Gallium-based liquid metals and their hybrids as smart electronic materials

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Gallium-based liquid metals and their hybrids as smart electronic materials

Long Ren, M.Sc.

Supervisors:
Yi Du, Dr.; Shi Xue Dou, Prof.; Xun Xu, Dr.

This thesis is presented as part of the requirement for the conferral of the degree:
DOCTOR of PHILOSOPHY

Institute for Superconducting and Electronic Materials
Australian Institute of Innovative Materials
Faculty of Engineering and Information Sciences
University of Wollongong, NSW, Australia

November, 2018
The re-emergence of room temperature liquid metals presents a forgotten exciting paradigm for an ideal combination of metallic and fluidic properties. The very unique fluid metal features of non-hazardous Ga-based liquid metals, including high surface energy, low viscosity, unlimited malleability, a wide temperature range of the liquid state, and desirable chemical activity for many applications, have been leading to remarkable possibilities and potentials for harnessing their properties and functionalities. The realization of stimulus-responsivity and multi-functionality makes Ga-based liquid metals a new family of “smart materials” – be regarded as the basis of multitudinous applications in frontiers covering from material science to engineering and medicine. Constructing hybrids of Ga-based liquid metals with other functional materials or groups can further extend this field-responsive capacity to incredible levels. An increasing number of reports on liquid metals have been published and revealed the abilities or activities of Ga-based liquid metals, as well as their alloys and constructed hybrids, as soft smart-response materials. However, development and systematic study of novel stimulus-responsive properties and the related unexplored application are still highly lacking.

Three different stimulus-responsive behaviors and the corresponding potential application with liquid metal-based nanodroplets and hybrids were studied in this doctoral thesis. For the first work, we reported a green and facile synthesis of the liquid metal nanoparticle by sonication liquid bulk sample in a thiol solution, which can be used as printing inks. Each liquid metal particle in the ink was protected by the oxide layer, which can be broken by external pressure. By using these liquid metal nanoparticle based inks, stretchable and flexible electronic devices have been fabricated and demonstrated on polydimethylsiloxane and polyethylene terephthalate plastic substrate by direct printing and laser etching. A continues and conductive thin film and path with defined micro- or nano-size can be obtained by applying localized pressure on the LM particles.

For the second work, we further investigated the temperature dependence electric and magnetic properties of the liquid metal constructed electronics. It was found that, below 6.6 K, the as-prepared liquid metal-based conductive electronics were superconductive and diamagnetic. A series of Ga-based liquid metals and corresponding nanodroplets, thus, have been developed to fabricate flexible...
Abstract

superconducting micro/nanoelectronics by direct printing. Those nanoparticles retain their bulk superconducting properties and can be dispersed and stored in various solvents, including ethanol, acetone, and water. By using these dispersions as inks, stretchable and flexible superconductive devices, including microsize superconducting coils, electric circuits, and superconducting electrodes, have been fabricated and demonstrated on the substrate by direct handwriting, inject printing and laser engraving.

Based on the first two works, it can be found that the Ga-based liquid metals and their nanoparticles are ideal conductive materials for building flexible electronics. Nevertheless, simply developing soft conductive matter is not the panacea for all the mechanical-mismatch induced challenges in electronics, especially for biosystems that displaying highly diverse combinations of mechanical properties. To smartly match the mechanical features of the targeted specific area, we developed liquid metal-based magnetoactive slurries by dispersing ferromagnetic particles in a Ga-based liquid metal matrix. Besides the benefits from the combination of conductivity and deformability, the stiffness and viscosity of the materials system designed here can be reversibly altered and subtly controlled within a very short time and over a wide range in response to the magnetic field applied.

In summary, these demonstrated Ga-based liquid metals and their hybrids make the Ga-based liquid metals promising to build multi-functional electronics for the varying field with different requirements, as a smart electric system which can be controlled by the external field applied.
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I would like to extend my sincere gratitude to my principal supervisor, Dr. Yi Du. During the past three years, Dr. Du created a free and warm work atmosphere which encouraged me to extend my horizons and develop my potential. Apart from his great support on my research work, Dr. Du also provided me various opportunities to participate international competitions and nominated me as different awards.

High tribute shall be paid to my co-supervisor, distinguished Prof. Shixue Dou. At the beginning of my PhD application in ISEM, Prof. Dou provided me with great support and guided me during the application process. I would like to thank Dr. Xun Xu, who is also my co-supervisor, provided me great support on my research work. Prof. Dou and Dr. Xu usually gave valuable suggestion and guidance on carrying out experiments and analysis the data, which gave me great benefits and inspirations. I really appreciate this special and valuable experience.

