 data points using a Qsine function in both dimensions.

2.3.8 Fabrication process of biodegradable electronics on galactomannan films

Cutting a piece of Kapton tape (Polyimide Film Tape 5413 Amber, 3M) with singlesided adhesive and a thickness of 75 m by a CO2 laser (Universal Laser System, M360) formed a shadow mask for Zn deposition. The Kapton film on a thermal release tape (Semiconductor Corp) was fixed on top of an alumina plate by using a Magic tape (3M). Attention was given to minimize air bubbles while laminating the Kapton film on the thermal release tape for enhanced laser cutting quality. The laser cutting conditions were 7 % power and 5 % speed to achieve a high-quality shadow mask. Careful removal of the excessive region in
the Kapton film by tweezers was followed by cleaning the Kapton shadow mask on the thermal release tape in an ultrasonic water bath (Branson Ultrasonic, Branson 200) for 1 minute. After water evaporation, leaving the sample on a hot plate (Scilogex, MS-H280-pro) at 90 °C released the Kapton shadow mask on the galactomannan films. Zn films deposited by magnetron sputtering (Kurt J Lesker CMS-18) formed patterned traces. The deposition conditions were 200 W, 5 T for 2000 s. These conditions minimize delamination and maintain high quality, uniform films with good yield. The adhesive on the Kapton shadow mask also helped ensure good contact between the shadow mask and the water-soluble substrate. Removal of the Kapton shadow mask left the sensor on the water-soluble substrate.

2.3.9 Experiments on human subjects

All experiments on human skin were conducted under approval from the Institutional Review Board of The Pennsylvania State University (protocol number STUDY00008003), and volunteer subjects gave informed consent.

2.3.10 Temperature mapping experiment

Temperature sensor array was connected to the SOIC-32 to DIP-32 SMT adaptor board by heat pressing (330 °F) ACF tape for 5 seconds onto the galactomannan film and board separately. L-shape 2.54 mm pitch pin headers were soldered onto the SMT pad to ensure a good connection between the adaptor board and relay board through DuPont male to female breadboard jumper wires (DuPont). The 16 channel relay had its switches connected to the SOIC-32 to DIP-32 SMT adaptor and its control panel pins connected to Arduino Mega 2560 microcontroller. The USB interface of Arduino Mega 2560 enabled the customized coding of the microcontroller by desktop using the Arduino IDE programming software. A multiplexing rate of 2 Hz was employed for the temperature mapping.

2.4 Conclusions

In summary, a simple extraction and purification method to obtain low-cost, energy efficient, environmentally friendly, fully water-soluble galactomannan films is developed.

Building on the galactomannan substrate, high-performance zinc-based sensors could be used for high-precision temperature mapping and high-fidelity electrophysiological signal monitoring. When combined with the device integration⁴⁴⁻⁴⁶ and cytotoxicity⁴⁷⁻⁴⁹ studies of this set of materials, the proof-of-concept demonstration presented in this study could easily be applied as disposable environmental sensors or biomedical devices. The resulting fully water-soluble sensors that disappear without a trace in water produce environmentally benign end products, which can even be used for alkaline soil amendments.⁶⁴ The materials explored for water-soluble sensors in this study are stable in organic solutions, which could further be explored in solvent-based fabrication. When taken together with novel additive manufacturing capabilities, this set of materials could open up a new manufacturing method of biodegradable electronics for the environment.

Chapter 3

Stretchable, Ultrasensitive, and Low-Temperature NO₂ Sensors based on MoS₂@rGO Nanocomposite

* The contents in this section have been pulished as Yi. N.. Cheng. Z.. Li. H.. Yang. L.. Zhu, J., Zheng, X., Chen, Y., Liu, Z., Zhu, H. and Cheng, H., 2020. Materials Today Physics, p.100265.

3.1 Introduction

Deformable gas sensors that can deploy on the skin or soft surfaces to detect various gaseous compounds are integral to accurate and real-time monitoring of health or environmental conditions. For instance, nitrogen dioxide (NO_2) , a common toxic gas formed by oxidation of emitted NO and N₂O from the internal combustion motor engines, frequently results in adverse respiratory health issues such as chronic bronchitis, emphysema, and irritation.⁶⁵⁻⁶⁷ It is reported that 10-20 parts per million (ppm) NO₂ is mildly irritating,⁶⁸ and exposure to 150 ppm or more may cause death from pulmonary edema or bronchospasm⁶⁹. Studies also reveal a significant association between long-term NO₂ exposure and mortality due to heart failure and dysrhythmia.⁷⁰⁻⁷¹ Therefore, it is necessary to develop wearable NO2 gas sensors to continuously detect the NO₂ level around individuals especially those living in urban area with elevated NO₂ concentration. With the prevalence of Internet of Things (IoT) in the future, the data collected from wearable NO₂ gas sensors can also guide the government or environmental department to better control air pollution. The requirements for wearable NO₂ sensors include high accuracy, fast response and recovery, good selectivity, low power consumption, small size, low cost, and mechanical robustness.⁷² Though widely commercialized electrochemical gas sensors exhibit fast response and recovery rates, low cost, and small power consumption.⁷³ they are not easy to miniaturize for wearable epidermal gas sensors and suffer from poor performance at an ultralow concentration relevant to health concerns.⁷⁴ As the most suitable modality for wearable devices, chemiresistive gas sensors have been explored for NO₂ sensing due to their simple fabrication process compared with electrochemical cells, field-effect transistors, and the other types of gas sensors.⁷⁵ Metal oxide-based chemiresistive gas sensors

have been extensively studied for gas detection, but they suffer from large power consumption, poor selectivity, and high noise.⁷⁶⁻⁷⁸ As an alternative, transition-metal dichalcogenides (TMD) with nanostructures as a new class of functional materials start to gain momentum in the development of high-performance gas sensors due to their large specific surface area, substantial surface activities, improved signal-to-noise ratio (SNR), and tunable electrical conductivity.⁷⁹⁻⁸⁰

Among the TMD materials, molybdenum disulfide (MoS_2) demonstrates excellent potential for NO₂ identification at room temperature.⁸¹ However, significant adsorption of ambient oxygen strongly influences the properties of pristine MoS₂, leading to dramatical degradation in its conductivity upon accumulative exposure to air.⁸²⁻⁸³ To overcome the limitation of MoS₂-based gas sensors for practical application, various materials (SnO₂,⁸⁴ Co₃O₄,⁸⁵ ZnO,⁸⁶ graphenes,⁸⁷ etc.) have been coupled with MoS₂ nanocrystals to improve their stability from decreased surface electron density and to enhance the gas sensing response from formed heterostructures. As widely reported in the literature, graphene prepared from multiple approaches that include mechanical exfoliation,⁸⁸ chemical vapor deposition,⁸⁹ and epitaxial growth⁹⁰ has shown a low limit of detection, small noise, and good reversibility. Due to the existence of reactive sites provided by the hydroxyl groups, reduced graphene oxide (rGO) usually has enhanced selectivity and sensitivity compared with pristine graphene.⁹¹ By combining the high specific surface area of graphene scaffold and the excellent sensitivity and selectivity from MoS₂ to NO₂, a graphene/MoS₂ hybrid aerogel consisting of MoS₂ and GO has been realized to detect the ultralow concentration of NO2 down to 50 ppb.92 However, these composites need to operate at a relatively high temperature of 200 °C to reach reasonable response and recovery rates. A slow recovery is one of the critical problems in the MoS₂-based NO₂ gas sensors at room temperature, and additional treatment such as UV light is always necessary to shorten the response and recovery time.⁹³ As fast response and recovery rate is desirable for many gas sensing applications such as toxic or explosive gas, it is of great interest to identify sensing materials with fast response/recovery rate at room temperature. Although efforts have been attempted (e.g., facilitated NO₂ reversible sensing behavior with oxygen

functional groups in GO⁹⁴ or vertically aligned MoS₂ because of the high aspect ratio and adsorption energy on exposed edge sites⁹⁵), the development of high-performance room temperature NO₂ gas sensor based on graphene/MoS₂ composites still remains elusive.

By leveraging the recent development of 3D highly porous laser-induced graphene (LIG), a novel gas sensing platform that is based on stretchable LIG patterns has been demonstrated as a simple alternative to interdigitated electrodes (IDEs) for integrating gassensitive nanomaterials.⁹⁶ While the novel LIG gas sensing platform is shown to be effective to integrate and test both metal oxides and low-dimensional nanomaterials, its direct performance comparison with the IDEs is not clear. Here we will directly compare the sensing performance of low-dimensional nanomaterials with various specific surface areas between the LIG patterns and IDEs. We first report the synthesis of nanostructured MoS_2 (a) rGO composites with various controlled specific surface areas and their applications for reversible, ultrasensitive, stretchable, room temperature NO₂ gas sensors. By adding the ball-milled NaCl crystal fillers in a solvothermal process, the controlled synthesis resulted in the $MoS_2@rGO$ composites with a specific surface area in a wide range. Integrating the composite sensing material on an IDE first confirmed the room temperature sensing capability of the $MoS_2@rGO$ composites to NO₂. The effect of the specific surface area of the porous MoS₂@rGO composites on their gas sensing performance was then investigated. The sample with the largest specific surface area demonstrated a significantly improved signal-to-noise ratio (SNR). The SNR was also enhanced from 60 to over 300 (to 2 ppm NO₂) as the spacing between the fingers in the IDE reduced from 200 to 80 m. The significantly enhanced SNR allowed the gas sensor to detect an ultralow concentration of 10 parts per billion (ppb) NO₂ with an SNR of 35.4 at room temperature. While it is possible to further reduce the spacing between the fingers, the process complexity to fabricate the IDE with reduced spacing would increase substantially. Being configured in a stretchable layout, the fabricated MoS₂@rGO gas sensor demonstrated robust mechanical operation upon stretching of 20%. The outstanding performance of $MoS_2@rGO$ gas sensors with controlled specific surface areas compares favorably against the previously

published literature reports (Table 1). As an alternative, the $MoS_2@rGO$ nanomaterial can be directly integrated on a 3D porous LIG line to eliminate the use of IDEs. The stretchable LIG-based $MoS_2@rGO NO_2$ gas sensor exhibited an extraordinarily high SNR of 1026.9 to NO_2 of 2 ppm with minimal interference from water vapor upon self-heating at a low temperature of 40 °C. Considering the high SNR of 62 to NO_2 of 10 ppb,⁹⁶ the new LIG gas sensing platform with a simple fabrication process is indeed very effective in testing nanomaterials and enable stretchable bio-integrated gas sensors.

Materials	Demonstrated LOD (ppb)	Operating temperature (°C)	Sensitivity	Calculated LOD (ppb)	Response/ recovery time	Sensing Mechanism	Interference gases used for selectivity	Wearable device	Ref
rGO/Cu ₂ O	400	150	33.9%/1ppm	82	5 min/ 12 min	CR	-	No	97
Black phosphorus	4	-	10%/10ppb	-	6 min/ 40 min	FET	-	No	98
SnO ₂ /ZnO	1000	25 (sense) UV light (recover)	238%/1ppm	-	3 min/ 5 min	CR	-	No	99
Graphene/MoS ₂	50	200	7%/0.5ppm	-	2.5 min/ 2.5 min	FET	H ₂ , CO	No	92
Ni	1000	25 (sense) 200 (recover)	1%/1ppm	-	83 s/20 s	FET	-	No	100
Sulfonated Graphene	1000	25	25%/1ppm	70	>10 min/ >20 min	EC	NH3, H2O, Toluene	No	101
Graphene	1000	25	5%/1ppm	6.87	>15 min/ >30 min	CR	NH ₃ , H ₂ O, C ₂ H ₅ OH, (CH ₃) ₂ CO	Flexible	72
phosphorene	20	25	150000%/100ppb	-	10 min/ 30 min	FET	CO, H_2S, H_2	No	102
PbS quantum dots	500	25	350%/50ppm	84	4 s/52 s	CR	SO ₂ , NO, H2S, NH ₃	Flexible	103
CVD MoS ₂	5000	25 + UV light	17%/5ppm	-	29 s/350 s	CR	$NH_3, H_2, H_2S, CO_2, CH_4$	NO	93
rGO	500	25	0.5%/0.5ppm	0.4	4 min/ 4 min	CR	NH ₃ , Cl ₂ , CH ₂ Cl ₂ , CH ₃ OH, C ₂ H ₃ OH, C ₆ H ₅ OH ₃ , C ₆ H ₁₄	Flexible	104
MoS2/Pt/rGO	500	25	6%/0.5ppm	2	1 hour/ >1 hour	FET	-	Flexible	81
ZnO nanorods	1000	200-225	750%/10ppm	2500	2 min/ 2.5 min	CR	-	No	105
Vertical aligned MoS ₂ /SiO ₂	1000	100	16.2%/1ppm	2.3	15 min/ 45 min	CR	NH ₃ , (CH ₃) ₂ CO	No	106
Al doped ZnO	10000	25	12%/100ppm	-	20 min/ 60 min	CR	CO, NH ₃	No	107
rGO/Fe ₂ O ₃	50	25	90%/5ppm	-	15 min/ 45 min	CR	H ₂ , H ₂ S, Cl ₂ , SO ₂ , NH ₃ , Benzene, Toluene	No	108
rGO/PEDOT	5000	80	12.5%/5ppm	-	50 min/ 50 min	CR	$\rm NH_3,H_2S,SO_2$	No	109
WO ₃ /YSZ	60	500	77mV/1ppm	-	50 s/100 s	EC cell	NO, CO ₂ , CO, NH ₃	No	110
NiO/YSZ	3000	850	40mV/100ppm	-	25 s/50 s	EC cell	NO, NH ₃ , C ₂ H ₂ , CH ₄ , CO, H ₂	No	111
SnS ₂	600	120	3633%/10ppm	20	170 s/140 s	CR	H ₂ , CH ₄ , CO ₂ , H ₂ S	No	112

Table 3-1. Performance comparison of representative NO2 gas sensors.

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TIPS-petacene	300	25	0.2µA/0.3ppm	20	200 s/ 400 s	CR	SO ₂ , H ₂ O, NH ₃	No	113
rGO/Co ₃ O ₄	50	25	3%/50ppb	-	5 min/ 40 min	CR	H_2 , H_2 S, NH_3 , SO ₂ , Cl_2 , (CH_3) ₂ CO, C ₂ H ₅ OH, Benzene, Toluene	No	114
MoSe ₂	1000	25	100%/10ppm	-	250 s/ 150 s	FET	NH ₃ , H ₂ S	Flexible, Stretchable	75
MoS ₂ @rGO	10	25	6%/1ppm	4.4	6 min/ 12 min	CR	SO ₂ , CO, NH ₃ , NO, C ₂ H ₅ OH, (CH ₂) ₂ CO	Flexible, Stretchable	This work [*]

CR: chemiresistor; EC: electrochemical. Note: ^{*}A static gas sensing characterization system has been used in the current study. In contrast, most of the literature reports have exploited a dynamic flow gas testing setup, which generally yields faster response/recovery processes from the flow in a much smaller chamber.

3.2 Results and discussion

3.2.1 Synthesis and Characterization of MoS₂@rGO nanocomposite

By using NaCl salt crystals with different sizes as the space filler to constrain the growth of MoS₂@rGO, the MoS₂@rGO composites with controlled morphologies were synthesized following an ethanol-thermal method (Figure 3-1a). In brief, molybdenum oxide (MoO3), thioacetamide (TAA), urea, and GO were used as the precursor for growing MoS2 on rGO by the ethanol-thermal method. Being stable in ethanol,¹¹⁵ a large quantity of NaCl crystal fillers added to ethanol was able to thoroughly disperse the small number of reactant suspension (i.e., MoO3, TAA, urea, and GO). As a result, the reactant suspension existed only in the interspaces between the NaCl crystal fillers. After thermal annealing, the size-regulated MoS_2 (a) rGO samples between the NaCl crystal fillers were harvested by dissolving the NaCl with water. Controlling the confined space between NaCl crystal fillers with different crystal dimensions yielded the MoS₂@rGO composite samples with various sizes. By using ball milling with different parameters, three different sizes of NaCl crystal fillers were prepared. We denote the as-received NaCl crystal as fillers, the NaCl crystal ball milled at 300 rpm for 5 mins as fine fillers, and the NaCl crystal ball milled at 400 rpm for 10 mins as ultrafine fillers. Following the same approach but without the use of the MoO₃/TAA/urea (or GO) in the precursor, pristine MoS₂ (or rGO) samples were obtained as the control.

The morphologies of the as-prepared rGO, MoS2, and MoS2@rGO samples were characterized by the scanning electron microscopy (SEM) (Figure 3-1 and Figure B-1). In contrast to a flake-like structure in the pristine rGO (Figure 3-1b) or a granular-like structure in the pristine MoS₂ (Figure 3-1c), the MoS₂@rGO composite (Figure 3-1d) showed a rough surface because of the interlaced MoS_2 flakes. The change from a granular-like shape to a uniform flake-like structure in MoS_2 was likely due to the presence of rGO in the composite. By ball milling the as-bought NaCl crystals into different sizes (Figure B-2), the confined space monotonically decreased in the following four samples: (1) MoS₂@rGO synthesized without NaCl crystal fillers (MoS₂@rGO without fillers, MoS₂@rGO), (2) MoS₂@rGO synthesized with as-bought NaCl crystal fillers (MoS2@rGO with commercial fillers, C-MoS2@rGO), (3) MoS₂@rGO synthesized with NaCl crystal fillers ball milled at 300 rpm for 5 mins (MoS₂@rGO with fine fillers, F-MoS₂@rGO), and (4) MoS₂@rGO synthesized with NaCl crystal fillers ball milled at 400 rpm for 10 mins (MoS₂@rGO with ultrafine fillers, UF-MoS₂@rGO). As confirmed by the SEM images (Figure 3-1e-g), the MoS₂@rGO samples became more uniform with reduced feature size as the confined space decreased. Forming flakes on the interconnected rGO framework, MoS2 not only enhanced the charge transport pathway but also increased the specific surface area of the composite from 217.34 m2/g to 283.72 m2/g.



Figure 3-1: MoS₂@rGO composites prepared by a solvothermal method with confined growth space and their corresponding SEM images. (a) Schematic of the synthesis process of the MoS₂@rGO samples with different surface morphologies. The surface morphology of the sample was controlled by changing the size of the confined space in the solvothermal process. SEM images of (b) rGO, (c) MoS₂, (d) MoS₂@rGO synthesized without adding NaCl salt crystals (MoS₂@rGO without fillers, MoS2@rGO), (e) MoS₂@rGO synthesized with adding asreceived NaCl salt crystals (MoS₂@rGO with fillers, C-MoS₂@rGO), (f) MoS₂@rGO synthesized with adding NaCl salt crystals ball milled at 300 rpm for 5 mins (MoS₂@rGO with fine fillers, F-MoS₂@rGO), and (g) MoS₂@rGO with ultrafine fillers, UF-MoS₂@rGO).