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The author is grateful for financial support from Australian Research Council (ARC) Discovery Projects (DP160102627 and DP170101467) and a BUAA-UOW Joint Research Centre Small Grant.
Certification

Long Ren, declare that this thesis submitted in fulfilment of the requirements for the conferral of the degree <DOCTOR of PHILOSOPHY>, from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Long Ren
3rd January 2019
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<tbody>
<tr>
<td>1D</td>
<td>One dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two dimensional</td>
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<tr>
<td>3D</td>
<td>Three dimensional</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
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<tr>
<td>Cs</td>
<td>Caesium</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>CuO</td>
<td>Copper monoxide</td>
</tr>
<tr>
<td>CuSO₄</td>
<td>Copper sulphate</td>
</tr>
<tr>
<td>CT</td>
<td>Computed tomography</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>EGaIn</td>
<td>Eutectic gallium-indium alloy</td>
</tr>
<tr>
<td>EDL</td>
<td>Electric double layer</td>
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<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
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<tr>
<td>Fe</td>
<td>Iron</td>
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<tr>
<td>FE-SEM</td>
<td>Field emission scanning electron microscopy</td>
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<tr>
<td>FC</td>
<td>Field-cooled</td>
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<tr>
<td>Fr</td>
<td>Francium</td>
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<tr>
<td>Ga</td>
<td>Gallium</td>
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<tr>
<td>Gd</td>
<td>Gadolinium</td>
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<tr>
<td>Hg</td>
<td>Mercury</td>
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<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Hydrogen peroxide</td>
</tr>
<tr>
<td>HA</td>
<td>Hyaluronic acid</td>
</tr>
<tr>
<td>HAADF</td>
<td>High-angle annular dark field</td>
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<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscope</td>
</tr>
<tr>
<td>In</td>
<td>Indium</td>
</tr>
<tr>
<td>JCPDS No.</td>
<td>Joint Committee on Powder Diffraction Standards card number</td>
</tr>
<tr>
<td>LM</td>
<td>Liquid metal</td>
</tr>
<tr>
<td>LMMS</td>
<td>Liquid metal-based magnetoactive slurries</td>
</tr>
<tr>
<td>MgB₂</td>
<td>Magnesium diboride</td>
</tr>
<tr>
<td>MUA-CD</td>
<td>Thiolated (2-hydroxypropyl)-β-cyclodextrin</td>
</tr>
<tr>
<td>Mg</td>
<td>Magnesium</td>
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</table>
List of Names or Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>NIR</td>
<td>Near-infrared</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>PPMS</td>
<td>Physical property measurement system</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>Rb</td>
<td>Rubidium</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Sn</td>
<td>Tin</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VSM</td>
<td>Vibrating sample magnetometer</td>
</tr>
<tr>
<td>WO₃</td>
<td>Tungsten trioxide</td>
</tr>
<tr>
<td>WHH</td>
<td>Werthamer–Helfand–Hohenberg</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray powder diffraction</td>
</tr>
<tr>
<td>ZFC</td>
<td>Zero-field-cooled</td>
</tr>
</tbody>
</table>
Table 3.1. Chemicals and materials used in this work.

Table 5.1. Summary of the onset Tc and offset Tc, as well as the upper critical field at 0 K and the coherence length, of the Ga-In-Sn alloy samples (2 mm × 5 mm × 1 mm) with different component proportions.

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**Figure 3.1** Schematic diagram of the ultrasonication process in the aqueous solution.

**Figure 3.2** Schematic diagram of the electron-matter interaction depicting its different products.

**Figure 3.4** Schematic drawing of the work principle and working modes of AFM.

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**Figure 4.4.** (a) EDX spectrum and analysis (inset) of the galinstan (65% Ga, 24 % In, 11% Sn by weight) nanodroplets at room temperature; the weight ratio Ga:In:Sn of these nanoparticles is 31.47:11.54:5.44, almost the same as for the original bulk sample; the signals of C and O correspond
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to the Ga oxide and organic coating; the Cu element is from the TEM grid. (b) HAADF-STEM image combined with different phase identifications of the galinstan nanodroplets at room temperature; based on the element mapping in Figure 3.3 (c): Phase 1 shows the eutectic alloy phase containing Ga/In/Sn, Phase 2 shows the Ga oxide shell of the droplets, and Phase 3 shows the outer organic matter layer of these droplets.

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**Figure 4.6.** Force–displacement curve obtained for one individual galinstan nanodroplet; the red line tracks the approach process between the AFM tip and the particle, while the blue line tracks the retraction of the AFM tip from the particle; the inset presents the I–V curves before and after the galinstan nanodroplet is broken by the applied external pressure.

**Figure 4.7.** (a) Digital image of galinstan bulk and SEM of galinstan nanodroplet. (b) – (d) Schematic and digital images of the electronics prepared by different routes including directly writing, inject printing and laser engraving, based on the droplets. (e) The image shows a flexible micro-coil and micro-gapped interdigitated electrode prepared by laser lithography from an EGaInSn nanodroplets film assembled on PDMS; (d) the resistance stability of the micro-coil on PDMS after mechanical sintering is demonstrated over a hundred rounds of bending and folding.

**Figure 5.1.** (a) and (b) are digital images of sintered flexible circles printed with the EGaInSn nanodroplet based inkjet and of the good electrical conductivity measured by a multimeter (inset image). (c) The image shows a flexible micro-coil and micro-gapped interdigitated electrode prepared by laser lithography from an EGaInSn nanodroplets film assembled on PDMS; (d) the resistance stability of the micro-coil on PDMS after mechanical sintering is demonstrated over a hundred rounds of bending and folding.

**Figure 5.2.** TEM images at different temperatures of EGaInSn nanodroplets. (a)TEM images (top) and the corresponding SAED patterns (bottom) of EGaInSn nanodroplets at representative temperatures: from left to right, 10 °C (283 K), −70 °C (203 K), −80 °C (193 K), −140 °C (133 K), and −150 °C (123 K). (b) STEM image of EGaInSn nanodroplets, as along with element mapping of the same EGaInSn nanodroplets at −150 °C (123 K): from left to right, the images show EGaInSn nanodroplets and mappings for C (yellow), O (Magenta), Ga (red), In (green), and Sn (blue).

**Figure 5.3.** SAED patterns of EGaInSn nanodroplets at (a) −80 °C and (b) −150 °C. The diffraction spots in the SAED pattern at −80 °C can be indexed to In and Sn, and no Ga related diffraction spots can be observed in this SAED pattern, indicating that In and Sn have started separating out and becoming crystalline, while Ga is still in a liquid amorphous phase at this temperature. When the temperature is reduced to −150 °C, Ga related diffraction spots appear, implying the crystalline nature of Ga and the full crystallization of the whole particle.

**Figure 5.4.** HAADF-STEM image combined with different phase identifications of the EGaInSn nanodroplets at -150 °C (123 K). Based on the element mapping in Figure 2(e), besides the Ga oxide shell phase and the outer organic matter layer (Phase 3 and Phase 4), the initial single phase of the core in the particle at RT is now divided into two phases. These two phases, Phase 1 and Phase 2, are related to Ga metal and InSn alloy respectively.

**Figure 5.5.** (a) Temperature dependence of the resistance between 2 K and 8 K for different Ga-In-Sn alloys with various component proportions, normalized by the resistance at 300 K. (b-f) Normalized
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temperature dependence of the resistance between 2 K and 8 K for the different alloys under different magnetic fields: (b) Ga\textsubscript{In\textsubscript{68}Sn\textsubscript{32}}, (c) Ga\textsubscript{In\textsubscript{61}Sn\textsubscript{29}}, (d) Ga\textsubscript{In\textsubscript{47}Sn\textsubscript{23}}, (e) Ga\textsubscript{In\textsubscript{24}Sn\textsubscript{11}}, (f) Ga\textsubscript{In\textsubscript{7}Sn\textsubscript{3}}.

**Figure 5.6.** Temperature dependence of the resistivity (ρ–T curves) between 2 and 300 K for the bulk sample (2 mm × 5 mm × 0.2 mm) and a printed nanodroplets pattern (2 mm × 5 mm × 0.1 mm) after mechanical sintering; inset: enlargement of the ρ–T curves between 2 and 8 K. The superconducting transition temperatures \( T_c \) of these two samples are both around 6.6 K.

**Figure 5.7.** Temperature dependence of the resistance between 2 K and 100 K for a bended printed Ga\textsubscript{30}In\textsubscript{47}Sn\textsubscript{23} nanodroplets pattern after mechanical sintering; inset: enlargement of the temperature dependence of the resistance curve between 2 K and 8 K. The superconducting transition temperatures \( T_c \) of this sample is also around 6.6 K.

**Figure 5.8.** Zero-field cooling and field cooling (ZFC, FC) magnetization curves from 2 to 300 K of the nanodroplets under a magnetic field of 50 Oe. The inset schematic illustrations show that the nanodroplet would make the transition to crystalline from amorphous as the temperature decreases from RT (300 K) to \( T^* \) (133 K, fully crystalline temperature point). The amorphous and then the crystalline nanodroplet remains paramagnetic when the temperature is above the \( T_c \) (=6.6 K), but the crystalline nanodroplet will change to diamagnetic when the temperature falls below \( T_c \) (=6.6 K) due to the Meissner effect in the superconducting liquid metal nanodroplet.