Raman spectroscopy analysis was further carried out to provide the structural information of the rGO, MoS₂, and MoS₂@rGO composites. The pristine rGO sample exhibited two peaks at 1350.6 and 1590.2 cm⁻¹ (Figure 3-2a), corresponding to the D band and G band of carbon. According to the intensity ratio of the D to G band, the degree of graphitic disordering ID/IG was determined to be 1.09 in rGO. As shown in **Figure 3-2b**, the pristine MoS_2 displayed four dominant peaks at 150.2, 285.3, 327.8, and 410.5 cm⁻¹, corresponding to the characteristic peaks of the phonon mode of metallic 1T phase MoS₂.¹¹⁶ Compared with the pristine MoS₂, the 1T phase MoS₂ mode peaks in the MoS₂@rGO composites¹¹⁷ (Figure 3-2c-f) became weak but still existed, indicating the existence of MoS₂ in the composites. Also, two distinct peaks at 1351.5 cm⁻¹ (D band) and 1590.6 cm⁻¹ (G band) in the region of higher wavenumbers (1200-1800 cm⁻¹) confirmed the presence of rGO in the $MoS_2(a)$ rGO composites. Using the relative intensity ratio of ID/IG as a convenient measurement of the reduction extent in carbon materials,¹¹⁸ the $MoS_2@rGO$ composites with a calculated ID/IG value of ~ 1.17 indicated that the GO was reduced to a great extent in the solvothermal process. The results from the above Raman spectroscopy analyses confirmed the concomitant presence of rGO and MoS₂ in the MoS₂@rGO composites.



Figure 3-2: Raman spectroscopy analysis of (a) rGO, (b) MoS_2 , (c) $MoS_2@rGO$, (d) C- $MoS_2@rGO$, (e) F- $MoS_2@rGO$, (f) UF- $MoS_2@rGO$. Red lines indicated the two characteristic peaks of MoS_2 at 150.2 and 410.5 cm⁻¹.

3.2.2 Gas sensing performance of MoS₂@rGO nanocomposite

The NO2 gas sensing performance of the synthesized MoS2@rGO composite was evaluated by drop-casting the suspension of the composite onto an IDE that was prepared by depositing metals through a polyimide (PI) shadow mask patterned by a CO_2 laser (Figure B-3). The gas-sensing performance of the MoS₂@rGO-based gas sensors was evaluated in a static gas sensing characterization system (Figure B-4) at both room temperature (Figure 3-3) and elevated temperature (Figure B-5) that has a sealed chamber with a volume of 10 L. The gas sensor was exposed to NO_2 gas for 500 s because the resistance decreased with a decaying rate, with the majority resistance drop completed within the time frame. Though the resistance of the gas sensor will continue to drop as the sensor was exposed for additional time, accurate NO_2 level detection can still be achieved by exposing the gas sensor to the environment only for the same time as the calibration test. It should be noted that the testing results obtained by a dynamic flow gas testing setup would generally improve (e.g., faster response/recover processes) over those obtained by a static gas sensing characterization system, their results may not be directly applicable to the practical applications. Elevated temperature induced a large response, possibly due to the change of gas adsorption and desorption process on the surface of sensing materials. However, it is interesting to see that no significant sensitivity change was observed for the UF-MoS₂@rGO samples when the temperature rises from room temperature to 82 °C. This implies the sensing materials ability to maintain stable gas sensing performance when the temperature of surroundings fluctuates under normal environment conditions. Different concentrations of NO_2 in the sealed chamber were prepared by diluting the 100 ppm NO₂ calibration gas (GASCO) and well mixing with the air in the chamber. The operation temperature of the MoS₂@rGO-based gas sensors was well controlled by a heater element underneath the sensing platform. As the temperature from the Joule heating increased linearly with the increasing input power, the temperature effect on the performance of the MoS₂@rGO gas sensors was quickly evaluated. After transferring the gas sensors from the ambient air to 2

ppm NO₂ circumstance, notable changes in the sensor resistance were observed. Because of the dominating p-type rGO 119 and the poor conductivity of MoS2, the MoS2@rGO samples exhibited p-type characteristics, as noted in the decreased resistance upon NO₂ absorption. Regardless of the morphologies of the MoS₂@rGO samples, their resistance changes all followed a similar trend that higher response and recovery rates occurred at elevated temperatures with lower sensitivity. The gas-sensing performance of various samples at room temperature was characterized (Figure 3-3a). Though pristine rGO samples were capable of reversibly detecting the NO₂ gas at a relatively fast response/recovery rate, their responses were small (0.18 %) with low sensitivity, and the considerable noise could not be used for accurate gas sensing (Figure 3-3b). Because the tremendous resistance of the pristine MoS_2 was over the measurement range of the source meter, its gas sensing performance was not included in the comparison. Compared with the pristine rGO sample, the $MoS_2@rGO$ composite without using fillers demonstrated higher sensitivity (13.7 %) (Figure 3-3c). The improved response was likely attributed to the enhanced charge transfer and formation of the heterojunction between rGO and MoS₂.¹²⁰ By applying NaCl fillers in the synthesis process, the resulting C-MoS₂@rGO composite with fillers showed a further enhanced sensitivity (19.0 %) (Figure 3-**3d**). The increased sensitivity can be attributed to the increased portion of heterojunction in the bulk material as the feature size of rGO and MoS₂ decreases. At the interface between p-type rGO and n-type MoS₂, both of the hole accumulation region in rGO and the charge depletion region in MoS₂ extend upon NO₂ adsorption due to the continuous electron withdrawal. Because NO₂ molecules preferably adsorb onto MoS₂ due to its rich active sites, the rGO at the junction plays a more prominent role compared with its bulk counterpart. As the charges transfer from rGO to NO₂, the carrier concentration in rGO conductive paths increases to result in a resistance drop. Though the $MoS_2@rGO$ samples with increased specific surface area showed a slightly decreased sensitivity that was likely due to the different ratios of MoS₂ in the $MoS_2@rGO$ composites ¹²⁰, their gas sensing measurements with a significantly reduced noise still demonstrated drastically increased SNR (i.e., the ratio of the mean value of the signal to the

standard deviation of the noise [R 0-R]/RMS baseline). In comparison to the SNR of 39.2 measured in the C-MoS₂@rGO, the SNR of the F-MoS₂@rGO and UF-MoS₂@rGO increased to 50.7 (Figure 3e) and 60.4 (Figure 3f), respectively. In contrast to the previous literature reports that the response/recovery processes have only been qualitatively described, the slope of the response was calculated in this study to better characterize the steady-state response conditions. As the slope of the response was calculated to be 0.154 %/min at 540 s (close to plateau in Figure 3f), it would be reasonable to assume that the sensor with a similar value in the slope of the response approximately reached the steady-state condition. Based on this consideration, a response time of 6 mins was selected in the following studies unless specified otherwise. It should also be noted that a direct comparison in the response/recovery rates hinges on a standard yet quantitative description of the response/recovery processes in the literature reports. The increase in SNR was believed to result from the reduced contact impedance between the IDE and the sensing materials that were associated with reduced feature size and more uniform distribution (consistent with the observation in the improved IDE design in the next section). The significantly increased SNR enabled the sample to respond to an ultralow concentration of NO₂, as demonstrated in the stretchable gas sensor to be discussed in the next section. Besides, the UF-MoS₂@rGO also showed reasonably well repeatability in the switching cycling test between 2 ppm NO_2 and the air (Figure 3g). The underlying mechanism of this outstanding recovery capability remains to be investigated, but could likely be the synergistic effect of rGO and MoS₂. Smaller MoS₂ clusters expose a higher ratio of edge sites that facilitate the adsorption of NO₂ molecules, leading to high sensing performance.^{95, 121} On the other hand, the reducing feature size leads to a more uniform contact between rGO and MoS₂, which facilitate the charge transfer between these two materials. The responses of the sensor to different concentrations of NO_2 (from 0.5 ppm to 2.5 ppm, with a step increase of 0.5 ppm) were also conducted in a continuous test (Figure 3h). The response of the sensor increased gradually with the increasing gas concentration, indicating its robust sensing performance. The incomplete recovery presented in the dynamic curve resulted from the given short recovery time and the

high-energy binding sites of rGO and MoS₂.^{91, 122}



Figure 3-3: NO₂ gas sensing performance of MoS₂@rGO composites. (a) Schematic illustration of the testing setup for the gas sensor, including a sealed chamber, interdigitated electrode, and a source meter (SM). Responses of five (b-f) samples to 2 ppm NO₂ at the room temperature. Signal to noise ratio (SNR) increased as the specific area of the MoS₂@rGO composite increased. (g) Cycle test of the UF-MoS₂@rGO shown in (f) to 1 ppm NO₂ showed reasonably good repeatability. (h) Calibration test of the UF-MoS₂@rGO shown in (f) to different concentrations of NO₂ demonstrated linear sensing performance.

3.2.3 Fabrication and characterization of stretchable NO₂ sensor

By eliminating the heater, the room temperature $MoS_2@rGO$ based gas sensor reduces power consumption and avoids the adverse thermal effect, enabling its application toward biointegrated electronic devices.¹²³ To conform to the hierarchically textured, non-developable topology of the skin surface and to deform with the natural motion of the underlying skin, the bio-integrated devices are expected to be not only flexible but also stretchable. By exploring a stretchable structure, the stretchable NO₂ gas sensor based on the MoS₂@rGO composite demonstrated the utility (**Figure 3-4**). With a simple fabrication process (**Figure B-6**), the stretchable sensor was capable of conforming to hand (**Figure 3-4a**), deforming to the fist (**Figure 3-4b**), and being twisted (**Figure 3-4c**) and stretched over an applied tensile strain of 20 % commonly experienced on the skin surface (**Figure 3-4d**).

The stretchability of the gas sensor mainly comes from the serpentine gold interconnects. When the gas sensor was stretched, the IDE will not undergo any significant deformation due to the rigid glass layer buried between the IDE and the soft Ecoflex substrate. Instead, the serpentine interconnects will accommodate the strain with limited resistance change due to the good conductivity of gold. To further test the hypothesis that the increased SNR was associated with reduced contact impedance between the IDE and the gas sensing materials, we reduced the spacing between the fingers of the IDE from 200 microns to 80 microns. Because of the increased conductive pathway in between fingers in the IDE, this new design further improved the SNR of the sensor (to 2 ppm NO₂) from 60.4 to 306.3 (**Figure B-7**) before stretching. Placing the stretchable sensor in the sealed chamber with different NO₂ concentrations from 0.5 ppm to 2.5 ppm before and after an applied tensile strain of 20 % demonstrated its robust operation even upon mechanical deformation (**Figure 3-4e**). According to the theoretical equation of the Limit of Detection (LOD) for a linear sensor: LOD= $3 \times noise (slope, the LOD of the stretchable gas sensor was calculated from the linearly fitted response versus NO₂ concentration curve as 4.4 ppb and 5.6 ppb before and after an applied tensile strain of 20 %.$

The resistance of the gas sensor was monitored when a tensile strain of 20% was applied to the sensor for 100 cycles (Figure 3-4f), indicating the resistance fluctuation of ~ 1%. The resistance fluctuation caused by 20% tensile strain is smaller than half of the sensor response to 0.5 ppm NO₂, which exhibits a much smaller influence of stretching compared to those in the literature reports.^{72, 107, 124} No significant change of sensitivity was observed before and after the cyclic deformation (Figure B-8). The effect of tensile strain on the gas sensing performance can be further minimized if a separate strain sensor is integrated to help deconvolute the gas response ¹²⁵⁻¹²⁶. Other than adding a separate strain sensor, placing the stretchable gas sensor onto a skin region with limited skin strain variation is another way to reduce the effect of skin deformation. As reported by literature, ¹²⁷⁻¹²⁸ the skin surface strain is largely concentrated at the region near the joint. The deformation of skin decrease significantly as the location moves away from the joint. It should be noted that the calibration curve of the stretchable gas sensor was not linear, and it had a much higher slope at a lower concentration than that at the higher concentration partially due to the saturation of NO₂ absorption on $MoS_2@rGO$ at high concentration. Therefore, the actual LOD of the stretchable gas sensor should be much lower than the above estimations.

To verify this hypothesis, we tested the sensing performance of the stretchable gas sensor at an ultralow concentration of 10 ppb at room temperature (**Figure 3-4g**). Because of the easy absorption and desorption at the ultralow concentration, fast response and recovery were observed. Though the response was only 0.125%, the sensor still exhibited an excellent SNR of 35.4. Because the measured SNR at 10 ppb was more than 10-fold of the SNR value needed to differentiate the signal from the noise, we believe that the stretchable gas sensor could be used for the detection of NO₂ even at ppt levels. Because of the possible inaccuracy to calibrate the ppt level concentrations of NO₂ in the current testing setup, the demonstration of ppt level detection was not investigated here. The excellent selectivity of the stretchable MoS₂@rGO-based gas sensor was confirmed by comparing its response to NO₂ with those to the other common air pollutants. In the demonstration, the response of the stretchable MoS₂@rGO-based gas sensor to 2 ppm NO₂ was significantly higher than those to NO, CO, NH₃, SO₂ of 1 ppm, or acetone and ethanol of 100 ppm (**Figure 3-4h**), highlighting the excellent selectivity. In addition to the common interfering gas species in the aforementioned discussion, humidity often dominates the response in many gas sensors reported in the literature, especially for those operating at room or low temperatures.

Exposing the gas sensor from the ambient environment to the relative humidity (RH) of 90% resulted in a resistance decrease of 15 %, indicating a large humidity effect (**Figure B-9**). However, several methods can be explored to mitigate the humidity effect. First of all, the humidity effect is significantly reduced from 15% to less than 2% when the sensor is operated at an elevated temperature of 40 °C after integrating a heater on the backside of the cover glass beneath the IDE. When the gas sensor is used in the environment with a range of different humidity levels, calibration of the gas sensor to various relative humidity levels is needed for the accurate detection of NO₂. The slightly elevated temperature is also below the tolerance threshold of human skin of 43 °C.¹²⁹ Secondly, a zeolite layer can be coated over the gas sensor as a moisture barrier layer to minimize the humidity effect.¹³⁰ Last but not the least, the algorithm from the electronic nose¹²⁵⁻¹²⁶ could be implemented to cancel the humidity effect with measurements from two sensors, where one is subject to gas and humidity and the other is only subject to humidity.

The stretchable NO₂ gas sensor was also demonstrated to be relatively stable in a longterm stability study by exposing the sensor to 2.5 ppm NO₂ every week for consecutive 6 weeks at 40 °C (**Figure B-10a**). The gas sensor exhibited a sensitivity of 7.1% with a small fluctuation because of the fluctuation in the relative humidity and other impurities in the ambient air environment (**Figure B-10b**). However, it should be noted that the repeatability of MoS₂@rGO stretchable gas sensor is not perfect possibly caused by the different distribution of MoS₂@rGO on the IDEs during the drop-casting process. The randomly distributed MoS₂@rGO on the IDE causes the difference of initial resistance of the sensor, the exposed surface area of the sensing material, and the conductive pathway between the sensing material and electrodes. 5 different samples made by UF-MoS₂@rGO were used to detect 2 ppm NO₂ (**Figure B-11**) but each of them shows different sensitivity ranging from 6.24% to 10.74%. Such repeatability requires each sensor to be calibrated before the actual use of the gas sensor and promoting the repeatability of IDE-based MoS₂@rGO should be considered as one of the primary goal for such device to be mass produced.



Figure 3-4. Stretchable NO_2 gas sensor for bio-integrated electronics. (a-c) Demonstration of the stretchable gas sensor deformed by (a) conforming to the hand, (b) bending to the fist, (c)

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twisting. (d) Optical images of the gas sensor stretched with an applied tensile strain of 0%, 10%, and 20%. (e) Responses of the stretchable gas sensor to different concentrations of NO₂ (from 0.5 ppm to 2.5 ppm with a step size of 0.5 ppm) before and after a tensile strain of 20%. The calculated limit of detections (LOD) of the stretchable gas sensor indicated its ability to detect an ultralow concentration of NO₂ in ppb level or close to ppt level. (f) Normalized resistance change with variation in the applied strain to the gas sensor for 100 cycles. (g) The measurement of the gas sensor to NO₂ of 10 ppb demonstrated an excellent SNR of 35.4, promising the detection of NO₂ with ppt concentrations (Note: The gap between fingers of IDE reduced from 200 μ m to 80 μ m in the stretchable gas sensor). (h) Selectivity of the stretchable MoS₂@rGO gas sensor.

3.2.4 Fabrication and characterization of LIG-based NO₂ sensor

Though being widely used in the testing of gas sensing materials, the IDE with smaller spacing between fingers was demonstrated to have a higher SNR. While it is feasible to fabricate the IDE with significantly reduced spacing to further enhance the SNR, the complexity and corresponding cost associated with the fabrication of the gas sensor would become prohibitive. As an alternative, a single conductive line with an appropriate resistance would allow accurate measurement of the resistance change in the gas sensing material cast on top. Considering laser-induced graphene (LIG)¹³¹⁻¹³² with a suitable sheet resistance of ~ 30 Ω /sq and an extremely large specific surface area (~350 m²/g),¹³³ the 3D porous graphene material fabricated from direct laser writing on the commercial polyimide (PI) represents a promising candidate as the conductive line for gas sensing applications. To prepare the LIG-based gas sensor, we first fabricated a highly porous LIG conductive line with a width of 200 μ m (**Figure 3-5a**) and a length of 1 cm by scribing a CO₂ laser (Universal Laser Systems) on the commercial polyimide tape (Kapton, 75 μ m thickness) with a laser power of 4% and a scanning speed of 1% on glass.

The SEM image indicates an interconnected fibrous-like porous structure for the laserablated PI film, exhibiting similar results as previously reported.¹³³ Raman spectrum of the single line showed characteristic peaks at ~ 1350 cm⁻¹ (D peak), ~ 1574 cm⁻¹ (G peak), and ~ 2700 cm⁻¹ (2D peak), consistent with the previously reported values of LIG to confirm its existence (**Figure B-12a**).¹³⁴ The G/2D intensity ratio in the Raman spectrum indicated the existence of multilayer (>23) graphite.¹³⁵ Casting UF-MoS₂@rGO onto the surface (**Figure 3-5b**) of the LIG sensing region by a microliter pipette completed the fabrication of the gas sensor. After the initial increase, the resistance decreased to a value smaller than its initial level as the organic solvent evaporated (**Figure B-12b**), indicating resistors connected in parallel between the LIG and MoS₂@rGO sensing materials. Considering the substantially larger resistance of the MoS₂@rGO than that of the LIG and the significant contribution of the bare LIG line (i.e., no MoS₂@rGO coating) to the total resistance, the response of this gas sensor to 2 ppm NO₂ at room temperature was only 0.1% (**Figure 3-5c**), as opposed to 11.0 % in that of IDE. However, the gas sensor still exhibited an excellent SNR of 138.3, due to the improved contact between the MoS₂@rGO sample and highly porous LIG.