**Figure 6.1.** Schematic illustration and photographs demonstrating the preparation of LMMS. The liquid galinstan becomes slurry-like and muddy after mixing with the Fe particles in the HCl solution. The viscosity of the LMMS sample clearly increases, and it can be molded into different shapes.

**Figure 6.2.** Digital photograph of Ga-based liquid metal droplets containing 100 nm Fe and 70 µm Fe in various amounts. The results indicated that the maximum molar percentage that could be successfully suspended in the liquid metal was ~ 15 % for 100 nm Fe, and ~ 50% for 70 µm Fe.

**Figure 6.3.** Digital photograph for the stiffness of the LMMS sample could be further enhanced by applying an external magnetic field. The cylinder molded under the field from a permanent magnet shows no deformation with a 50 g weight on the top. The high cylinder toppled over immediately, however, after the magnet was removed.

**Figure 6.4.** (a) XRD patterns of LMMS sample containing 15% 100 nm Fe particles (LMMS-S15%) and 50% 70 µm Fe particles (LMMS-L50%) after 1 d from the preparation, as well as the patterns of pure Fe and pure LM for reference. (b) – (d) SEM image of the surface of the LMMS-L50% sample, and related element mapping of Ga and Fe in the LMMS-L50%.

**Figure 6.5.** Typical STEM image of a small piece from LMMS-S15% with phase mapping and element mapping of the same location. The inset in (a) is the corresponding SAED pattern of the selected area. (b) Combined phase mapping, with two possible phases represented on the same small piece. From (c) to (f), the images show the maps for Fe (yellow), Ga (red), In (blue), and Sn (green). (g) Line profile analysis of distribution of elements in LMMS-S15%.

**Figure 6.6.** SEM images of the surface of the LMMS-L50% sample, and related element mapping of Fe in the LMMS-L50%, (a) – (b) before and (c) – (d) after the application of magnetic field.

**Figure 6.7.** (a) Variation of storage modulus (G’) and complex viscosity for the LMMS samples containing different molar fractions of Fe. (b) Magnetic field dependence of G’ and complex viscosity.
at 0.2% strain amplitude for the sample containing an LMMS-L30%. The magnetization curves of pure LM, pure Fe, and LMMS-L30% are shown in the inset.

Figure 6.8. (a) Schematic illustration of the movement of Fe particles in LMMS samples with and without magnetic field applied. Chains of Fe particles are proposed to be formed under the alignment force of magnetic field, similar to the behavior of other magnetorheological fluids. (b) Variation of stress induced at different strains for the LMMS-L50% sample with and without magnetic field applied.

Figure 6.9. Demonstration of penetration of the LMMS-based electrode into the bio-electrolyte covered by an artificial bio-membrane: (a) without magnetic field applied and (b) with magnetic field applied. (c) The electrochemical current response to the LMMS electrode successfully inserted in and withdrawn from the electrolyte.

Figure 6.10. (a) Schematic illustration of the pressure on the implanted electrode from the tissue movement and external force. (b) The relationship between stress and applied magnetic field for the LMMS-based electrode. The relationship between the electric current response and the applied magnetic field also shows similar rising tendency as the observation for stress. Each plots for stress (upper left) and current response (lower right) versus strain are also shown in the insets in (b). (c) Schematic illustration of the test system based on the bio-electrolyte. The bio-electrolyte forms a dielectric layer between the inserted LMMS electrode and the contrast electrode, and the pressure would induce a change in the thickness of this dielectric layer.
Chapter 1: Introduction

1. Introduction

1.1. Research Background

It is believed that the ongoing technological revolution in artificial intelligence and robotics will have an irrevocable impact on all human lives and the lives of future generations. The definition of robotics in this revolution is close to that of a ubiquitous “smart machine”, with abilities ranging from perceiving and exploring outer space to tracking and killing cancer on the nanoscale.\(^1\) Besides creating human-like intelligence, building artificial robotic organisms is leading the development of this revolution. There are expectations of making such machines soft and compatible, exhibiting unprecedented adaptation, sensitivity, and agility, which are highly suited to interactions with delicate entities including the human body.\(^2\) The key challenge to achieving this fully expected potential is exploring and developing suitable building blocks, namely smart materials, which will be adaptive and smart enough to respond with more freedom to the signal or stimulus from the control center.\(^3-4\)

Smart materials are defined as materials that are capable of reacting or responding to the changes in their surroundings or fields.\(^5-6\) It means one or more properties of these smart materials can be significantly and reversibly changed in a controlled fashion by an external stimuli, such as mechanical stress or tensile, temperature, electric or magnetic fields, light, moisture, pH value. Different types of smart materials, which classed by the stimuli, are already common in the advanced devices with applications in electronics, optic-devices, memories, sensors, actuators, and so on. Being notably, the smart materials associated with electricity offer a big advantage for the new generation electronics, which facilities the building of Electronic Smart Systems for utilizing in transportation, healthcare, energy, safety and security, logistics, information communications, and manufacturing.