To make a stretchable NO₂ sensor with self-heating capability, we further fabricate a LIG pattern with a small single line (with a reduced width of 75 μ m and length of 2 mm) connected by lines with a width of 400 μ m. The serpentine area was coated with silver nanoparticle ink (Novacentrix AJ-A191), followed by curing at 180°C for 10 mins, to significantly reduce their resistance and the single line area was decorated by UF-MoS₂@rGO. Such a design makes sure the overall resistance of the sensor is mainly the resistance of the LIG single line.

Because of the location-dependent conductivity in the LIG pattern, the voltage applied by the source meter for the resistance measurement induced localized heating (60 °C in **Figure 3-5d**) at the single line area. The self-heating in the LIG yielded a significantly enhanced SNR of 1026.9 at 2 ppm, as well as a 5-fold increase in the response. Considering the high SNR of over 60 to NO₂ of 10 ppb,⁹⁶ the new LIG gas sensing platform with a simple fabrication process is indeed very effective to test various nanomaterials and enable stretchable gas sensors. The extraordinary SNR would further enable the detection of NO₂ with an ultralow concentration (i.e., ppt level). The elevated temperature also facilitated fast response and recovery (e.g., a shorter recovery time of 400 s as opposed to > 1500 s). More importantly, the wavy LIG pattern created by the simple laser scribing process would easily yield stretchable gas sensors to follow arbitrary skin motions such as bending of fingers (**Figure 3-5e-f**). As the gas sensor going through deformation, the wavy LIG region was able to accommodate strains with limited resistance change due to its significantly reduced resistance compared to the single line area. Meanwhile, the stiff PI substrate beneath the LIG single line area was able to minimize the strain introduced to the LIG single line, making the wearable sensor less sensitive to deformations. The LIG sensing region can also be decorated with other gas-sensitive nanomaterials either before or after the laser ablation process. The novel LIG-based gas sensing platform will enable the integration and testing of various nanomaterials through a simple fabrication process to conveniently yield chemiresistive gas sensors, which can detect various target gas species for health monitoring.



Figure 3-5. Wearable $MoS_2@rGO$ -based NO_2 gas sensor on a highly porous laser-induced graphene (LIG) conductive line. SEM images of the LIG single line on the polyimide film (a) before and (b) after casting with $MoS_2@rGO$ composite. The responses of the $MoS_2@rGO$ -based gas sensor on a LIG pattern to various NO2 concentrations: (c) LIG with a length of 1 cm and a width of 200 µm at room temperature, and (d) LIG with a length of 2 mm and a width of 75 µm connected to wavy LIG patterns with a width of 400 µm upon self-heating to 60 °C. Optical images of wearable $MoS_2@rGO$ -based NO_2 gas sensor on a stretchable LIG pattern (e) before and (f) after bending of the finger.

3.3 Experimental procedures

3.3.1 Synthesis of MoS₂

In a typical procedure, 24 mg sodium molybdate (Sigma \geq 99.5%), 28 mg thiourea (Sigma \geq 99.0%), and 0.2 g urea were dispersed in 20 ml ethanol by stirring for 1 h. The suspension was loaded in a 25 ml autoclave reactor, which was placed in an oven at 200 °C for 16 h. After the

reaction, the autoclave reactor was allowed to naturally cool down in an ambient condition. The black dispersive MoS2 reaction product was collected and washed with deionized water and ethanol sequentially for at least three times, followed by storage in the mixture of deionized water and ethanol at the volume ratio of 1:1 before use.

3.3.2 Synthesis of GO and rGO

The GO was prepared according to the modified Hummers' method as discussed in the literature.¹³⁶⁻¹³⁷ Briefly, 3.0 g graphite flakes and 1.5 g NaNO3 were mixed in the 98 % H2SO4 of 69 ml, followed by cooling to 0 °C in an ice-water bath. Next, 9.0 g KMnO4 was slowly added, and the reaction was kept at 35 °C with stirring for 30 min. Upon slow addition of 138 ml water, the reaction temperature was maintained at 98 °C for 30 min. After removing the heating, the reaction was cooled down using a water bath for 10 min. After adding additional water, 3 ml H2O2 was slow added. Filtering the suspension followed by sequential rinsing with 10 % HCl aqueous solution and deionized (DI) water removed ion species. The final sediment was dialyzed with DI water until the pH of the water became neutral. The dialyzed suspension was then centrifuged at 10,000 rpm with GO remaining in the supernatant. Finally, the samples were sonicated to yield a solution of exfoliated GO.

The rGO dispersion was prepared by the thermal reduction method. The well-exfoliated GO solution was first transferred to an autoclave and loaded into an oven. The temperature of the oven was maintained at 200 °C for 16 h. Next, removing the autoclave from the oven rapidly cooled down the solution to room temperature and terminated the reaction. The obtained rGO sheets were sonicated and stored before further processing.

3.3.3 Synthesis of MoS₂@rGO composite

The $MoS_2@rGO$ composites were prepared by a solvothermal method. In brief, 24 mg MoO3, 28 mg thioacetamide, and 0.2 g urea were dissolved in 16 ml ethanol with continuous magnetic stirring for 1 h, followed by adding 4 ml GO suspension of 3.5 mg/ml. Next, the well-mixed solution was transferred to an autoclave and loaded into a furnace (MTI). Heating the

furnace to 200 °C and then the temperature was maintained for 16 h. Removing the autoclave from the oven rapidly cooled down the solution to room temperature and terminated the reaction. The as-prepared $MoS_2@rGO$ composite was collected and washed with deionized water and then ethanol, followed by storage in the mixture of deionized water and ethanol at the volume ratio of 1:1 before use.

The confined growth of the MoS₂@rGO composites followed the same recipe as above. 12 mg MoO3, 14 mg thioacetamide, and 0.1 g urea were dissolved in 8 ml ethanol with continuous magnetic stirring for 1 h, followed by adding 2 ml GO suspension of 3.5 mg/ml. After transferring the 10 ml reactant suspension into the autoclave reactor, 20 ml NaCl crystal fillers (Morton Salt, as-bought or ball-milled) were added into the reactor slowly with agitation. After the reactor was placed still for 5 min, the supernatant liquid was removed (the liquid existed only between the crystal fillers). After maintaining the temperature at 200 °C for 16 h, the asprepared MoS₂@rGO filled in the confined spaces formed by crystal fillers. The crystal fillers were dissolved by water to collect the products, and the obtained products were washed by deionized water for at least five times. Finally, the black dispersive MoS₂@rGO product was dialyzed with deionized water for at least seven days using regenerated cellulose dialysis membranes until no smell.

3.3.4 Raman spectroscopy

Raman spectroscopy was carried out on a LabRam HR800 UV NIR with 532 nm laser excitation.

3.3.5 SEM imaging

The morphologies of the as-prepared rGO and MoS₂@rGO were characterized by the SEM (Hitachi S4800) at an accelerating voltage of 10.0 kV.

3.3.6 Surface area measurement of MoS₂@rGO composite

UV-vis spectroscopy with methylene blue (MB) dye as the probe was used so as to measure the surface area of the $MoS_2@rGO$ composite.¹¹⁶ Six different concentrations of MB

aqueous solution (0.5, 1, 2, 3, 4, and 5 mg L–1) were used to first obtain the standard plot. Next, 5.0 mg MoS₂@rGO sample was added into 10 mL MB solution with a concentration of 10 mg L–1, followed by magnetic stirring in darkness for 24 h. Finally, the MoS₂@rGO mixtures were filtrated to collect the filter liquor for the measurement of the MB concentration. In this measurement, all the MB molecules were assumed to be flat, and the surface area of 1.30 nm2 per molecule of MB¹³⁸ was used to calculate the surface area.

3.3.7 Fabrication of MoS₂@rGO-based gas sensors

The IDE was first created on thin cover glass (globe SCIENTIFIC INC) by depositing metals through a polyimide (PI) shadow mask patterned by a CO2 laser. The PI tape (Kapton 3M) was laminated on the cover glass with its adhesive layer bonded to the glass. After patterning with a CO2 laser (Universal Laser Systems), removal of the carbon residue from the laser processing completed the shadow mask. Electron beam (e-beam) evaporation (Semicore) of 10 nm Cr and 100 nm Au, followed by peeling off the PI shadow mask, yielded the IDE on the cover glass. Dropping the well-dispersed MoS₂@rGO suspension onto the IDE and connecting the IDE to the source meter (Keithley 2401) through copper film and silver epoxy paste (MG chemicals 8331) completed the fabrication process of the gas sensor. A Ti heater was also fabricated by following the same shadow mask deposition approach. Integrating the heater beneath the IDE with scotch tape allowed us to investigate the temperature effect on the performance of the MoS₂@rGO gas sensor.

3.3.8 Fabrication of stretchable MoS₂@rGO based gas sensor

The IDEs were designed to have five fingers with a width of 350 microns spaced by 200 or 80 microns to ensure good sensitivity.¹³⁹ Fabrication of the IDE was carried out by the metal evaporation through a shadow mask or by a UV laser cutting (Suzhou Tianhong Laser Co., Ltd). Briefly, 5 nm Cr as an adhesive layer and 100 nm Au as the electrode were first deposited on an ultrathin polyimide film of 8 microns (CS Hyde Company). Spin-coating a thin layer of soft polydimethylsiloxane (PDMS) (mixing ratio of 10:1) on a 6-inch Si wafer served as a temporary substrate to bond the ultrathin polyimide film. Laminating the polyimide film on PDMS (with the

Au layer facing down) yielded a flat surface for the UV laser cutting. Coating a cover glass with a thin layer of a softer PDMS (mixing ratio of 20:1) by doctor blade served as the receiver substrate. Pressing the cover glass against the patterned polyimide film on the Si wafer, followed by lifting, transferred the patterned polyimide film from the Si wafer onto the cover glass with the Au electrode facing outside. The successful transfer was enabled by the difference in adhesion (i.e., the softer PDMS with a stronger adhesion to the polyimide film). Bonding the cover glass to a strip of Ecoflex (Smooth-on) with a thickness of 2 mm through a thin layer of uncured Ecoflex yielded the IDE on a stretchable substrate. Finally, the serpentine conductive ribbons patterned by the UV laser were used to connect the IDE to two contact pads, which were subsequently connected to a source meter through alligator clamps and silver epoxy.

3.4 Conclusions

By adding NaCl crystal fillers with various sizes for the confined growth of MoS₂@rGO composites in a simple solvothermal method, we synthesized the MoS₂@rGO gas sensing material with a controlled specific surface area. The synthesized MoS₂@rGO composites became more uniform with reduced feature size and increased specific surface area as the confined space reduced. Integrating the resulting MoS₂@rGO composites on an IDE yielded chemiresistive NO₂ sensors. Characterization of the MoS₂@rGO-based gas sensor demonstrated room temperature sensing capability and the MoS₂@rGO samples with the increased specific surface area also exhibited significantly improved sensing performance in terms of the fast response/recovery, good selectivity, and drastically enhanced SNR for detection of NO₂ with ultralow concentrations. The MoS₂@rGO-based NO₂ gas sensor designed in a stretchable form demonstrated its utility as a stretchable gas sensor toward bio-integrated devices. The sensing performance of the stretchable gas sensor was evaluated before and after the applied tensile strain, confirming its robust operation upon mechanical deformation. Additionally, the IDE design with reduced spacing between fingers created by a simple laser cutting process further increased the SNR to 306.3 at a NO₂ concentration of 2 ppm. Capable of detecting NO₂ with a concentration of 10 ppb with an SNR of 35.4 and fast response/recovery, the stretchable gas sensor enabled the detection of an ultralow concentration to be even in the ppt level. In contrast to the above stretchable gas sensors that rely on the use of IDEs, the novel gas sensing platform that is based on a stretchable 3D porous LIG pattern significantly simplifies the fabrication process of the sensors. With the 3D highly porous and interconnected fibrous network structure, the LIG exhibits a high specific surface area and improved contact with the gas-sensitive nanomaterials. When combined with synthesized ultra-fine $MoS_2@rGO$, the resulting stretchable gas sensor exhibited an extraordinary SNR of 1026.9 to NO2 of 2 ppm and > 60 to 10 ppb.

Chapter 4

Novel Gas Sensing Platform based on a Stretchable Laser-induced Graphene Pattern with Self-heating Capabilites

* The contents in this section have been pulished as Yang, L., Yi, N., Zhu, J., Cheng, Z., Yin, X., Zhang, X., Zhu, H. and Cheng, H., 2020. Journal of Materials Chemistry A, 8(14), pp.6487-6500.

4.1 Introduction

The recent development of wearable electronics has drawn considerable attention from both academia and industry. Because wearable electronic devices can conform to and follow the deformation of the skin, they are capable of capturing various essential mechanical,¹⁴⁰ thermal,¹⁴¹ chemical,¹⁴² electrical,¹⁴³ and biological signals,¹⁴⁴ demonstrating an excellent potential for future healthcare monitoring applications. Though continuous recording and analysis of gaseous compounds bear significant importance in healthcare, the study of wearable gas sensors for toxic gas detection,¹⁴⁵ environmental air quality monitoring,¹⁴⁶ and breath analysis¹⁴⁷ has only commenced recently. As one representative example, nitrogen dioxide (NO_2) is one of the most prominent toxic air pollutants from the combustion of fossil fuel. Inhaling at low concentration can cause symptoms such as asthma, bronchitis, and emphysema.^{112, 148} Long-term exposure can lead to heart failure and dysrhythmia.¹⁴⁹ Therefore, there is an increasing demand for the development of wearable gas sensors to provide accurate and continuous recording of NO₂. Wearable gas sensors can also enable the direct monitoring of the odours released from the human body to help inform the health conditions. Compared to their industrial counterparts, the development of wearable gas sensors needs to address additional challenging requirements, including lightweight and small form factor, low operating temperature, low energy consumption, and mechanical robustness upon various skin deformations.

Realizing the full potential to detect ultralow gas concentrations hinges on the effective use of nanomaterials because of their significantly increased surface to volume ratios. Previous studies of nanomaterials in the development of various gas sensors include metal oxide nanoparticles and nanowires,¹⁵⁰ quantum dot,¹⁵¹ and two-dimensional (2D) materials such as graphene-based¹⁵² and graphene-like layered nanomaterials^{88, 153-154}. Though graphene-based sensors exhibit high electrical conductivity, high mechanical strength, and low noise,¹⁵⁵⁻¹⁵⁹ they are often associated with low sensitivity and poor selectivity.^{88, 101, 154, 160-162} Because of their rich active sites, selective molecular adsorption, semiconducting behaviours, and high yield preparation,¹⁶³⁻¹⁶⁵ other graphene-like 2D materials such as molybdenum disulfide (MoS₂) have been explored as a promising material in the field of gas sensors. As the pristine MoS₂ has poor electrical conductivity, 3D MoS₂/graphene hybrid structures⁹² or MoS₂@rGO composites¹²⁰ have been investigated to overcome the limitation. More importantly, the possible formation of the p-n junction between p-type rGO and n-type MoS₂ leads to enhanced sensitivity, selectivity, and signal-to-noise ratio (SNR) for the detection of target gas specious at an ultralow concentration.¹⁶⁶

Most of the highly sensitive gas sensors often suffer from a small response and slow response/recovery processes (or even no recovery) when operated at room temperature.¹⁶⁷⁻¹⁶⁹ Elevated temperature from the integrated heating element is commonly used to expedite the desorption process of the adsorbed gas molecules. Though the heating elements can be conveniently fabricated with silicon (Si) micromachining technologies,¹⁷⁰⁻¹⁷¹ their performance suffers at high operating temperatures because of the instability from electromigration. The limited lifetime from chemical degradation¹⁷² also hinders their practical use. In a separate effort, the use of metal nanowires (NWs) such as silver or copper has produced transparent heaters.¹⁷³⁻¹⁷⁴ However, metal nanowires are prone to oxidation, leading to a degraded heating performance over time. Though gold (Au) coating can be used to prevent oxidation and improve biocompatibility, the increase in material costs poses a substantial obstacle for commercialization.¹⁷⁵ Additionally, the integration of a separate heating element complicates the fabrication process to construct a gas sensing system.

Among different configurations of gas sensors that explore field-effect transistor (FET),⁹¹ surface work function (SWF),¹⁷⁶ and surface acoustic wave (SAW),¹⁷⁷ the ones based on the chemiresistor¹⁷⁸ are the most promising modality for the wearable gas sensors because of their simple design, relatively easy fabrication methods, and simplified data acquisition system from the straightforward measurement. Upon surface binding or adsorption of target gas molecules, the chemiresistor changes its electrical resistance due to the variation in the carrier concentration. Though simple in the design of the conventional chemiresistive sensor, noble metal or carbon-based interdigitated electrodes (IDEs) are still required to achieve an improved signal quality in the sensitive nanomaterials. However, the fabrication of IDEs often relies on a shadow mask deposition, screen printing, or inkjet printing. Because reducing the spacing between the fingers in IDEs increases the SNR of the resulting gas sensor,¹⁶⁶ photolithographic processes are used to create the intricate IDEs designs, which complicates the fabrication process and increases the cost.

As a simple alternative to IDEs for integrating gas-sensitive nanomaterials, the highly porous laser-induced graphene (LIG) pattern¹⁷⁹⁻¹⁸¹ is systematically investigated as a novel gas sensing platform in this study. In a fast, cost-effective, and environmentally friendly process to fabricate the LIG, a transient CO₂ laser heating converts sp³-hybridized carbon in the substrate such as polyimide into porous sp²-hybridized carbon that is the carbon allotrope commonly found in graphene.¹⁸² Though the LIG has been explored in numerous sensing applications,¹⁸³⁻¹⁸⁶ the exploitation of the highly porous and p-type semiconducting LIG for gas sensing material to detect oxygen, nitrogen, and carbon dioxide.^{133, 186-187}. Additionally, the testing of the LIG and many other gas sensors was mostly carried out in a vacuum background rather than an ambient environment, posing a challenge for practical applications.

Leveraging the Joule heating or resistive heating (i.e., self-heating) of the LIG as in the previous study, ^{133, 188-189} we describe the approach to fabricate the LIG gas sensing platform

with self-heating capabilities to characterize the gas sensing performance of various nanomaterials in this report. Eliminating the need for IDEs and separate heaters, the novel LIG gas sensing platform demonstrates its utility for characterizing various gas-sensitive nanomaterials (e.g., MoS₂, MoS₂@rGO, or ZnO/CuO core/shell nanomaterials). Dispersing nanomaterials with different selectivity in the sensing region easily results in a high-density gas sensor array, which could potentially be used to deconvolute various gaseous components in the mixture relevant to the environmental or healthcare applications in the future studies. As a representative example to demonstrate the unique advantages of the LIG gas sensing platform, we systematically investigated the gas sensing performance of the LIG decorated with MoS₂@rGO nanomaterials in various self-heating conditions. At a proper self-heating condition to 60 °C, the MoS₂@rGO-LIG gas sensor exhibits fast response/recovery and ultrasensitive detection of NO₂, with a limit of detection of 1.5 parts per billion (ppb) at low power. When designed in a stretchable pattern, the LIG gas sensing platform can withstand a uniaxial tensile strain of 20 % that is comparable to the level of maximum deformation on the skin surface to open new opportunities for the epidermal electronic devices.

4.2 Results and discussion

4.2.1 Fabrication of the stretchable LIG gas sensing platform

The LIG gas sensing platform is designed to consist of a straight sensing region and a serpentine interconnect region where the wavy LIG pattern is coated with a thin metal (e.g., Ag) layer. The self-heating of the LIG results from the Joule heating (or resistive heating) during the resistance measurement of the chemoresistive LIG gas sensors upon the externally applied voltage. As the thin metal layer coated on the wavy LIG significantly reduces the resistance in the serpentine interconnect region when compared to that of the sensing region, the Joule heating leads to localized heating in the LIG sensing region. The stretchable, highly porous LIG gas sensing platform is created by using a simple laser scribing process with a selective coating of

metal layer in the serpentine interconnect region (Fig. 1a). In brief, computer-designed layouts of porous LIG patterns on polyimide (PI) films rapidly formed with high precision in an ambient environment by using a laser system (Fig. 1a-i), with the remaining PI underneath the LIG to ensure its mechanical integrity. Transferring the LIG pattern onto a soft elastomeric substrate (Fig. 1a-ii) was followed by drop casting Ag ink (Novacentrix AJ-191) in the serpentine interconnect region to yield a stretchable LIG gas sensing platform (Fig. 1a-iii). As the Ag coating significantly reduces the resistance in the serpentine interconnect region to result in localized heating in the sensing region, the power consumption is minimized. While it is possible to separately fabricate the LIG sensing region and the Ag wavy serpentine interconnect region, the creation of the Ag pattern would involve more complicated fabrication processes. Additionally, the significantly reduced contact area and quality at the Ag/LIG interface would lead to poor mechanical robustness, especially upon mechanical perturbations such as various skin deformations. Drop-casting various highly sensitive nanomaterials (e.g., rGO, MoS₂, MoS₂@rGO, or ZnO/CuO core/shell nanomaterials) in the LIG sensing region (Fig. 1a-iv) of the individual gas sensor in the array completed the fabrication of the stretchable gas sensing platform. In a representative demonstration, four different sensing units (S1-S4) arranged in an array of two by two were prepared (Fig. 1b-i). The array conformed to the wrist even upon the skin deformation from holding the fist (Fig. 1b-ii). Each sensing unit is capable of bending to a cylinder (Fig. S1) and following various deformations applied to it (Fig. 1b-iii, iv).



Figure 4-1. Schematic illustration of the fabrication process and demonstration of the wearable gas sensing platform. (a) Schematic illustration of the steps to prepare the stretchable LIG gas sensing platform: (i) porous LIG pattern on a PI film created by a laser scribing process, (ii) LIG/PI pattern transferred onto a soft elastomeric substrate, (iii) serpentine regions coated with conductive metal such as the Ag ink, (iv) gas-sensitive nanomaterials drop cast at the sensing region. (b) Optical images of the LIG gas sensing platform and its demonstration to follow various deformations applied to it. Various sensitive nanomaterials dispersed at the LIG sensing region could be designed with high selectivity to detect a specific component or with different selectivity to various components in the gaseous mixture upon various self-heating conditions. Collectively, the sensing response from the sensor array enables combinatorial sensing of multiple gas components in the mixture. Images of (i) a representative sensing platform with four sensing units arranged in an array of two by two on a soft substrate, (ii) sensing platform that followed the skin deformation from holding the fist, and deformations of a single sensing unit (iii) on the human wrist and (iv) in bending.

4.2.2 Characterization of the LIG gas sensing platform

The laser scribing process yielded continuous, porous LIG structures (Fig. 2a). Raman spectrum of the LIG (Fig. 2b) also exhibited the D peak (~ 1350 cm⁻¹), G peak (~ 1572 cm⁻¹), and 2D peak (~ 2697 cm⁻¹), with a relative large ratio of I_G/I_{2D} to indicate the presence of few-layered porous graphene, consistent with the literature reports.¹⁹⁰ The sensitive nanomaterial with high selectivity will be chosen to detect a specific gaseous component in the mixture. Collectively, the sensing response from different sensors in the high-density array enables deconvolution of multiple gaseous components in the mixture relevant to the healthcare or environmental applications. As the first step toward this goal, here in this study, we will first demonstrate the design rationale of the LIG gas sensing platform and systematic investigations of an ultrasensitive NO_2 gas sensor to highlight the feasibility of the LIG sensing platform. The design example of the NO_2 gas sensor includes the use of low-dimensional nanomaterials such as MoS_2 and $MoS_2(a)rGO$ with controlled surface morphologies. Considering the intrinsic p-type semiconducting LIG¹³³, introducing n-type MoS₂ nanomaterials⁸¹ on LIG could form p-n junctions to enhance the sensing performance.^{59,60} In the next step, we will demonstrate the versatility of the LIG gas sensing platform by exploring it to characterize heterostructure metal oxides. As a representative heterostructure metal oxide, ZnO/CuO core/shell nanomaterials prepared by calcination of a Cu-Zn bimetallic metal-oxide framework (MOF) will be explored.

We will specifically focus on the selectivity of this class of nanomaterials, which will help illustrate the feasibility to deconvolute the gaseous components in a mixture with the LIG gas sensing platform.

The preparation of the $MoS_2(a)$ rGO composite solution followed the previously reported procedure.¹⁶⁶ In brief, as received NaCl crystal fillers were added to a mixture of precursors (i.e., molybdenum oxide, thioacetamide, urea, and GO). The NaCl crystal fillers created the confined space among them, allowing the MoS₂@rGO to synthesize only within such a confined space. The morphology of the $MoS_2@rGO$ was also regulated by the size of the confined space, as in the previous report.¹⁹¹ In the following study, two different MoS₂@rGO samples were synthesized without or with as-bought NaCl crystal fillers. As characterized by the scanning electron microscopy (SEM), the MoS₂@rGO composites exhibit hierarchical flower-like structures consisting of a large number of petals (Fig. 2c-d). The resulting MoS₂@rGO nanoflower is associated with large specific surface area, consistent with the previous literature report.¹⁹² The MoS₂@rGO nanoflower synthesized with as-bought NaCl crystal fillers exhibit smaller sample size and higher specific surface area (Fig. 2d, "small petal") than that synthesized without salt (Fig. 2c, "big petal"). As the literature report ¹²⁰ indicates an optimized gas sensing performance when the rGO concentration is over 0.5 mg/ml and the MoS₂ concentration is in the range from 0.64 to 1.28 mg/ml. A proper ratio of rGO to MoS₂ is also desired, because too much rGO will shield gas sorption sites on MoS₂ and too little rGO will reduce the conducting pathway. While the optimized MoS₂@rGO ratio is not investigated in this study, both of the MoS₂@rGO samples have a MoS₂ concentration of 1.33 mg/ml and an rGO concentration of 0.7 mg/ml, to be consistent with the above report. The $MoS_2@rGO$ composite solutions were then drop cast in the LIG sensing region to yield the stretchable gas sensor. The successful integration of MoS₂@rGO nanoflowers on the porous LIG sensing region was confirmed by the SEM (Fig. 2e-f). The formed interconnected network has a small contact resistance, which is beneficial for gas sensing performance. The elemental compositions of the LIG gas sensors before and after dispersing MoS₂@rGO were also examined by X-ray photoelectron spectra (XPS) (Fig. S2). Ascribing the Si 2s, Si 2p, and O 1s peaks to the siloxane of the PDMS substrate, the survey spectrum of bare LIG samples (**Fig. S2a**) indicates the presence of the LIG on PDMS. Compared with survey spectrum of bare LIG samples (**Fig. S2a**), the survey spectrum of LIG with MoS₂@rGO synthesized using NaCl crystals (**Fig. S2b**) informs the presence of MoS₂ on the LIG. The characteristic features of MoS₂ have been observed: Mo 3d doublet centered at the binding energy of 232 eV and 228 eV (**Fig. S2c**) and the S 2p peak centered at 162 eV (**Fig. S2d**).¹²⁰ It should be noted that it is difficult to control and calculate the ratio of MoS₂@rGO over LIG though the volume of the MoS₂@rGO solution could be accurately controlled in drop casting.



Figure 4-2. Characterization of the LIG gas sensing platform. (a) SEM image and (b) Raman spectrum of porous LIG electrode. SEM images of $MoS_2@rGO$ nanoflowers synthesized (c) without ("large petal") and (d) with ("small petal") the as-bought NaCl salt crystals. SEM images of $MoS_2@rGO$ nanoflowers with (e) "large petal" and (f) "small petal" structure dispersed on the porous LIG electrodes

4.2.3 Evaluation of the self-heating function of LIG

Though room temperature gas sensors eliminated the adverse thermal effect, moderate heating in gas sensing materials (e.g., graphene/MoS₂) would still be favourable to enable fast response/recovery and enhanced reversibility.⁹² As the Joule heating of the LIG material itself has been reported, ^{133, 188-189} we will first investigate the localized self-heating effect of the LIG gas sensing platform with a LIG sensing region and an Ag/LIG serpentine interconnect region. Different from the other gas sensors (even including LIG gas sensors) that integrate additional heaters,¹⁸⁸ the self-heating effect of the LIG gas sensing platform could be exploited to reduce the device complexity for characterizing various gas-sensitive nanomaterials.

The self-heating effect of the LIG gas sensing platform hinges on its geometric parameters and location-dependent conductivity (i.e., Ag coated LIG in the serpentine interconnect region). A strong self-heating effect requires the resistance of the LIG sensing region to be significantly larger than that of the serpentine region. Similar to the conventional design of heaters, a smaller linewidth and a longer length in the LIG sensing region increased its relative resistance to the serpentine interconnect region. However, the Ag ink coating in the serpentine interconnect region drastically reduced its resistance, obviating the need for a significantly reduced linewidth and increased length in the LIG heating region. While the laser processing parameters change the sheet resistance of the LIG, the additional change in the linewidth and length of the LIG sensing region further provides ways to tune the resistance of the LIG sensing region. Given the same laser processing parameters, the resistance of the LIG sensing region was found to be proportional to its length (Fig. S3a), yielding a sheet resistance of 78 Ω /sq. Though the resistance decreased as the width increased (Fig. S3a), the inverse proportional relationship was not observed, because of the change in the sheet resistance (ranging from 110 Ω /sq to 60 Ω /sq with the increasing width from 150 µm to 292 µm) from creating the
LIG pattern of different widths.

The transient Joule heating was characterized for the LIG sensing region with a length of 2.5 mm and width of 120 μ m (an initial resistance of ~ 2.3 k Ω) (**Fig. 3a**). The peak temperature rapidly increased to equilibrium for an applied voltage in the range from 0.5 V to 12 V (**Fig. 3a**). The time to equilibrium of less than 20 s is much shorter than the other heaters based on graphene or nanowires of 50-300 s.¹⁹³⁻¹⁹⁵ As the Joule heating induced temperature rise linearly scales with the input power applied on the LIG sensing region, a higher applied voltage in this range induced a higher temperature (**Fig. S4**). The infrared thermal images of the LIG surface also confirmed the localized heating and temperature rise from Joule heating in the LIG sensing region due to its relatively high resistance in comparison with the Ag/LIG serpentine interconnect region (**Fig. S5**). The temperature of the gas sensing region was controlled to 20.1 °C, 39.8 °C, 60.4 °C, and 80.1 °C, by applying a voltage of 0.5 V, 7 V, 10 V, and 12 V, respectively.

The steady-state characteristics of the LIG gas sensing platforms were analyzed by measuring their current-voltage (I-V) curves with different sizes in the LIG sensing region (**Fig. 3b**). In the I-V curve measurement, the voltage was ramped up from 0 V to 11 V in a step-wise manner (i.e., step increase of 1 V per 20 s). Though the I-V curves were relatively linear despite the temperature rise from self-heating, there was still a small change in the resistance of the LIG gas sensing platform. Taking the LIG sensing region with a length of 2.5 mm and width of 120 µm as an example, its resistance was shown to decrease (**Fig. 3c**) because of the negative temperature coefficient in the graphitic materials.¹⁹⁶ However, the resistance reduction was small to be negligible, as the resistance of the LIG gas sensing platform only gradually decreased from 2.331 k Ω to 2.220 k Ω by 4.7 % in the voltage range from 0 V to 11 V. By considering the small variation in the electrical resistance of the LIG gas sensing platform, an improved agreement was observed between the temperature rise and the input power (**Fig. S3**). Because of the relatively stable resistance, the current in the LIG gas sensing platform was observed to ramp up in a stepwise manner from 0 mA to 5.44 mA (**Fig. 3c**).



Figure 4-3. Characterization of the LIG electrode with self-heating capabilities. (a) The time-dependent temperature profile of the LIG electrode when different input voltages were applied during the resistance measurement of the chemiresistor. The inset shows the zoom-in of the measurement in the first 10 s. (b) Current-voltage (I-V) curves of three LIG electrodes with different sizes. (c) The change in resistance of and current in the LIG electrode with a length of 2.5 mm and width of 120 μ m as a function of the time

4.2.4 Gas sensing performance of the LIG-based gas sensor

The sensing mechanism of the chemiresistive gas sensor relies on the direct charge transfer between the target gas molecules (e.g., NO₂) and sensitive nanomaterials (e.g., MoS₂, MoS₂@rGO, or ZnO/CuO core/shell nanomaterials). In the MoS₂@rGO nanoflowers, while the p-type rGO sheets provide the overall conductivity, the n-type MoS₂ on the rGO sheets has multiple active sites with selective affinity to NO₂ gas molecules for sensing. The adsorption of NO₂ on the surface of MoS₂@rGO nanoflowers continuously withdrew electrons from MoS₂@rGO, which extended both of the electron depletion and hole accumulation regions at the interface of the p-n junction. The accumulation of holes increases the major carrier

concentration of the gas sensor, thereby decreasing the overall resistance.

It should be pointed out that the carrier concentration of the LIG changes upon NO_2 adsorption is evidenced by its response to NO_2 gas molecules (Fig. S6). The gas sensor response was defined as the ratio of its electrical resistance R in the presence of target gas to that R_0 in the air. The gas sensing response of pristine porous LIG sensing regions to NO₂ was observed to depend on the laser scribing parameters. When a power of 16 % and a speed of 10 % were used in the CO₂ laser scribing process, the resulting LIG sensing regions showed a poor sensitivity (~ 0.3 ‰) and apparent baseline shift when exposed to 1 ppm NO₂ at 20 °C (Fig. S6a). Reducing both the power and speed in the laser scribing process (power of 3 % and speed of 0.8 %) yielded pristine porous LIG sensing regions with significantly improved performance (i.e., response of 12 ‰ and SNR of 434) (Fig. S6b). It should be pointed out that the obtained SNR is significantly larger than those of the previous studies based on 2D material¹⁹⁷ due to the significantly reduced noise levels though the response may be small. Meanwhile, the excellent selectivity of the sensor to NO_2 over a wide range of other inferencing gas species (e.g., acetone, ethanol, ammonia, SO₂, CO, and NO) was also confirmed (Fig. S6c). In addition to the change in laser scribing parameters, dispersing highly sensitive materials such as MoS_2 (Fig. S7) or $MoS_2@rGO$ (Fig. 4a) in the LIG sensing regions also improved the gas sensing performance to NO₂. For instance, the response of the porous LIG line (power of 16 %, speed of 10 %) coated with MoS₂@rGO (or MoS₂) exhibited significant increase to 7 ‰ (or 5 ‰), corresponding to ca. 20-fold increase when compared to the pristine porous LIG sensing regions without nanomaterial coating. Upon NO_2 exposure of 6 min, a high SNR of 482 (or 285) was also observed in the LIG sensing region coated with $MoS_2@rGO$ (or MoS_2). Considering the vast difference between sensors with and without the highly sensitive nanomaterials, the response of the gas sensor should be mainly contributed by the nanomaterials.

The $MoS_2@rGO$ nanoflowers with the small petal structure was selected to investigate

the width effect on the gas sensor performance, because it demonstrated a more substantial response of 4.0 % than that with the big petal structure of 1.8 % to NO₂ of 1 ppm at 60 °C from self-heating (10 V applied on the LIG with a linewidth of 120 µm and length of 2.5 mm) (Fig. 4a). The more significant response in the LIG with the small petal structure than that with the big petal structure was also observed at other temperature values, i.e., 6.6 ‰ vs. 2.8 ‰ at 20 °C, 5.1 ‰ vs. 2.0 ‰ at 40 °C, and 2.0 ‰ vs. 0.4 ‰ at 80 °C (Fig. S8). The LIG with the small petal structure is associated with the reduced feature size and more uniform distribution of the nanomaterials. The increased specific surface area and the possibly formed p-n junction lead to a more substantial response and faster response/recovery processes. In contrast to the previous literature reports that the response/recovery processes have only been qualitatively described, we have introduced the angle of the plateau (defined as the tangent angle of the response/recovery curves at the end of adsorption/desorption) to quantitatively capture these processes. The smaller the angle of the plateau, the faster the response/recovery processes. With such a new definition, the response process in the LIG with the small petal structure (angle of the plateau of 2°) was indeed faster than that with the big petal structure (slope of the plateau of 3°).