The future of electronics is believed to be soft, elastomeric, miniaturized, and biocompatible.\(^7\) Exploration of soft and biocompatible electronic materials that respond to the environmental changes and manifest their own functions according to the optimum conditions will undoubtedly be an essential task in the development of smart materials and the smart electronic system. Conventional, rigid materials including stiffness metal and dielectric ceramics remain the key electronic building blocks of most modern smart electronic devices, but show limited abilities towards to the soft smart
electronics. Among the large number of smart materials, the term “soft” is well presented by the field-responsive fluids that typically divided into magnetorheological fluids and electrorheological fluid. However, the fluids carriers used in these smart fluids are usually non-conductive, being the barrier for the smart electronics.

The ideal cases for combination of conductivity and deformability are metals that are liquid at or near room temperature, featured with both metallic and fluidic properties. The unique low viscosity as well as the desirable high thermal and electrical conductivity properties of liquid metals, makes them suitable for use in soft, stretchable devices such as soft robotics, e-skin, wearables, and stretchable electronics.\[^{8-10}\] Furthermore, they can be patterned at room temperature in unique ways and incorporate readily into microfluidic networks as pumps, electrodes, and valves. Perhaps the most promising and distinct property of liquid metals is their ability to be reversibly shape-reconfigured at room temperature;\[^{11}\] this opens up the possibility for devices that can change their function based on the switchable shape or position of their liquid metal components.

Ga has low viscosity, high electrical and thermal conductivity, and negligible vapor pressure at room temperature. Its melting point is \(\sim 30 ^\circ \text{C}\), but this can be depressed by incorporating other metals such as In (EGaIn, melting point: 15.7 \(^\circ\) C) and Sn (galinstan, melting point: \(-19 ^\circ\) C). Both alloys have a volumetric electrical conductivity of \(3.4 \times 10^6 \text{ S} \cdot \text{m}^{-1}\) and thermal conductivity of \(26.4 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\) at about \(30 ^\circ\) C. The existence of these basic properties offers huge possibilities to be regulated by applying related stimuli.\[^{12}\] For example, the highly sensitive amphoteric oxide layer offers the possibility of tuning the surface tension of liquid metal droplets, which means that the liquid metal droplets can respond mechanically (even shape shifting) under the applied external stimulus, such as a chemical reaction, the pH of the surroundings, and electrochemical control.\[^{13}\]

Besides Ga-based liquid metals themselves, the hybrids or material systems composed of EGaIn/galinstan and other functional materials also present novel physical and chemical properties. An excellent autonomously electrically self-healing composite has been achieved by suspending liquid metal droplets in soft elastomers, which can re-route the electrical connections when mechanical damage is applied.\[^{14}\] The soft polymer matrix with a particular distribution of the liquid metal units, along with the system’s response to the mechanical forces, makes such smart activities to occur.
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The realization of stimulus-responsive and multi-functionality present Ga-based liquid metals a new family of “smart materials”. Furthermore, constructing hybrids of Ga-liquid metal and other functional materials or groups can even extend this smart capacity to incredible levels. An increasing number of reports on liquid metals have been published and revealed such abilities or activities of Ga-based liquid metals, their alloys and constructed hybrids as intelligent liquid, but critical research activities on the mechanisms describing their stimulus-response activity, electronics, their interaction with other functional entities as well as their efficient of intimate integration still need to be further undertaken.

1.2. Objectives of the Research

There are many exciting and promising applications that harness the unique properties of liquid metals. Most of these applications are focused on electronics, but few studies are focused on smart electronic materials.

In this thesis, we are expected to achieve the following goals:

(1) Preparation of Ga-based liquid metal nanodroplets and the related nano-hybrids or nanocomposites;

(2) Investigation of the field-responsive physical and chemical properties of the as-prepared Ga-based nanodroplets and nano-hybrids;

(3) Construction of smart electric system by the as-prepared Ga-based nanodroplets and nano-hybrids.

1.3. Thesis Structure

For developing liquid metal-based smart materials, the synthesis of Ga-based liquid metal and the hybrids as well as their nanodroplets are explored in this work. Moreover, in order to study the field-responsive properties and performance of these liquid metals and relatives, detailed structural characterizations, electric and magnetic measurements are also performed with changing field applied. The scope of this thesis work is briefly outlined as follows:

Chapter 1 introduces the background and potential of Ga-based liquid metal as smart electronic materials and expounds the significance of this work.
Chapter 1: Introduction

Chapter 2 presents a literature review on recent progress in Ga-based liquid metal for electronics and smart materials.