Different voltage inputs were first applied to the LIG sensing region with various linewidths to ensure their temperatures remained the same such as at 60 °C. In particular, a voltage of 20 V, 15 V, 12 V, and 11 V was applied on the LIG with a linewidth of 120 μ m, 160 μ m, 200 μ m, and 240 μ m, all with the same length of 6 mm. Next, dispersing MoS₂@rGO nanoflowers with small petal structure on the LIG sensing region with various linewidths prepared chemiresistive gas sensors. The electrical resistance of the resulting gas sensors decreased upon exposure to NO₂ of 1 ppm and recovered in the air due to the desorption of NO₂ (**Fig. 4b**). The magnitude of the response to NO₂ of 1 ppm at 60 °C increased from 3 ‰ to 8 ‰ as the linewidth of LIG sensing region increased from 120 μ m (**Fig. 4b**). Consisting of the electrical resistance R_{sensing} in the sensing region, $R_{\text{serpentine}}$ in the serpentine region, and the contact resistance R_{contact} between nanomaterials (e.g., MoS₂@rGO) and LIG,

the total resistance R_{total} of the resulting gas sensor would be the sum of the three. Forming a parallel connection between the LIG and the nanomaterial such as MoS₂@rGO would indicate a more significant response in the LIG with a smaller linewidth, which cannot explain the trend in the experiment. The increased response with the increasing linewidth could be likely attributed to the non-uniform temperature distribution in the LIG sensing region (**Fig. S4**). Consistent with the literature reports on ohmic microheaters,¹⁹⁸ non-uniform temperature distribution resulted in a lower temperature at the edge than that at the central region of the LIG sensing region. Because the MoS₂@rGO sensing material showed a more substantial response at a lower temperature (**Fig. 4c-d**), the lower temperature at the edge region of the LIG sensing region with a larger linewidth gave rise to the more significant response. Additionally, the incomplete recovery to NO₂ observed in the LIG with a larger linewidth could be explained by the limited recovery at a lower temperature (**Fig. 4c-d**) at the edge region from the non-uniform temperature distribution as well.

After uncovering the width effect, we further investigated the temperature effect on the gas sensor performance. By leveraging the self-heating effect in the LIG sensing region, the gas sensing behaviours of the MoS₂@rGO-LIG sensor to NO₂ of 1 ppm were compared at various operating temperatures from 20 °C to 80 °C (**Fig. 4c-d**). The operating temperature was selected to be below 100 °C because of the stability consideration of the ionosorption of gas species in the charge transfer involving MoS₂.¹⁰⁶ While a complete recovery was observed in the LIG gas sensing platform with MoS₂@rGO nanoflowers of the small petal structure, the recovery time of 2830 s to 1 pm NO₂ at 20 °C was significantly larger than that at 80 °C (580 s) (**Fig. S9**). Also, it is crucial to sensitively detect low concentrations of NO₂ (~ 53 ppb) in the envisioned applications, as this level of exposure can cause chronic bronchitis, emphysema, and respiratory irritation.⁹² The repeatability test indicates that the response of the gas sensor to the same target gas concentration is independent of whether the gas sensor is fully recovered. Thus, the gas sensor does not necessarily need to fully recover when used for the long-term monitoring of low-level exposures. Considering a recovery time of 720 s is sufficient to

capture the gas sensor characteristics, this value is used in the subsequent tests for rapid testing (as in literature studies) unless otherwise specified. As the operating temperature was increased from 20 °C to 80 °C, the response of the sensor with the big petal structure gradually decreased from 2.8 % to 0.4 % upon exposure to NO₂ for 6 min (**Fig. 4c**). As the maximum response is often observed at optimum operating temperature for many low-dimensional and metal oxide nanomaterials, the reduced response at the elevated temperature is consistent with the previous study on MoS₂/graphene hybrid structure.⁹² While the temperature-dependent response is related to the equilibrium of the NO₂ adsorption, further experiments are still needed to directly uncover the underlying mechanism. However, the elevated operating temperature led to improvements in the response/recovery processes of the gas sensor. The decreased slope of the plateau from 11° to 0.7° indicated the significantly improved response process (**Fig. S10a**). Defining the recovery ratio as the ratio of responses at the end to the start of desorption in given time duration, the recovery rate also increased from 20 % to 200 % for desorption of 12 min as the operating temperature was increased from 20 °C to 80 °C. The improved desorption

A balance has to be struck as the significant response and fast response/recovery cannot be achieved simultaneously by tuning the operating temperature alone. This observation also held for the LIG with the small petal structure. While the response of the sensor decreased from 6.6 ‰ to 2.0 ‰ as the operating temperature was increased from 20 °C to 80 °C, the angle of plateau decreased from 8° to 0.6° (**Fig. S10b**), and the recovery rate increased from 58 % to 113 % (**Fig. 4d**). Considering the balance between the significant response and fast response/recovery processes, the operating temperature of 60 °C was selected in the subsequent studies unless specified otherwise. The room or low temperature sensing capability was particularly attractive for wearable gas sensing applications due to low energy consumption and the elimination of the adverse thermal effect on the skin surface. Though the operating temperature of 60 °C seems to be slightly higher than the desired temperature in the epidermal applications, incorporating a heat sink or combining the thermal isolation layer in the

gas sensor could readily reduce the temperature at the sensor/skin interface to avoid the adverse thermal effect on the skin surface.



Figure 4-4. Effects of the width and operating temperature from self-heating on the gas sensing performance. (a) the typical response curves of $MoS_2@rGO$ nanoflowers with the small petal and big petal structure on the LIG sensing platform at 60 °C to NO₂ of 1 ppm. (b) Time-dependent response curves of $MoS_2@rGO$ nanoflowers with the small petal on the LIG with various widths at 60 °C. (c) Sensor response of $MoS_2@rGO$ nanoflowers with the big petal to 1 ppm NO₂ at various temperatures from self-heating. (d) Sensor response of $MoS_2@rGO$ nanoflowers with the small petal to 1 ppm NO₂ at various temperatures from self-heating.

In the typical dynamic response test, the MoS₂@rGO-LIG sensor showed a response of 1.80 ‰, 2.90 ‰, 3.96 ‰, 4.70 ‰, 5.30 ‰, 7.60 ‰, and 9.50 ‰ as the concentration of NO₂ was progressively ramped up from 0.2 to 0.4, 0.6, 0.8, 1.0, 2.0, and 5.0 ppm, respectively (**Fig. 5a**). The monotonically reversible sensing result demonstrated a relatively wide detection range for NO₂ to meet the requirements of air quality monitoring and exhaled breath detecting.¹⁴⁸ Exposing the gas sensor to NO₂ of 1 ppm for five consecutive cycles also indicated excellent repeatability, with a relatively stable response of 5 ‰ and fast response/recovery processes of 360 s/720 s (**Fig. 5b**). Additionally, the stable response of 5 ‰ was observed regardless of the incomplete recovery, indicating the full recovery is not

necessarily needed for the envisioned applications of long-term monitoring of low-level exposures.

In addition to the response and response/recovery processes, the signal-to-noise ratio (SNR) is another critical parameter in the performance assessment of gas sensors, especially relevant to the calculation of the limit of detection (LOD). In spite of the relatively small responses of a few ‰, the SNR of the MoS₂@rGO-LIG with the small (or big) petal structure to 1 ppm NO₂ gas was 269/482/213/339 (or 331/421/530/132) at 20/40/60/80 °C (**Fig. S11**), which is significantly higher than most of the values in the previous reports based on 2D material.¹⁹⁷ The highly porous LIG and the MoS₂@rGO nanoflowers with a high specific area resulted in low contact resistance, thereby leading to low noise and high SNR.

One parameter to represent the level of noise is its standard deviation RMS_{noise} in the baseline of the response curve. Calculating the RMS_{noise} value from 100 data points in the response curves (Fig. S12) of the $MoS_2@rGO-LIG$ sensor with the small (or big) petal structure to NO₂ in the concentration range from 200 ppb to 600 ppb yielded 0.0030 % (or 0.0036 %). The slope of the simple linear fit in the linear calibration curves (i.e., between the response and NO₂ concentration) was obtained to be 7.49 ‰/ppm (or 5.42 ‰/ppm) for the one with the small (or big) petal structure (Fig. 5c). Defining the LOD as $3 \times RMS_{noise}/slope$,⁷⁰ the theoretical estimation of the LOD could be extrapolated from the above linear calibration curves and calculated to be 1.2 ppb (or 2.0 ppb) for the sensor with the small (or big) petal structure. In the validation experiment, an SNR of 62 was still measured with fast response and nearly complete recovery in the sensor with the small petal structure in the presence of 10 ppb NO_2 (Fig. 5d). Because the LOD could also be interpreted as the concentration with a signal to be approximately three times of the noise, the measured SNR of 62 in Fig. 5d indicated an actual LOD of less than 1 ppb into the parts per trillion (ppt) range. Though this actual LOD is challenging to be validated with our current static gas testing setup, it will be demonstrated with a more precise testing setup in future studies. The NO_2 gas sensors with an ultralow LOD

and self-heating capabilities demonstrated with a simple fabrication method in this study compared favourably to previous gas sensor introduced in Chapter 3.

The selectivity of the MoS₂@rGO-LIG sensor to NO₂ was confirmed in comparison to the responses to a wide range of other interfering gas species that include acetone, ethanol, methanol, ammonia, SO₂, CO, and NO (Fig. 5e). While the sensor response to NO₂ of 1 ppm was 5.1 ‰, its response was only -0.34 ‰ to ammonia (NH₃) of 1 ppm, 2.0/-0.19/-0.11 ‰ to NO/SO₂/CO of 1 ppm, and -0.3/-0.19/-0.5 ‰ to acetone/ethanol/methanol (CH₃COCH₃/C₂H₅OH/CH₃OH) of 100 ppm. Though the concentration of the volatile organic compounds (VOCs) was much higher than that of NO_2 , the sensor response was still much smaller because of their weak interaction with the gas sensing nanomaterials.^{72, 199} The sensor responses to NH₃/SO₂/CO of 1 ppm were small yet considerable, but they were in the opposite direction because of their reducing characteristics.^{72, 199} In addition to the common interfering gas species such as NH₃, NO, CO, SO₂, and VOCs in the target application environment, humidity often poses significant concern on the gas sensors, especially for those operating at room or low temperatures. Exposing the gas sensor at a high level of relative humidity (RH) demonstrated the humidity effect. After being exposed to an RH of 88 % for 6 min, the humidity response was considerable at 20 °C (i.e., 1.96 ‰). However, the response was significantly reduced at elevated temperatures (i.e., 0.83/0.45/0.29 ‰ at 40/60/80 °C) (Fig. $\mathbf{S13}$), indicating a small interfering effect of RH on NO₂ response at elevated temperatures. Coating metal-organic framework (MOF) such as a layer of hydrophobic and catalytic Zeolitic Imidazolate Framework-CoZn (ZIF-CoZn, isostructural with ZIF-8(Zn) or ZIF-67(Co)) thin film on the gas sensor could also drastically improve the sensor performance under humidity interference.²⁰⁰ Additionally, the concept from the electronic nose could be applied to deconvolute the gas response in the presence of humidity based on the measurements from two sensors with one subject to both gas and humidity and the other one subject to humidity alone.201

When used in epidermal applications, the LIG gas sensing platform also expects to be mechanically robust with minimum resistance change upon mechanical perturbations such as natural skin motions. As stretchable structures have been extensively studied and explored to ensure stretchable properties in the epidermal devices, they will be exploited to yield a stretchable LIG gas sensing platform. Leveraging the simple laser scribing process, the stretchable serpentine interconnect region can be created during the sensor fabrication in a single step. Because of the serpentine interconnect region, the MoS₂@rGO-LIG gas sensor on an elastomeric substrate such as Ecoflex exhibited a robust mechanical property (Fig. 5f) to withstand a uniaxial tensile strain ε of 20 % that is comparable to the level of the maximum deformation on the skin surface.²⁰² The mechano-chemiresistive properties of the MoS₂@rGO-LIG gas sensor with the small petal structure to NO_2 of 1 ppm were investigated. The static tensile strain was applied from a custom-built stretcher with a step motor controlled by Arduino Uno, and the gas sensor was evaluated at both room temperature and 40 °C from self-heating. In addition to maintaining its mechanical integrity, the sensor subject to a uniaxial tensile strain of 20 % demonstrated an increased response and faster recovery when compared to the unstretched (i.e., $\varepsilon = 0\%$) at both room temperature and 40 °C. As the tensile strain was increased from 0 % to 20 %, the sensor response increased from 5.5 ‰ to 6.2 ‰ (or from 2.8 ‰ to 4.0 ‰) at 20 °C (or 40 °C). The increased response and faster recovery upon mechanical deformation could be attributed to the deformation-induced structure change in the highly porous LIG and the strain engineering of the semiconducting nanomaterials. As a simple and straightforward strategy, strain isolation with a stiff material in the sensing region was explored to demonstrate ways to reduce the strain interfering. A tensile strain of 20 % was applied from a custom-built stretcher on the LIG gas sensing platform with three different strain isolation designs (Fig. S14a). As the existing PI beneath the LIG has Young's modulus much larger than that of the elastomeric substrate, it naturally served as the stiff material for strain isolation. Progressively increasing the size of the PI pattern (i.e., single line, small circle, and large circle) enhanced the strain isolation effect. As a result, the resistance change in the LIG gas

sensing platform reduced from 11.3 ‰ for the single line design to 0.47 ‰ for the large circle design, when a strain of 20% was applied perpendicular to the sensing region. The resistance fluctuation was also greatly suppressed for the large circle design compared with the other two designs (Fig. S14c-d). The enhanced strain isolation effect by larger PI substrate can be explained by the uneven distribution of strain at the PI-PDMS interface. It has been revealed that for an interface between a soft substrate and a rigid island, the strain will concentrate near the edge of the rigid island.²⁰³⁻²⁰⁶ The large circle design ensures the LIG sensing element away from the edge of rigid PI island and thus minimize the strain introduced to LIG. While the LIG gas sensing platform could be attached to the skin surface with its sensing line perpendicular to the major deformation direction, the strain along the parallel direction of the sensing line may not be ignored. In the LIG gas sensing array, the spacing between two sensors could actually follow most of the strain applied to the array with different strain isolation designs. When a strain of 20 % parallel to the LIG sensing line was applied, the resistance change in the LIG gas sensing platform reduced from 77.8 ‰ for the single line design to 4.4 ‰ for the large circle design. Replacing the spacing with a much compliant material would certainly improve the strain isolation effect to result in a much smaller resistance change. When using the sensor to detect ultralow concentration of NO_2 , the strain-induced resistance fluctuation may not be ignored. Integrating a strain sensor with the gas sensor can help deconvolute the sensor response due to NO_2 adsorption from the overall sensor response. Other than the demonstrated strain isolation strategy, many other stretchable strategies (e.g., pre-strain,²⁰⁷ self-similar interconnect patterns,²⁰⁸ and kirigami patterning of the substrate²⁰⁹ can also be applied to further minimize the strain and reduce the resistance change in the LIG sensing region. The demonstrated stretchable gas sensors could enable the conformal contact to the hierarchically textured skin surface for applications in epidermal electronic devices.



Figure 4-5. The dynamic response, limit of detection, selectivity, and mechanical robustness of the gas sensor. (a) Dynamic response test of the gas sensor with the small petal structure in the presence of NO₂ from 0.2 ppm to 5 ppm at 60 °C from self-heating (applied voltage of 10 V). (b) Demonstration of repeatability to NO₂ of 1 ppm for five consecutive cycles. (c) A linear fit to the calibration curves obtained from the sensor response to NO₂ of 200 ppb, 400 ppb, and 600 ppb at 60 °C from self-heating. (d) Experimental demonstration of the ultralow limit of detection to NO₂ of 10 ppb at 60 °C, where a high SNR of 62 was still measured. (e) The selectivity of the stretchable MoS₂@rGO-LIG gas sensor to NO₂ over a wide range of other inferencing gaseous molecules at 60 °C before stretching. (f) Response of the stretchable gas sensor in (e) to NO₂ of 1 ppm before and after a uniaxial tensile strain of 20 % was applied at room temperature and 40 °C, respectively.

The deconvolution of multiple gaseous components from a mixture requires the use of

a high-density gas sensor array with each of the different selectivity. As the first step to demonstrate such a capability of the LIG gas sensing platform, we will demonstrate the application of the LIG gas sensing platform goes from characterization of low-dimensional nanomaterials to a different class of nanomaterials such as heterostructure metal oxides. As a representative heterostructure metal oxide, ZnO/CuO core/shell nanomaterials were first prepared by calcination of a Cu-Zn bimetallic metal-oxide framework (MOF) (**Fig. S15**). Dispersing the ZnO/CuO core/shell nanomaterials in the LIG sensing regions (power of 16 %, speed of 10 % in the laser scribing process) in a different sensing unit in the array yielded a gas sensor with a response of 1.5 ‰ and an SNR 390 of to NO₂ of 1 ppm (**Fig. S16a**). In contrast to the sensing unit with MoS₂@rGO (or MoS₂), the sensing unit with ZnO/CuO core/shell nanomaterials exhibited a different selectivity with significant responses to VOCs (**Fig. S16b**). Considering the other nanomaterials with a different selectivity to VOCs (e.g., ZnO based ammonia gas sensor^{90,91}), an array of sensing units with different selectivity in various sensing units of the array is required to detect gaseous components from a mixture based on the algorithm from the electronic nose, the result from this study also paves the ways for applying the novel LIG gas sensing platform in an array layout to the electronic nose.

4.3 Experimental procedure

4.3.1 Fabrication of the gas testing platform on laser-induced graphene

A polyimide (PI) film (Kapton HN, 90 μ m thickness) laminated on a water-soluble tape (3M, 5414 tapes) was first attached on glass slides by a double-sided tape. Upon direct CO₂ laser (Universal Laser, 10.6 μ m) scribing with a power of 16 % and speed of 10 %, porous laser-induced graphene (LIG) patterns formed on the top surface of the PI by photothermal ablation. The same laser system with a lower power of 5 % and lower scanning rate of 1 % enabled the cutting of LIG patterns. Immersing the resulting sample in water dissolved the water-soluble tape and released the LIG patterns from the glass substrate. Rinsing the LIG surface with ethanol and water subsequently with mild agitation removed the dust and contaminants. After attaching the LIG to a water-soluble tape with gentle pressure, a thin Ecoflex (Smooth-on,

Ecoflex 00-30) layer with a thickness of 500 μ m was cast on the back of PI surface and cured at 60 °C on a hot plate for one hour. Dissolving the water-soluble tape exposed the LIG pattern with two serpentine lines (width of 2 mm) and a single straight line with various lengths and widths. Coating the serpentine lines with silver ink (Novacentrix AJ-191) reduced their electrical resistances to provide electrical connection to the external data acquisition system. Drop casting nanomaterials such as MoS₂, MoS₂@rGO, or ZnO/CuO core/shell nanomaterials in the LIG single line sensing region completed the fabrication of a highly sensitive stretchable gas sensor.