Chapter 3 presents the detailed preparation methods, as well as the structural and mechanical characterization techniques for Ga-based liquid metals and their droplets.

Chapter 4 introduces a facile way to prepare Ga-based liquid metal nanodroplets and active the as-constructed flexible electronics by applying local mechanical force.

Chapter 5 presents temperature induced phase, electro-conductive and magnetic response of Ga-based liquid metals and the related droplets.

Chapter 6 investigates liquid-metal-based hybrids for magneto-responsive mechanically adaptive electrodes.

Chapter 7 summarizes the work in this thesis and provides some prospects for the liquid metal and the hybrids as smart electric materials.

1.4. References

Chapter 1: Introduction


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2. Literature Review

2.1. Introduction of Ga-based liquid metal

Metals that are liquid at room temperature should be an ideal combination of fluidic and metallic properties. There are five known metallic elements that are in the liquid state at or near room temperature: Fr, Cs, Rb, Hg, and Ga. Featured by the virtually no vapor pressure at room temperature and low toxicity, Ga is the only one among these metals that can be handled safely.\(^{[1]}\) Ga, discovered in 1875, is in group-13 of the periodic table as a post-transition metal. The melting point (~ 30 °C) of Ga is slightly higher than room temperature, but the addition of other post transition metals such as In and Sn make the Ga-based eutectic alloys (EGaIn (75% Ga, 25% In) and galinstan (68.5% Ga, 21.5% In, and 10% Sn)) that melt below room temperature.\(^{[2]}\) EGaIn has a melting temperature of 15.5 °C, which means that it remains in liquid state at room temperature. The melting temperature of Galinstan is −19 °C, making it a better candidate for cold environments.\(^{[3]}\) The tuneable melting temperatures of these eutectic alloys represent one of the most significant steps toward application of Ga-based alloys as liquid metals.

2.2. Responsive characters of Ga-based alloy and its hybrids with outside field applied

The unique low viscosity, as well as the desirable high thermal and electrical conductivities of Ga-based liquid metals, makes them suitable for use in soft, stretchable devices such as soft robotics, e-skin, wearables, and stretchable electronics.\(^{[4]}\) It is believed, however, that the most attractive and distinct property of Ga-based liquid metals is their ability to be reversibly shape-reconfigured at room temperature.\(^{[5]}\) Ga-based liquid metals exhibit a high surface tension (EGaIn: 624 mN⋅m\(^{-1}\), Galinstan: 534 mN⋅m\(^{-1}\)), but when meet an oxygenated environment (including ambient air and water), Ga-based alloys form a self-passivating Ga-oxide skin that dramatically reduces the surface tension as a responsive result.\(^{[2]}\) The existence of the distinct basic properties offers huge possibilities to be regulated by applying related stimuli, such as a chemical reaction, the pH of the surroundings, and
electrochemical control. Such smart behavior opens up the possibility of devices that can change their function based on their switchable shape or the position of their liquid metal components. Some other stimulus-responsive properties of the Ga-based liquid metals and their hybrids have also been demonstrated, which make the Ga-based liquid metals promising to meet the requirement of future soft-electronics, robot design, and bio-systems.

2.2.1. Temperature dependence properties

As a liquid, the first explored stimulus-responsive character of Ga-based liquid metal could be volume expansion with increasing temperature.\[6\] The thermometer is also the first application that commercial Galinstan was used for, as a replacement for the toxic Hg. Ga has the widest liquid range of any metal (30 °C − 2400 °C), with the coefficient of thermal expansion increasing by several hundred percent upon melting. Besides the thermal expansion, most properties of Ga, as well as its liquid metal alloys, are strongly temperature-dependent, particularly near the melting point, such as its supercooling/superheating behavior, negative thermal expansion in the transition from liquid to solid, and its superconductivity at very low temperature. Such characteristics give the Ga-based liquid metal good temperature responsive smart activities.

2.2.2. Electro- and electrochemical modulation

Voltage is an attractive stimulus due to its controllability and accessibility method since it is easy to apply and miniaturize. The Lippmann’s equation and Lippmann–Young’s equation show and explain the way to electrically changing the wettability and dielectric properties of the liquid media, then inducing a surface or interface tension difference.\[^{7,8}\]

\[
\left( \frac{\partial \gamma}{\partial E_A} \right)_{T, p, \mu_i \sigma} = -Q_A
\]

(Lippmann’s equation)

where \(\gamma\) is the interfacial tension, \(E_A\) is the potential of a cell in which the reference electrode has an interfacial equilibrium with one of the ionic components of A, \(Q_A\) is the charge on unit area of the interface, \(\mu_i\) is the chemical potential of the combination of species \(i\) whose net charge is zero, \(T\) is the thermodynamic temperature and \(p\) is the external pressure.

\[
\cos(\theta) = \cos(\theta_0) + \frac{\varepsilon_d}{2\sigma_i \varepsilon_d} v_d^2
\]

(Lippmann–Young’s equation)
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where \( \theta \) is the apparent contact angle of the liquid with applied field, \( \theta_0 \) is the native contact angle (without field), \( \sigma_{gl} \) is the surface tension of the gas-liquid interface, \( \varepsilon_d \) is the permittivity of the dielectric, \( t_d \) is the thickness of the dielectric layer, and \( v_d \) is the voltage across the layer.