4.3.2 Preparation of the ZnO/CuO core/shell nanomaterials

Intergrowth Cu₂(nbdc)₂(dabco) on Zn₂(nbdc)₂(dabco) was synthesized by the conventional seeded growth method. In a typical procedure, $Cu(NO_3)_2$ ·3H₂O was dissolved in N,N-dimethylformamide (DMF). Next, acid linker 3-Nitrophthalic (3acid nitrobenzenedicarboxylic acid, nbdc) was dissolved in DMF. Base (pyridine) was then added with micropipette into base linker dabco (1,4-diazabicyclo[2.2.2]octane) solution in DMF. 66 μ L seed dispersion (0.1 % conventional Zn₂(nbdc)₂(dabco) pillared metal-organic framework (MOF) suspension in DMF (wt %)) was added into the base solution. Once linkers and metal salt were completely dissolved, metal solutions and acid linkers were added into the seed solution. The final mixture with a molar ratio of metal salt: nbdc: dabco: base: DMF = 2.8: 2: 2: 40: 24000 was shaken on an orbital shaker at 200 rpm for 48 hours. The solid in the resulting suspension was separated using centrifugation (4000 RCF). The obtained bimetallic MOF was then used to prepare the mixed metal oxide nanomaterials. Intergrowth MOF Cu₂(nbdc)₂(dabco)-on-Zn₂(nbdc)₂(dabco) of 100 mg was heated in N₂ (50 SCCM) at 400 °C (ramp rate of 1 °C/min) for 10 hours followed by dry air (50 SCCM) at 400 °C for another 10 hours. The obtained ZnO/CuO core/shell nanomaterials were cooled to room temperature in dry air.

4.3.3 Synthesis of MoS₂@rGO composite

The $MoS_2@rGO$ composites were prepared by a solvothermal method. In brief, 24 mg

 MoO_3 , 28 mg thioacetamide, and 0.2 g urea were dissolved in 16 ml ethanol with continuous magnetic stirring for 1 h, followed by adding 4 ml GO suspension of 3.5 mg/ml. Next, the wellmixed solution was transferred to an autoclave and loaded into a furnace (MTI). Heating the furnace to 200 °C and then the temperature was maintained for 16 h. Removing the autoclave from the oven rapidly cooled down the solution to room temperature and terminated the reaction. The as-prepared $MoS_2@rGO$ composite was collected and washed with deionized water and then ethanol, followed by storage in the mixture of deionized water and ethanol at the volume ratio of 1:1 before use.

The confined growth of the $MoS_2@rGO$ composites followed the same recipe as above. 12 mg MoO₃, 14 mg thioacetamide, and 0.1 g urea were dissolved in 8 ml ethanol with continuous magnetic stirring for 1 h, followed by adding 2 ml GO suspension of 3.5 mg/ml. After transferring the 10 ml reactant suspension into the autoclave reactor, 20 ml NaCl crystal fillers (Morton Salt, as-bought) were added into the reactor slowly with agitation. After the reactor was placed still for 5 min, the supernatant liquid was removed (the liquid existed only between the crystal fillers). After maintaining the temperature at 200 °C for 16 h, the as-prepared $MoS_2@rGO$ filled in the confined spaces formed by crystal fillers. The crystal fillers were dissolved by water to collect the products, and the obtained products were washed by deionized water for at least five times. Finally, the black dispersive $MoS_2@rGO$ product was dialyzed with deionized water for at least seven days using regenerated cellulose dialysis membranes until no smell.

4.3.4 Testing of gas sensor

The gas sensing performance of various gas sensors was characterized in a static gas sensor testing system with a commercial computer-controlled sourcemeter (Keithley 2400, Keithley Instruments, USA). Different concentrations of NO_2 in the sealed chamber were prepared by diluting and well mixing the 100 ppm NO_2 calibration gas (GASCO) with the air in the chamber with a volume of 10 L.

The morphologies of the as-prepared rGO and MoS₂@rGO were characterized by the SEM (Hitachi S4800) at an accelerating voltage of 10.0 kV.

4.4 Conclusions

In summary, we have developed a novel gas sensing platform based on porous laserinduced graphene (LIG) with a metal surface coating. Consisting of an LIG sensing region and an Ag/LIG serpentine interconnect region, the LIG gas sensing platform as a chemiresistor provides an alternative to interdigitated electrodes with separate heaters for integrating and characterizing the performance of gas-sensitive nanomaterials. The metal surface coating on the LIG in the interconnect region has induced location-dependent conductivity to significantly reduce its resistance, which enables highly localized Joule heating (i.e., self-heating) during the measurement of the chemiresistor. The fast (to reach equilibrium within 20 s) and wellcontrolled (by externally applied voltage) self-heating capability in the LIG gas sensing platform eliminates the need for a separate heating element, which significantly reduces the fabrication complexity. As one demonstration to show the capabilities of this new gas sensing platform, highly sensitive nanomaterials such as MoS₂ and MoS₂@rGO have been dispersed on the LIG sensing region to result in an ultrasensitive chemiresistive NO_2 gas sensor. Due to the large specific surface area in the nanomaterials and highly porous LIG, rich yet specific active sites in the MoS₂, and possible formation of p-n heterojunctions in MoS₂@rGO, the resulting gas sensor exhibits relatively large response, fast response/recovery processes, and excellent selectivity at slightly elevated temperature from self-heating in a static testing setup. The drastically reduced noise levels resulted in a significantly increased SNR (e.g., close to 900 to NO₂ of 1 ppm), which enables the sensor to detect NO_2 at a concentration of a few ppb. Based on the experimental demonstration, the actual limit of detection is believed to be smaller than 1 ppb. The effects of the LIG sensing region geometric parameters, operating temperature, and various nanomaterials on the gas sensing performance have also been systematically investigated. Configuring the serpentine interconnect region in a stretchable layout, the resulting LIG gas sensing platform

becomes mechanically robust even under a uniaxial tensile strain of 20 % that is comparable to the maximum deformation on the skin surface. Considering the other stretchable strategies, the strain interfering could be further minimized. When incorporating a heat sink or combining the thermal isolation layer in the gas sensor to avoid the adverse thermal effect on the skin surface, the novel LIG gas sensing platform that could deconvolute multiple gaseous components in a mixture opens new opportunities for the epidermal electronic devices.

Chapter 5

Fabricating Functional Circuits on 3D Freeform Surfaces via Intense Pulsed Light-induced Zinc Mass Transfer

5.1 Introduction

Currently, most electronic devices are fabricated by vacuum-based integrated circuits processes ²¹⁰, screen printing ²¹¹, or additive manufacturing methods ²¹², all of which require a planar substrate for patterning functional materials. Because a convex or concave surface is not compatible with lithography processes and traditional printers, the technique of transfer printing has been explored for heterogenous integration of the thin film electronics onto curvilinear structures ²¹³. In addition to the complicated fabrication processes, the electronics also need to be flexible and moldable to ensure robust performance over the shape transformation.

To achieve direct fabrication of electronic circuits on an arbitrary shape, advanced printing techniques have been developed, including omnidirectional printing ²¹⁴, aerosol jet printing ²¹⁵, and adaptive 3D printing ²¹⁶. However, disadvantages still exist for these direct writing methods. Omnidirectional printing relies on the precise motion control of the printing head and a perfect match between the target surface and the printing quality can be affected if there is a mismatch between the actual surface and the moving path of the printing head. High-resolution scanning of the target surface is necessary for other arbitrary surfaces. The design of ink formulations and the exploration of bending nozzles with specific angles are also needed to ensure successful dispensing of the ink onto the surface. Unlike other direct-write printing processes, aerosol jet printing is a non-contact process where the ink droplets are jet onto the target substrate through an aerodynamic process. Although aerosol jet printing has a larger tolerance for the working distance (i.e., the gap between the printing head and target substrate), the working distance variation can also exert influence on the uniformity of the printed features

²¹⁷, causing poorly defined edges and overspray ²¹⁸. Because it is an aerodynamic process, aerosol jet printing also suffers from the splash of sprinkles, which causes a fuzzy edge along the printed line. As a method to address the geometry variation in the target surface, an adaptive 3D printing method explores a closed-loop feedback system to automatically adjust the printing head position, which also allows the 3D printer to print conductive silver ink onto moving freeform surfaces ²¹⁶. However, the patterning accuracy and feature size are limited partially due to the requirement for the real-time high-accuracy scanning device. Furthermore, sintering of nanomaterials in the ink from these printing techniques often requires a high temperature. This is not compatible with the soft elastomeric substrates commonly used in stretchable/wearable electronics.

More importantly, most of these printing techniques have been explored for noble metal nanomaterials such as silver ^{217, 219}, copper ²²⁰, and carbon-based inks such as graphene ²²¹. The electronic waste that has been generated as a direct result of these techniques has been increasing at an accelerated rate every year. This is causing environmental concerns and health issues as they penetrate into our ecosystem²²². As a potential solution to mitigate or eliminate the electronic wastes, transient or degradable electronics can safely dissolve in water or biofluids with environmentally friendly and biologically safe end products after their function. The demonstrated fully degradable electronics include antennas ²²³, printed circuit boards (PCBs) ²²⁴, epidermal sensors ²²⁵, implantable sensors ²²⁶, supercapacitors ²²⁷ and therapeutic devices ²²⁸. This class of emerging electronics relies on a set of degradable functional materials, including conducting materials, semiconducting materials, insulating and dielectric materials. Transient metals (e.g., Zn, Mg, Mo and W) are among the most popular composition for conductors due to their good electrical conductivities and fast water dissolution rates ⁹. Zn is an important trace metal accounting for various biological functions in the human body, it has been reported to serve as the conductive material for constructing transient electronics²²⁵. While fabrication of transient electronics has been attempted on flat substrates either with lithographic processes or printing approaches, ^{211, 229} direct writing of transient electronics on the arbitrary freeform surface has never been achieved to the best of our knowledge.

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Here we present a novel approach to directly fabricate electronics on freeform surfaces through the use of intense pulsed light-induced mass transfer (IPLMT), leveraging the evaporation-condensation effect of Zn nanoparticles ²³⁰ and intense pulsed light sintering ²³¹. The fabricated conductive Zn pattern can be used as conductive traces, interdigitated electrodes, sensing components, or antennas as building blocks for transient electronics on 3D freeform surfaces. Applying an encapsulation layer on top of the transient circuits can help program the operation timeframe before their functional degradation. The transient circuits can also be conveniently converted into long-lasting circuits with noble metals such as Ag or Cu through a single replacement reaction by immersing the circuits into copper sulfate or silver nitrate solution followed by photonic sintering. The simple replacement process can also result in a higher conductivity in the long-lasting circuits compared to that of the transient ones. The IPLMT with high-fidelity and versatility has been demonstrated by constructing various types of sensors onto freeform surfaces. Examples include glass beakers for smart Internet-of-Things (IoTs) and seashells for integration on complex biological surfaces.

5.2 Results and discussion

5.2.1 Investigation of the effect of process parameters

As shown in **Figure 5-1**, exposure of the Zn nanoparticles (Zn NPs) to the intense pulsed xenon light (IPL) can cause light-induced heating and increase their temperature to result in mass transfer and deposition of Zn layer on the target surfaces (**Figure 5-1a**). Immersing the Zn patterns into a copper sulfate (CuSO₄) or silver nitrate (AgNO₃) solution can further convert the zinc layer into a long-lasting copper or silver layer with good conductivity after an additional photonic sintering process (**Figure 5-1b**). Such a deposition method can be used to prepare functional circuits not only on planar surfaces but also on 3D freeform surfaces such as seashells (**Figure 5-1c**). In brief, after applying the temporary carrier layer with the Zn NPs ink over a shadow mask pliably laminated on a freeform surface (e.g., 3D objects or complex biological

surfaces), various types of sensing circuits (either transient or long-lasting) can be directly fabricated in a fast and convenient way. Smart IoTs, a network of physical objects with embedded electronics, sensors, or software that can communicate with each other, is becoming morepopular as the IT revolution continues to shape the world ²³². Smart IoTs with the ability of sensing, actuating, controlling and responding can find wide applications in transport, healthcare and energy ²³³⁻²³⁵. The proposed fabrication technique is well suited to prepare sensing, communicating and even energy harvesting units on various kinds of objects with complicated shapes. The influence of various process parameters during the IPLMT of Zn was first investigated through the fabrication of Zn patterns onto a flat target surface. The fabrication of conductive Zn patterns starts with the preparation of Zn NPs ink by dispersing Zn NPs in ethanol with the help of polyvinylpyrrolidone (PVP) surfactant. As a widely used surfactant for metal nanoparticle, PVP can stabilize nanoparticles in the solvent to prevent aggregation ²³⁶. Without the addition of PVP, the sedimentation of Zn NPs occurs in ethanol (Figure D-1). Before depositing the Zn NPs ink on the temporary carrier layer, the surface of the temporary carrier layer needs to be exposed to the UV-ozone treatment for enhanced wettability. Without the UVozone treatment, the Zn NPs ink deposited on the PI film exhibits significant non-uniform distribution due to the coffee ring effect (Figure D-2a). In contrast, UV-ozone treatment of the PI thin film substrate for 5 mins can modify the surface wettability to facilitate a relatively uniform distribution of Zn NPs ink on the PI thin film with a thickness of 8 µm (Figure D-2b). After ethanol fully evaporates, a thin layer of Zn NPs forms on the PI film (Figure 5-1a-ii). To generate a specific pattern on the target substrate (e.g., glass slides), a thin-film shadow mask (e.g., dumbbell shape) prepared by laser cutting of Kapton tape is sandwiched between the glass slide and the PI temporary carrier layer with the Zn NPs ink facing inward (Figure 5-1a-iii). Next, turning on an intense pulsed light instrument (Xenon light X-1000, Xenon Corp Inc) generates a strong light exposure to the Zn NPs through the temporary carrier layer within 100 µs. The short period of exposure of the Zn NPs to the high-intensity light transiently raises their local temperature to be above their melting point, causing the evaporation of Zn beneath its surface

oxide (i.e., ZnO shell) possibly through the cracks on the ZnO shell ²³⁰. The evaporated Zn atoms then transport through the opening in the patterned shadow mask and condense at the surface of the glass slide (**Figure 5-1a-iv**). Removing the Kapton shadow mask and the temporary carrier layer completes the fabrication of the conductive Zn pattern on the surface of the target substrate.



Figure 5-1 Schematic and demonstration of directly fabricating transient and long-lasting devices on planar and freeform substrates. (a) Schematic illustration of the fabrication process to deposit the transient Zn layer through the intense pulsed light-induced mass transfer (i) After adding the zinc nanoparticles (Zn NPs) to ethanol with (IPLMT) process. polyvinylpyrrolidone (PVP) surfactant to prepare the Zn NPs ink, (ii) dispensing the Zn NPs ink onto UV-ozone treated polyimide (PI) thin film yields a uniform coated temporary carrier layer. (iii) After applying the temporary carrier layer onto the target surface with the Zn NPs layer facing the target substrate with a sandwiched shadow mask, (iv) the intense pulsed light induces the mass transfer of Zn from the temporary carrier layer to the target substrate. (v) Removal of the shadow mask and temporary carrier layer finishes the fabrication process. (b) The transient Zn-based sensing device can be converted into a long-lasting device through a single replacement reaction of Zn with Ag or Cu formed on the 3D freeform surface such as a glass vial, by immersing the transient Zn-based device in a saturated AgNO₃ or CuSO₄ solutions. The Cu layer can also be selectively coated with another Ag NPs ink layer, followed by a photonic sintering with the same intense pulsed light. (c) Multifunctional sensing circuits can be directly fabricated on a complicated 3D freeform surface such as a seashell.

Such a simple yet versatile method can conveniently and quickly evaporate conductive

Zn patterns onto various types of substrate surfaces, including glass slides, polystyrene (PS) petri

dishes, polyethylene terephthalate (PET) thin films, and PI thin films (Figure 5-2a). The

temporary carrier layer is critical because its transparency and thermal properties will affect the actual photonic energy absorbed by Zn NPs and the local temperature of Zn NPs, respectively. Since the local heating of the Zn NPs is strongly associated with the photonic energy absorbed by the Zn NPs, the energy of the IPL is also a key parameter in the process. Because of its effects on the absorbed photonic energy and heat conduction, the concentration of Zn NPs in the Zn NPs ink may also play an important role through its influence on the layer thickness of Zn NPs on the temporary carrier layer. As the electrical conductivity is key to the conductive circuits and resistance-based sensors, we first investigate the effect of these three parameters on the electrical conductivity separately in the experiment. The calculation of the electrical conductivity of IPLMT-evaporated Zn layer is based on its electrical resistance value and dimension parameters. After evaporating the Zn pattern in a dumbbell shape with a neck width of 4 mm and a neck length of 10 mm on the target substrate by the IPLMT method, its resistance is measured by a digital multimeter. An optical profilometer (Zygo) scans the thickness and confirms the width of the Zn pattern (Figure D-3). The effect of the temporary carrier layer on the electrical conductivity of Zn pattern is demonstrated through the use of three different temporary carrier layers, namely PI films of 8 μ m, PI films of 12 μ m, and PET films of 3 μ m (Figure 5-3, 10 samples in each group). As the xenon light energy gradually increases from 1800 J to 2400 J, the electrical conductivity of the evaporated Zn layer on the PI thin films of 8 µm increases from 0 S/m to 3.2×10^5 S/m. Because of the significant high local temperature even just at the Zn/PI interface, the PI thin film of 8 µm slightly crumples from an initially flat shape after the xenon light exposure (Figure D-4a). In contrast, the PI films of 12 µm are unable to generate the conductive Zn pattern at all levels of xenon light energy, possibly due to the significantly attenuated photonic energy from their larger thicknesses and increased opacity and heat capacity compared to PI films of 8 µm. This postulation is further confirmed by the observation that the Zn NPs layer on the PI films of 12 μ m remain unchanged after the IPL exposure (Figure D-4b). The significantly attenuated photonic energy from the temporary carrier layer can result in a lower local temperature of the Zn NPs such that the evaporation of Zn atoms is not favorable.

While the clear PET films of 3 μ m are associated with increased light transmittance and decreased heat capacity, no successful Zn evaporation appears over the wide range of xenon light energy, and the PET thin film is burned into ashes when the xenon light energy level is above 2200 J (**Figure D-4c**). Such unsuccessful results may be ascribed to the significant low glass transition temperature of the PET compared to that of the PI²³⁷.



Figure 5-2 Zn thin layers with dumbbell shapes are successfully evaporated onto different types of substrates, including (i) glass slides, (ii) polystyrene (PS) petri dish, (iii) polyethylene terephthalate (PET) thin film, and (iv) PI thin film.



Figure 5-3 Calculated conductivity of the thin Zn layer evaporated onto glass slides from different types of temporary carrier layers, where only the thin PI temporary carrier layer with a thickness of 8 µm yields successful Zn evaporation with a gradually increased conductivity as the exposure energy from xenon light increases.