**Figure 2.1.** Summary of primary methods for electro-induced liquid metal modulation. (a) Continuous electrowetting creates surface tension gradients to actuate liquid metal within channels. (b) Electrowetting-on-dielectric uses large voltages to achieve modest changes in wetting behavior on a substrate. (c) Electrocapillarity utilizes charges in the electrical double layer to realize modest changes in surface tension. (d) Electrochemically controlled capillarity utilizes interfacial reactions to achieve enormous changes in surface tension.\(^9\) (Reproduced with permission from ref. 9, copyright 2016, AIP Publishing.)

The derived methods, as schematically shown in Figure 2.1, include electrocapillarity, continuous electrowetting, electrowetting on dielectric, and electrochemically controlled capillarity.\(^{4, 9}\) Therefore, liquid metal droplets, such as Hg, can be handled and actuated in an ionic electrolyte upon exposure to an appropriate voltage by controlling surface tension.\(^{10}\) Electrocapillarity is one of the earliest reported methods for tuning the interfacial tension of liquid metals, which utilizes the charges at the interface between the metal and electrolyte to lower interfacial tension. This change of interfacial tension is induced by an electrical potential at the boundary between liquid metal and liquid electrolyte, and the potential gradients would lead to the gradients in the interfacial tension. Although the electrocapillary phenomena result in only modest changes in interfacial tension, the electrochemical reactions which may happened at surfaces of Ga-based liquid metal can further significantly lower the surface tension, achieving wide range adjustment on the interfacial tension. Ga-based eutectic liquid metals are mainly composed of Ga which is very sensitive to an oxygenated
environment including ambient air and water, which can be easily controlled by the electrochemical route. The self-passivating Ga-oxide skin that dramatically reduces the surface tension of liquid metal can be also dissolved by electrochemical reaction, which promise a wide range of possibility for modulation of Ga-based liquid metal by these routes.

Figure 2.2. (a) A drop of liquid metal being oxidized electrochemically in 1 M NaOH. (b) Surface tension of a eutectic gallium indium drop in 1 M NaOH. The vertical dotted line represents the electrochemical formation of the oxide layer.\(^5\) (Reproduced with permission from ref. 5, copyright 2014, National Academy of Sciences.) (c) Schematic of apparatus and experimental images of a 30μL EGaIn droplet undergoing the fingering instability; (d) box-counting plot shown as a function of time for this same droplet, spreading at 1.3 V.\(^{11}\) (Reproduced with permission from ref. 11, copyright 2017, American Physical Society.)

Figure 2.2 (a) shows that the EGaIn liquid metal sphere disperses to an asymmetric layer when change the applied potential from 1.5 V to 0.5 V in a solution of 1M NaOH, with the surface area is several times that of its original area. The potential applied at the boundary between liquid metal and NaOH electrolyte lead to electrochemical oxidation of the metal, which further lowers the interfacial tension besides the standard electrocapillary effects.\(^5\) Figure 2.2 (b) shows the interfacial tension measurements of the sessile EGaIn droplet in 1 M NaOH as a function of potential applied. In the
absence of the oxide layer, the surface tension of the droplet varies parabolically with respect to voltage, behaving in a manner consistent with classic electrocapillarity. However, due to the formation of oxide layer on the surface via increasing the potential, the interfacial tension dramatically drops, and even further approaches to near-zero when further increasing the potential to positive. The high-energy interface between the metal and electrolyte is then replaced with two new interfaces, metal–metal oxide and metal oxide–electrolyte, resulting very low interfacial tensions and yields to the gravity. The continually growing oxide layer, competing with dissolution by the basic electrolyte, allows liquid metal droplet flowing and spreading despite being covered with a solid film.

Further experiments and mechanism studies have been done by characterizing changes in morphology and dynamics as functions of droplet volume and applied electric potential, as shown in Figure 2.2 (c) – (d). It indicates that surface electrochemical oxidation generate compressive interfacial forces that opposes the tensile forces at a liquid interface and drives instabilities in the Ga-based liquid metal alloy, until the oxide grows too thick and retards further oxidation. Controlling the competition between this oxidation induced compressive stress and the tension at the interface offers a big potential to develop reconfigurable electronic, electromagnetic, and optical devices based on metallic liquid metals.