The investigation of the effect of Zn NPs concentration involves the use of the Zn NPs ink with three different Zn NPs concentrations (i.e., 20%, 25%, and 30%) prepared and dispensed on the PI film of 8 μ m. Gradually increasing the power of the xenon light results in increased conductivity of the deposited Zn layer for all three types of Zn NPs ink. The Zn NPs ink with a concentration of 25% or 20% exhibits a significantly higher conductivity than that of 30% (**Figure 5-4a**). Such a phenomenon may result from the difference of the Zn NPs layer thickness. As the concentration increases, the thickness of the Zn NPs on the PI thin films would likely

increase at the same time. Because the photonic energy is mainly absorbed by the Zn NPs close to the Zn/PI interface, a thicker Zn NPs layer impedes the escape of Zn atoms from inside to the top surface. To further verify this hypothesis, Zn NPs layers with different thicknesses are used for the IPLMT process by applying different numbers of drops (1, 2, and 3, with a volume of ??? in each drop) of the Zn NPs ink with a concentration of 25% on the temporary PI carrier layer. The Zn NPs layers formed by two or three drops of the ink are not able to generate conductive Zn pattern even when the xenon light energy is increased to the maximum (Figure D-5a). While the highest conductivity of the Zn layer from the IPLMT process (i.e., 3.5×10^5 S/m) is about 2% of its bulk counterpart (i.e., 1.81×10^7 S/m), it is already 15% of sputtered Zn (2.3 x 10⁶) and 35% of E-beam evaporated Zn (1 x 10^6) (Figure D-5b). Such a conductivity of the Zn layer from the IPLMT process ranks top among other fabrication processes for Zn based transient electronics (Table D-1). Nevertheless, no significant difference of conductivity is observed for the Zn layers deposited onto a variety of different target substrates, including glass, PS, PET, and PI, indicating the versatility of the IPLMT process (Figure 5-4b). In summary, the above results indicate that the IPLMT of Zn is a fast and simple method for fabricating Zn-based transient electronics, which addresses the challenges from lithographic processes and printing approaches. In the following discussion, the Zn NPs ink with a concentration of 25 wt% on the temporary PI carrier layer of 8 µm exposed to a xenon light energy of 2400J is used in the IPLMT of Zn for device fabrication unless otherwise specified.



Figure 5-4 (a) Calculated conductivity of the thin Zn layer evaporated onto glass slides from the Zn NPs inks with different concentrations of Zn NPs. (b) The conductivity of the Zn layer

evaporated to different types of target substrates is ca. 3 X 10^5 S/m, showing negligibly small differences among target substrates.

The dissolution of the Zn from the IPLMT process is first investigated to reveal its functional degradation. The demonstration involves the use of a glass vial as the target surface. Because the dissolution rate of Zn is relatively fast, the Zn-based electronics can only operate for less than hours before breakdown after their immersion in water. Though such a quick dissolution process makes Zn an ideal material candidate for devices with temporary use purposes, additional encapsulation layer provides programmed lifetime for different applications. As a demonstration, Zn-based resistors are fabricated with the IPLMT on the outer surface of a glass vial, with one encapsulated by a water barrier layer (e.g., PDMS or other degradable polymers) and the other without encapsulation. After the resistors are immersed in water at the room temperature, their resistances are constantly monitored by a digital multimeter to inform the degradation process (Figure D-6a). While the Zn-based resistor without encapsulation can only function for ca. 40 mins after immersion in water (followed by a gradual increase in the resistance to indicate its breakdown), the resistor with encapsulation shows negligible resistance change during the test (Figure D-6b). Easy removal of the Zn-based sensors (without encapsulation) is also demonstrated by wiping off the sensor with gloves after taking it out from the water (Figure **D-6c-d**). While the PDMS layer is used as an encapsulation layer in this demonstration, it can be easily replaced with other transient or biodegradable thin films, whose thickness or choice can help program the operation time of Zn-based transient electronics⁴. The transient sensors based on the Zn from the IPLMT process exhibit high-fidelity performance, comparable with their commercial counterparts. The demonstrated examples include sensors and electrodes to monitor electrophysiological signals such as electrocardiogram (ECG) and electromyogram (EMG). After depositing the Zn pattern from the IPLMT process on polyvinyl alcohol (PVA) thin films, the sensors can be pliably attached to the skin surface. The pliable attachment with a strong adhesion is achieved through a partial dissolution and softening of the PVA thin film to conformally adhere to the textured skin surface. The successful deposition of the Zn on the PVA thin film changes its surface roughness, as shown by SEM images of before and after the deposition (Figure D-8-a-b).

The partial dissolution of the PVA beneath the transient electrodes indeed replicates the microstructures of the skin surface (**Figure D-8c**), further confirming the conformal contact between the electrode and skin. The improved contact quality at the electrode/skin interface ensures a good signal-to-noise ratio (SNR) for both ECG and EMG signals (19.74 and 8.52, respectively) (**Figure D-7**). After use, the transient sensor easily detached from the skin surface slowly dissolves in water and completely disintegrates after 24 hours of soaking at the room temperature (**Figure D-9**).

5.2.2 Fabrication of electronics on a smooth surface for smart IoTs

Though the thickness and choice of the encapsulation layer can program the operation time for Zn-based transient electronics, demand still exists for long-lasting electronics on a 3D freeform surface for smart contact lens, smart IoTs, and non-planar devices ²¹³. As a step toward such a need, we then demonstrate the viability of the IPLMT process to pattern noble metal such as copper (Cu) and silver (Ag) on a 3D freeform surface. However, this seems challenging because the IPLMT of Cu or Ag is not successful when Zn NPs inks are switched to Cu NPs or Ag NPs. The unsuccessful evaporation of the Ag and Cu NPs by the IPLMT may likely result from the elevated melting temperatures of Ag of > 1200 K 238 and Cu of > 825 K 239 compared to that of Zn of > 700 K when they have similar size (~70nm). In order to address this seemly challenging task, the single-replacement reaction has been explored to replace the evaporated Zn layer with Ag or Cu. As a demonstration, the patterned Zn layer is first prepared onto a glass beaker by the IPLMT method. The substitution of Zn with Ag or Cu has then been achieved by immersing the target substrate with Zn patterns in the saturated silver nitrate (AgNO₃) and copper sulfate (CuSO₄) solution for 1 minute. While the Zn pattern can be successfully replaced by Ag or Cu, a significant resistance increase is observed, possibly due to the loose interconnection between the Ag or Cu dendrite formed during the single replacement reaction. Such a compromised conductivity is not favorable in constructing conductive traces for long-lasting electronics. Because photonic sintering with intense pulsed light has been widely used to induce rapid heating of metal NPs and nanowires ²⁴⁰⁻²⁴¹ for sintering, the same setup used for the IPLMT process can be used for photonic sintering of the formed Ag or Cu dendrite ²⁴². In fact, photonic sintering of the replaced Ag layer by a xenon light energy of 900 J has successfully decreased the resistance by three orders of magnitude (from ~ 2.0 M Ω to ~ 2.5 k Ω) (Figure 5-5).



Figure 5-5 Resistance evolution of the conductive lines from the Zn layer to intermediate substituted Ag or Cu layer and finally to the sintered Ag layer. Scanning electron microscopy (SEM) images of the PI temporary carrier layer.

Other than direct sintering of the noble metal dendrite, coating of the Ag NPs ink (JS-A191, Novacentrix) on the replaced Cu layer can also be achieved through a picoliter dispenser (Microplotter, Sonoplot) due to the increased wettability (**Figure D-10**) of the Cu dendrite layer. Sintering of the coated Ag NPs ink on top of Cu results in resistance of less than 10 Ω that is much lower than the original Zn layer and the replaced Ag layer. To help reveal the underlying mechanism behind the IPLMT process and the subsequent replacement reaction, scanning electron microscope (SEM) images have been taken for both the temporary PI carrier layer and the target surface. Compared to the solid Zn NPs before their exposure to intense pulsed light (**Figure 5-6a**), hollow spheres of the NPs observed (**Figure 5-6b**) on the temporary PI carrier layer after the IPLMT process imply the evaporation of the Zn in the core of the NPs beneath their native oxide shells.



Figure 5-6 Scanning electron microscopy (SEM) images of the PI temporary carrier layer (a) before and after (b) IPLMT of Zn, which highlights hollow spheres of Zn NPs on the PI temporary carrier layer post exposure to intense pulsed light.

In addition to Zn on the glass (i.e., Zn and Si signals), carbon (C) is also observed on the target glass substrate as shown in the energy-dispersive X-ray spectroscopy (EDX) mapping (**Figure 5-7a**), possibly due to the decomposition of the PI thin film. The Zn evaporation and PI decomposition also partially support the existence of transient high temperature at the Zn/PI interface. After immersion of the Zn layer in the CuSO₄ solution, the Cu layer is then confirmed by the EDX with the C layer remaining on the glass (**Figure 5-7b**). Following the coating and photonic sintering of the Ag NPs ink, a conductive single line a width of 200 μ m exhibits well-defined edges for the composition of C, Cu, and Ag. The well-defined feature at the edge comes from the significant difference in surface wettability between the replaced Cu layer and its surrounding area of glass for spontaneous wicking of the Ag NPs ink (**Figure 5-7c**).



Figure 5-7 SEM and energy-dispersive X-ray spectroscopy (EDX) images of (a) the Zn layer evaporated on glass vial, (b) the Cu layer formed by a single replacement reaction in the evaporated Zn layer in the CuSO4 solution, and (c) the Ag layer further formed by coating Ag NPs ink on the Cu layer followed by a photonic sintering.

A system level demonstration of the multifunctional electric circuit on a 3D glass beaker consists of a dipole antenna, electrodes for ECG measurements, humidity sensor, temperature sensor, and their corresponding pads for connection. After laminating the kirigami-patterned soft semi-transparent PI film with Zn NPs on both the bottom and side surfaces of the glass beaker, carrying out multiple exposures through the IPLMT of Zn deposits Zn onto both the bottom (Figure 5-8a) and sidewall (Figure 5-8b) of a glass beaker. A follow-up Ag NPs replacement and photonic sintering process further converts the transient Zn device into the long-lasting Ag device, resulting in a smart beaker. The performance of each sensing element in the multifunctional circuit compares favorably against their commercial counterparts. Contact impedance between the electrodes and human skin is first analyzed by an LCR meter (Hewlett Packard 4284A) from 20 Hz to 2 MHz (Figure 5-8c). When compared to the commercial gel electrodes, a higher contact impedance is observed from the electrodes, which is consistent with previous literature reports on metal-based ECG electrodes ²²⁵. Placing two thumbs on the electrodes on the 3D glass beaker enables the real-time monitoring of the ECG signal from the human subject through a data acquisition system (ADInstruments). A comparison of the ECG signals collected from the smart beaker and commercial gel electrodes attached to the wrist of the

human subject indicates a slight baseline shift from the former, likely ascribed to the changing contact impedance at the electrodes/thumbs interface (Figure 5-8d). Though the ECG signal from the smart beaker exhibits a slightly smaller signal-to-noise ratio (SNR) compared to that of the commercial gels, the PQRST wave is still evident and sufficient for clinical diagnostics. The humidity sensor on the smart beaker involves the use of ZnO NPs drop-cast on an interdigitated electrode (IDE). Calibration and testing of the humidity sensor have been accomplished by placing the smart beaker inside a controlled chamber with a given relative humidity (RH) level (i.e., 49% RH, 55% RH, 59% RH, 66% RH, or 72% RH) for 2 minutes. The humidity sensor on the smart beaker linearly increases with the increasing RH level with a sensitivity of 0.51%/RH% (Figure 5-8e). The humidity sensor also exhibits a good response ($\sim 2 \text{ min}$) and fast recovery rate (< 20 s) at the room temperature (Figure 5-8f). The Ag-based resistance temperature detector (RTD) on the smart beaker can also conveniently measure the water temperature in the glass beaker. After obtaining the linear calibration curve between the RTD resistance and the temperature by filling the beaker with hot water (Figure 5-8g), the RTD can detect the temperature change as hot water is poured into the beaker and keep track of the cooling process (Figure 5-8h). In addition to its future use for wireless communication and RF energy harvesting, the antenna located at the middle of the sidewall on the smart beaker is also able to detect the level of water in the beaker. The resonance frequency of the dipole antenna shifts to a lower value as water is filling up the beaker (Figure 5-8i) due to the change of the permittivity in the dielectric environment.



Figure 5-8. Multifunctional sensing circuits fabricated on the sidewall and bottom surfaces of a glass beaker toward smart Internet-of-Things (IoTs). Photographs of (a) multifunctional Ag-based sensing circuits on the sidewall and (b) their contact pads (for external connections) patterned on the bottom surface of the glass beaker. A: antenna; H: humidity sensor; T: temperature sensor; E: electrode to measure electrophysiological signals. (c) Contact impedance measured by the Ag electrodes and gel electrodes that are in contact with two thumbs from a human subject. (d) Comparison of the electrocardiogram (ECG) signals captured by Ag electrodes on the beaker and commercial gel electrodes. (e) Sensitivity of ZnO-based humidity sensor and (f) its representative humidity sensing curve. (g) Calibration curve of the Ag-based temperature sensor and (h) its recorded temperature change of the glass beaker after the addition of hot water. (i) Shift in the resonance frequency of the dipole antenna (red) and then to completely immerging the dipole antenna (blue).

5.2.3 Fabrication of electronics on complicated biological structure

Though the successful fabrication of circuits on a 3D glass beaker demonstrates the potential of IPLMT for smart IoTs, the application of IPLMT on biological surfaces can still be challenging due to their complicated surface morphologies. Biological surfaces that have been

91 explored to integrate sensing circuits include flower pedals²⁴³, leaves²⁴⁴, and wood²⁴⁵. The applications for directly fabricating circuits on these biological surfaces range from environmental monitors to devices with wireless communication modules. By using a leaf sensor, farmers would be able to track the biochemical processes of their crops in real time²⁴⁴. Many industries could also benefit from ultra-high frequency (UHF) radio frequency identification (RFID) tags fabricated on wood to allow for battery-free tracking of objects.²⁴⁵ As a good candidate for biological structures, seashells are selected here to demonstrate the feasibility and performance of the IPLMT process on complicated freeform surfaces. The same set of transient Zn circuit components as above has been fabricated on the complex surface of a seashell using the IPLMT method. Due to the complicated shape of the seashell and large curvatures, the shadow mask based on a thermal release tape double layer does not conform on the surface of the seashell due to the compromised flexibility of the thermal release tape with a large thickness. To ensure good contact between the shadow mask and seashell, the Kapton tape is retrieved from the thermal release tape to reduce the thickness before application to the surface of the seashell. Figure 5-9a shows the photograph of the Zn layer deposited on the surface of a seashell. The granular morphology of the Zn deposited by the IPLMT process is similar to that of Zn from sputtering or e-beam evaporation (Figure D-11). Since the seashells have numerous grooves on their surfaces (Figure D-12), selective wetting of the Ag NPs ink on the seashell surface is not successful due to the uncontrollable flow of the Ag NPs ink along the grooves. The single replacement reaction of Zn in the AgNO₃ solution is explored to convert the Zn pattern into Ag, followed by photonic sintering (Figure 5-9b). As observed in the SEM images, densification of the sintered Ag in the formed large silver films exhibits a similar morphology as those thermally sintered ²⁴⁶. To verify the functionality of the Ag-based circuit directly patterned on the seashell, the performance of a gas sensor based on an IDE and a temperature sensor has been examined. The gas-sensitive MoS₂@rGO composite nanomaterial synthesized by the solvothermal method as described previously²⁴⁷ is dispensed on the IDE to construct a NO₂ gas sensor. The responses of the gas sensor gradually increase as the concentration of NO_2 increases

from 1 to 4 ppm at room temperature (**Figure 5-9c**). The slow and relatively incomplete recovery of the signal can be addressed by adding a heating element to increase the working temperature of the MoS₂@rGO sensing material, as in our previous work²⁴⁸. A polynomial fitting curve with a diminishing slope toward a higher concentration of NO₂ agrees well with the power law of chemiresister-based gas sensors (**Figure 5-9d**). The temperature sensor with a sensitivity of 0.055 Ω /°C can track the heating and cooling of the seashell by an air blower (**Figure 5-9e**). The seashell is first placed at the room temperature for 1 min before blowing hot air. A sharp increase and a slow decline of the seashell temperature are observed during the hot air blowing of 1 min and the cool down process of 2 minutes, respectively. The blowing of cool air for 1 min after the natural cooling process further decreases the temperature of the seashell. Both the gas sensor and the temperature sensor show more fuzzy signals compared to their counterparts fabricated on the glass beaker. It is highly possible that the reduced or non-uniform conductivity of the Ag conductive trace formed by the single-replacement reaction introduces a higher level of noise relative to the signal, causing degraded performance of the sensors.



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Figure 5-9. Multifunctional sensing circuits patterned on a seashell as a representative biologically complex surface. (a) (i) Optical image and (ii) SEM image of the Zn layer patterned on the seashell with (iii) the magnified SEM image showing the granular shape of the deposited Zn. (b) (i) Optical image of the Ag layer formed on the seashell by a single-replacement reaction after immersing the Zn-based device in a saturated AgNO₃ solution. (ii) SEM image and (iii) its magnified view to show the morphology of the Ag layer on seashell after photonic sintering and the large Ag film formed by the densification of Ag NPs. (c) Sensing response curve of the MoS₂@rGO-based NO₂ gas sensor follows the power law of chemiresistive gas sensors. (e) Temperature change of the seashell recorded by the temperature sensor during the heating and cooling processes of seashell induced by continuous air blowing.

5.3 Experimental procedure

5.3.1 Preparation of the Zn NPs inks

PVP of 0.0025 g was first added to ethanol of 2 g in a glass vial followed by a 15 min sonication to thoroughly dissolve the PVP. After the PVP was fully dissolved in ethanol, Zn NPs (35-45 nm, US Research Nanomaterials) of 0.5 g was added into the glass vial with sonication to ensure good dispersion of Zn NPs in the solvent, yielding the Zn NPs ink of 25 wt%. The Zn NPs inks with other concentrations of Zn NPs or Zn NPs without PVP were prepared using the same procedure with corresponding concentrations of Zn NPs or without the addition of PVP.

5.3.2 Preparation of the PVA substrate

The PVA thin film substrate was first prepared by dissolving PVA powder of 3 g (Sigma-Aldrich) in deionized water of 27 g, follow by stirring for 2 hours at 70° C and then tape casting on glass slides. The doctor blade coating was used to control the thickness of the PVA thin film to be 40 μ m. Placing the film at room temperature for 2 hours fully evaporated the water and cured the PVA thin film.

5.3.3 IPLMT of Zn thin film on flat surface

Target substrates (e.g., glass, PS, PET, PI, or PVA) were first cleaned with ethanol before the IPLMT process. Next, the Zn NPs ink was applied onto the temporary carrier layer (i.e., 3 µm-thick PET, 12 µm-thick PI, and 8 µm-thick PI films) after the temporary carrier layer was exposed to UV-ozone (UV10 Ozone cleaner system, Novascan Technologies, Inc) for 5 mins. After aligning the temporary carrier layer with the target substrate, a height-adjustable stage was used to bring the samples close (<1 cm) to the xenon light (X-1000, Xenon Corp, Inc) for IPLMT.

5.3.4 SEM imaging

SEM images were taken by Verios XHR SEM (Thermal Fisher Scientific, Inc). Iridium layer of 5 nm was coated on the top surface of the samples to prevent the potential charging effect.

5.3.5 Fabrication of sensing circuits on glass beakers

A shadow mask was first fabricated by patterning a Kapton tape with a commercial CO2 laser (Universal Laser Systems). Briefly, a Kapton tape with a thickness of 25 µm and the adhesive facing outward was carefully aligned on the thermal release tape (REVALPHA, Nitto) to avoid trapped air bubbles. The thermal release tape functioned as a temporary substrate to keep the Kapton tape flat during the laser patterning process. After generating a predefined pattern in AutoCAD, a CO2 laser (power: 7%, speed: 4%) was used to pattern the Kapton tape. Peeling off the excessive region yielded the shadow mask. Next, the Kapton shadow mask was taped onto the glass beaker. Heating the thermal release tape with a hot air blower left the shadow mask onto the target substrate and completed the transfer printing process of the shadow mask. After fixing the Zn NPs ink on the PI temporary carrier layer over on the Kapton shadow mask on the glass beaker with tapes, xenon light was applied to initiate the IPLMT of Zn NPs. Removal of both temporary carrier layer and shadow mask finished the IPLMT of Zn. The substitution of Zn with Ag or Cu was achieved by immersing the Zn pattern on the glass beaker into saturated AgNO3 or CuSO4 solution for 1 min. After converting the Zn into Cu through the single replacement reaction, a picoliter dispenser (Microplotter II, Sonoplot) was used to selectively coat the conductive pattern with AgNP ink due to its enhanced wettability. The glass tip with a diameter of 20 µm attached to a piezoelectric motor from the Microplotter ensured both precise control of the contact location and continuous flow of AgNP ink. Photonic sintering (energy: 900J) was then used to fully sinter the coated AgNP to yield the final functional sensing circuit on the glass beaker.
5.3.6 Fabrication of sensing circuits on a seashell

The Kapton shadow mask was first fabricated following the same procedure as previously described. A small amount of ethanol was applied to the surface of the seashell before placement of the shadow mask that was first retrieved from the thermal release tape. The surface tension between the ethanol solution and shadow mask helped bring the shadow mask to the proximity of the seashell surface after the ethanol solution was fully evaporated. The same IPLMT process as described above was then applied to generate the functional Zn pattern on the seashell.

5.3.7 Testing of the temperature/humidity sensor, electrodes for measuring electrophysiological signals and dipole antenna

The sensors were first connected to conductive copper traces through the conductive silver paste. Calibration and testing of the temperature sensor and humidity sensor were achieved by connecting the copper traces to a digital multimeter (Keithley 2401) through alligator clips. Data acquisition software (I-V software) acquired the resistance values from the digital multimeter and recorded them in computers. The electrophysiological signals (e.g., ECG or EMG) were acquired from the electrodes by a commercial biological data acquisition system (Bioamp, ADInstruments). The S-parameters (e.g., return losses S11) of the antenna were measured by a vector network analyzer (Keysight E5071C) and the resonance frequency of the dipole antenna was determined from the S11 curve.

5.4 Conclusions

We have reported a novel IPLMT process to deposit Zn for constructing transient circuits onto various types of flat and non-flat 3D freeform surfaces. After elucidating the effect of various processing parameters on the performance of the IPLMT Zn, the optimal set of parameters has been identified to yield highly conductive Zn patterns for fabricating electronics on 3D complicated surfaces. The single-replacement reaction and/or selective coating of the Ag NPs ink has also been explored to convert the patterned Zn layer into long-lasting Cu or Ag. The versatility of this powerful method has been showcased through a system level demonstration with electronics that include antennas, electrodes, temperature sensors and gas sensors on 3D surfaces for smart IoTs and integration on complicated biological surfaces. This novel method can generate circuits on complicated surfaces with well-controlled yet small feature sizes, overcoming several obstacles faced by traditional lithographic processes or various advanced printing approaches. As a result, the IPLMT process possesses a huge potential to create novel transient and long-lasting devices and systems for applications in a variety of fields including optoelectronics, telecommunication and medicine.

Chapter 6

Concluding remarks

Different than traditional sensors that are bulky, rigid, and undeformable, wearable electronics with stretchability are compatible with the soft human tissues. Various stretagies have been explored to build stretchable sensor circuits on human skins. The future application of such on-skin, deformable, and light-weight wearable sensors ranges from motion tracking to personalized healthcare. Finding low-cost and easy-to-implement fabrication methods for wearable electronics is therefore important for the future commercialization of wearable electronics. The key findings of this thesis are summarized as follows:

1. Discovered a new water soluble substrate (Galactomannan film extracted from plant endosperm) and demonstrated the feasibility of building a transient multifunctional sensor pad to capture key physiological information from human skin.

2. Designed and fabricated a stretchable gas sensor based on $MoS_2@rGO$ nanocomposites with high sensitivity, selectivity, good selectivity, and fast response/recovery rate. The room temperature NO_2 detection capability and the stretchability of the gas sensor can be applied to human skin, with a robust sensing performance even under stretched conditions.

3. A further simplified structure of stretchable gas sensor with self-heating capability based on laser-induced graphene was proposed and verified by experiments. The self-heating function of the gas sensor can significantly improve the response/recovery rate of the gas sensor. Strain isolation layer between the sensing element and soft substrate can ensure minimal strain can be introduced to the gas sensor.

4. Developed a new fabrication method for direct printing of functional circuits on complicated 3D surface. The fast, convenient, and versatile method enables by the photon-induced evaporation of zinc is promising for future Internet-of-Things applications.

Appendix A

Supplementary Materials for Chapter 2



Figure A-1. (a) Optical image of temperature sensor array. (b) Bending of the temperature sensor array. (c) SEM image of sputtered zinc thin layer on galactomannan film. (d) SEM image of e-beam evaporated zinc thin layer on galactomannan film. (e) SEM image of individual temperature sensor fabricated through e-beam evaporation. The inset shows the detail of the zinc traces.



Figure A-2. (a) Circuit diagrams of the four by four temperature sensor array and the multiplexing circuit. (b) Photo of the experimental setup of the multiplexing circuit with a voltage source and a heater.



Figure A-3. Resistance measurement of the Zn electrode subject to a compresive strain (0-30 %) to induce bending with different radii of curvature. Negligible resistance change (< 2 %) was observed upon bending.



Figure A-4. (a) EMG signal from Zn electrode and Gel electrode after 15 days storage of the zinc electrodes. **(b)** ECG signal from Zn electrode and Gel electrode after 15 days storage of the zinc electrodes. The baseline drift of the ECG signal is more severe compared with the signal collected from fresh electrodes. A magnified view of the signal is shown in the inset.



Figure A-5. (a) Impedance between the Zn (or Cu) electrodes and the skin surface, measured after 15 days of its fabrication. The result was compared to that measured from the commercial gel electrode. **(b)** Contact impedance as a function of frequency for commercial gel electrode with different sizes. Small electrode size yields a higher impedance value.



Figure A-6. (a) EMG signals from Cu electrode and Gel electrode. **(b)** ECG signals from Cu electrode and Gel electrode. Baseline drift of ECG signal is more obvious from Cu electrode. A magnified view of the signal is shown in the inset.

Supplementary Materials for Chapter 3



Figure B-1. SEM images of (a)pure MoS_2 , (b) rGO/MoS₂ synthesized without the addition of NaCl salt, (c) rGO/MoS₂ synthesized with addition of as received NaCl salt crystals, (d) rGO/MoS₂ synthesized with addition of NaCl salt crystals ball milled at 300 rpm for 5 mins, and (e) rGO/MoS₂ synthesized with addition of NaCl salt crystals ball milled at 400 rpm for 10 mins.



Figure B-2. SEM images of different sizes of the NaCl crystals. (a) As-bought NaCl crystal. **(b)** The ball-milled (300 rpm, 5 min) NaCl crystals. **(c)** The ball-milled (400 rpm, 10min) NaCl crystals.



Figure B-3. Fabrication process of the interdigitated electrode (IDE) on the cover glass. (i) The cover glass is rinsed by ethanol. (ii) Applying PI tape onto clean cover glass. (iii) Cutting pattern on PI tape with CO_2 laser. (iv) Peeling off the excessive region. (v) E-beam evaporating 100nm gold onto cover glass. (vi) Removing PI tape shadow mask. (vii) Drop casting sensing material onto IDE. (viii) Connecting IDE to source meter(SM).



Figure B-4. (a) Photograph of a gas sensor (gold) integrated with a heater (titanium). **(b)** Photograph of the gas sensor and heater fixed onto a homemade acrylic lid. **(c)** Photograph of the testing chamber (green box), source meter (red box), and direct current (DC) voltage source (blue box). **(d)** The temperature of gas sensor has a linear relation with the power of the heater.



Figure B-5. Effect of temperature on the NO₂ sensing performance of $MoS_2@rGO$ sensors fabricated with different confinement spaces: (a) With no fillers. (b) With Fillers. (c) With fine fillers. (d) With ultrafine fillers. The gas sensor operated at elevated temperature is associated with faster response and recovery, but smaller response. The highest response of the gas sensor at the room temperature indicates that its operating temperature is room temperature (All the samples are tested in 2ppm NO₂).



Figure B-6. Fabrication process of stretchable room temperature rGO/MoS_2 based NO_2 gas sensor. (i) Polyimide film. (ii) E-beam evaporation of Cr and Au. (iii) Lamination of polyimide/Cr/Au film onto "hard" PDMS (mixing ratio 10:1) with the Au layer facing down. (iv) Cover glass. (v) Coating of cover glass with "soft" PDMS (mixing ratio 20:1). (vi) UV laser cut the pattern of IDE and serpentine ribbons on the polyimide film. (vii) Peeling off the excessive part of the polyimide film yields the IDE and serpentine ribbons for the final assembly of stretchable gas sensor. (viii) Attaching the cover glass with "soft" PDMS contacting the polyimide film accomplishes the transfer of the patterned polyimide film from a silicon wafer to cover glass. (ix) Bonding the cover glass to a thick Ecoflex strip fixes the IDE. (x) Connecting the serpentine ribbons with IDE complete the fabrication process.



Figure B-7. NO_2 gas sensing performance of stretchable gas sensor to different concentrations (from 0.5 ppm to 2.5 ppm) at room temperature (a) before and (b) after stretching.



Figure B-8. Average response magnitude of 5 stretchable gas sensors to 2 ppm NO_2 before and after the cyclic deformation test.



Figure B-9. Sensing performance of rGO/MoS_2 gas sensor to H_2O vapor. The sensor was placed in a chamber with 90% relative humidity for the sensing process and placed in an ambient environment with 40% relative humidity for recovery. Three temperatures were achieved by tuning the power of the heater.



Figure B-10. Long-term stability of rGO/MoS_2 gas sensor. The sensing curve (a) and the response magnitude fluctuation (b) of stretchable rGO/MoS_2 gas sensor towards 2 ppm NO₂ over the period of 6 weeks.



Figure B-11. Repeatability test of rGO/MoS_2 gas sensors. The sensing curves of five different rGO/MoS₂ gas sensors show different response magnitude to 2 ppm NO₂.



Figure B-12. (a) Representative Raman spectrum of a LIG single line. **(b)** Resistance change of the LIG single line upon drop-casting of the rGO/MoS₂ composite synthesized with the addition of ultrafine NaCl fillers.

Appendix C

Supplementary Materials for Chapter 4



Figure C-1. Optical images of the gas sensor (a) bent over a cylinder with a radius of 5.53 mm and (b) attached to the back surface of the hand.



Figure C-2. XPS survey scan for (a) bare LIG samples and (b) LIG with the addition of rGO/MoS₂ synthesized with the addition of NaCl crystals (c) the Mo 3d doublet centered at the binding energy of 232 eV and 228 eV (d) the S 2p peak centered at 162 eV.



Figure C-3. Dependence of the temperature in the LIG electrode from self-heating on the input power, in which the solid black line assumes a constant resistance over time and the dashed red line uses the real-time resistance that decreased with the increasing temperature.



Figure C-4. Spatial distributions of the temperature in the LIG electrode from different self-heating conditions.



Figure C-5. Dependence of the resistance of the LIG electrode on its (a) length and (b) width. The solid red line in (a) represents the linear fit to the experimental data. Calculating the slope gave a sheet resistance of 78 Ω /sq.



Figure C-6. The gas sensing performance of pristine LIG lines to NO₂ of 1 ppm at 20 °C. Gas sensing response observed in the pristine LIG when (a) a power of 16 % and a speed of 10 % or (b) a power of 3% and a speed of 0.8 % was used in the laser scribing process. (c) The selectivity of the pristine LIG line in (b).



Figure C-7. The response of the MoS_2 -LIG gas sensor to NO_2 of 1 ppm at 20 °C.



Figure C-8. Comparison of the gas sensing performance between gas sensors with the big and small petal structures at (a) 20 °C, (b) 40 °C, and (c) 80 °C from self-heating.



Figure C-9. Comparison of the gas sensing performance for the LIG with the small petal structure between 20 °C and 80 °C with complete recovery time.



Figure C-10. Comparison of the angle of the plateau calculated from response curves of gas sensors with the big and small petal structures at 20 °C, 40 °C, 60 °C, and 80 °C from self-heating.



Figure C-11. Comparison of the SNR between gas sensors with the big and small petal structures at different temperatures from self-heating.



Figure C-12. Dynamic response test of the gas sensors with the big and small petal structures in the presence of NO_2 from 200 ppb to 600 ppb.



Figure C-13. Effect of the high relative humidity (RH) of 88 % on the response of the rGO/MoS_2 -LIG gas sensor at different temperatures.



Figure C-14. Stretchability of LIG gas sensor wih different designs (a) optical images of the setup for tensile test (upper) and three different PI substrate pattern(lower). (b) the averaged electrical resistance variation for different PI substrate designs under 20% tensile strain on both parallel and perpendicular direction with respect to the LIG single line. The resistance variation curves of LIG gas sensing device with (c) 20% tensile strain in the parallel direction and (d) 20% tensile strain in the perpendicular direction.



Figure C-15. STEM image (HAADF) of $Cu_2(nbdc)_2(dabco)$ -on- $Zn_2(nbdc)_2(dabco)$ metalorganic framework (MOF) with accompanying EDS spectrum images to show the elemental distribution. After calcination, the MOFs formed CuO-on-ZnO nanoparticles, where CuO shell was visible on ZnO core from the EDS spectrum images.


Figure C-16. (a) Response and (b) selectivity of the ZnO/CuO-LIG gas sensor, in which ZnO/CuO core/shell nanomaterials were dispersed on LIG.

Appendix D

Supplementary Materials for Chapter 5



Figure D-1. Effect of PVP on the stability of Zn NPs ink. Sedimentation occurs in the Zn NPs ink without the addition of PVP (left), whereas the Zn NPs ink with PVP remains homogeneous.



Figure D-2. Optical profilometer map of deposited Zn. Distributions of 10 μ L Zn NPs on the PI thin film (a) without and (b) with 5-min UV-ozone treatment.



Figure D-3. Optical profilometer map of deposited Zn. (a) Top view and (b) side view of a straight line of deposited Zn layer. (c) 2D height profile of the Zn layer obtained from the intersection labeled in (b).



Figure D-4. Optical images of the temporary carrier layer (i) before and (ii) after the xenon light exposure for (a) a PI layer with a thickness of 8 μ m, (b) a PI layer with a thickness of 12 μ m, and (c) a PET layer with a thickness of 3 μ m.



Figure D-5. (a) Dependence of the conductivity of the IPLMT deposited Zn layer on the thickness of the Zn NPs layer and **(b)** the comparison of the conductivity of the Zn layers deposited by different fabrication approaches (i.e., bulk, sputtered, and E-beam evaporated).



Figure D-6. Resistance measurement of the IPLMT Zn layer during the water dissolution process. (a) Experimental setup for continuous monitoring of the resistance of the Zn layer upon water dissolution. (b) Resistance change of the Zn layer over time. (c) Zn resistor remains attached to the glass vial after immersion in water for 1.5 hours. (d) The upper part of the resistor can be easily wiped off from the glass vial by gloves.



Figure D-7. Water-soluble electrodes based on the IPLMT Zn on a PVA substrate to measure ECG/EMG signals. (a) Conformal contact of the electrodes on the skin of the forearm. Comparison of the (b) ECG and (c) EMG signals captured by transient Zn/PVA electrodes and commercial gel electrodes.



Figure D-8. SEM images of Zn-based electrodes on the PVA substrate. SEM images of the PVA films (a) before and (b) after the xenon light-induced evaporation of Zn to show a dense layer of Zn, as well as (c) microstructures of the skin surface reproduced on the PVA thin film after its partial dissolution and attachment on the human skin.



Figure D-9. Dissolution process of the Zn-based electrode on PVA in water at room temperature: (a) 0 min, (b) 10 mins, (c) 12 h, and (d) 24 h after immersion in water.



Figure D-10. Changes in the contact angle upon copper substitution reaction. Contact angle of Ag ink on (a) deposited Zn and (b) the Cu layer after the Cu-Zn substitution reaction.



Figure D-11. SEM images of (a) sputtered and (b) E-beam evaporated Zn layers.



Figure D-12. SEM image of the micro-grooves on the surface of a seashell.

Fabrication method	Conductivit y (S/m)	Surface type	Referenc e
Laser printing/sinterin g	1.124 x 10 ⁶	Planar	Wan ¹
Electrochemical sintering	> 10 ⁵	Planar	Lee ²
Room- temperature sintering	7.24 x 10 ⁴	Planer	Li ³
Photonic sintering	44,643	Planer	Mahajan ⁴
Room temperature curing	0.024	Planer	Huang ⁵
Photonic sintering	60,213	Planer	Li ⁶
Photonic sintering	22,321	Planer	Mahajan ⁷
IPLMT Zn	3.5 x 10 ⁵	Planar/Freefor m	This work

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