The results show that the formation of the oxide was actually the cause of the spreading, rather than standard electrocapillary effects. While, in the other side, it is also possible to use electrochemical reactions to estimate the oxide layer, leading the system back to the state of high interfacial tension. This concept can be used to actuate liquid metal from channel, as shown in Figure 2.3 (a), by locally inducing the withdrawal of liquid metal from a low interfacial tension state. Furthermore, by combining these electro-hydrodynamic phenomenon and effects with desirable electro-stimulus, the ability to decrease and increase the interfacial tension provides a method to pump and manipulate the shape of liquid metal, and be applied in the micro-fluid area, such as the production of liquid metal droplets with controllable sizes in the micro-channels (typical design as shown in Figure 2.3 (b)).

The electrolyte surrounding and the voltages applied to the liquid metal droplets play the key roles in the dynamic process of manipulation, while the shapes and composition of the electrodes can also make effective influences. As shown in Figure 2.3 (c), a nonlinear shape of alphabet “S” was
gradually created by using a 7x7 electrode array to dynamically manipulate one droplet of liquid metal.

**Figure 2.3.** (a) Reduction of the oxide layer at the interface of the channel increases the interfacial tension of the metal, causing rapid withdrawal.\(^{[12]}\) (Reproduced with permission from ref. 12, copyright 2015, John Wiley and Sons.) (b) A schematic of voltage applied for forming liquid metal micro-droplets, and the microscopy images of the production of EGaIn micro-droplets at corresponding voltages.\(^{[13]}\) (Reproduced with permission from ref. 13, copyright 2014, AIP Publishing.) Programmable transformation of liquid metal, (c) demonstration of making desirable shape through basic electrode array control algorithm; (d) schematic diagram showing the mechanism of the electric field creates deformation.\(^{[14]}\) (Reproduced with permission from ref. 14, copyright 2017, Association for Computing Machinery.) (e) Schematic diagram of the mechanism of voltage-induced liquid metal droplet locomotion on the Cu surface.\(^{[15]}\) (Reproduced with permission from ref. 15, copyright 2018, Royal Society of Chemistry.)
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When applying suitable voltage between two electrodes (Figure 2.3 (d)), the liquid metal droplet contacting to one electrode (Anode, high voltage) would deform in the direction of the electric field, heading to the other electrode (Cathode, low voltage) which is similar with many reports about 1D motion in confined channels. Through the construction of multi-electrodes array, the program that controlling only one selected electrode as Cathode (low voltage) and setting all other electrodes as Anodes (high voltage), makes the liquid metal droplet continually deform and spread from Anode to Cathode, achieving such full manoeuvrability in 2D motion.\textsuperscript{14} Such design with electrodes array can dynamically transform from a simple droplet shape to many other complex geometry in a controllable manner. The composite of the electrode may also have a big influence due to the possible alloying process between Ga and many other metals. The electrochemically enabled reactive wetting, such as the formation of an intermetallic CuGa\textsubscript{2} compound when the Ga-based liquid metal contacting Cu substrate (Figure 2.3 (e)),\textsuperscript{15} could accelerate the spreading rate of liquid metal on the substrate and even can produce a continuous perfusion of liquid metal within 3D porous substrate.

Applying an external electric field to discrete drops of the liquid metal in aqueous solution can create a surface tension gradient across the liquid metal surface. This gradient is caused by a potential drop through the electrolyte surrounding the metal and, according to the principles of electrocapillarity, which can drive fluid motion inside of the channel without directly contacting the liquid metal with an electrode. As shown in Figure 2.4 (a), a spreading liquid metal film could merge into a large sphere when applying an electric field to the water surrounding the liquid metal.\textsuperscript{20} Self-rotation and planar locomotion of the liquid metal droplet were also demonstrated with enough electric field applied (Figure 2.4 (b) – (c)). To achieve this directional movement, the driving forces including the surface tension gradient force and the rotational force, should overcome the retardation induced by the viscous friction. In an alkali solution, a slow chemical reaction can occur between Ga and alkali producing gallate salts such as \([\text{Ga(OH)}_3]^-\) anion. Thus, the surface of Ga-based liquid metal is negatively charged, resulting in the formation of electric double layer (EDL, modelled as a charged capacitor) with an accumulation of positively charged ions in the diffuse layer, which can be representatively displayed in Figure 2.4 (d). When no external potential is applied, due to the high conductivity of the liquid metal, the potential and charge distribution should approximately uniform throughout the droplet. In the presence of an external potential, a potential gradient will be generated
along the channel due to the finite conductivity of electrolyte. The potential difference across the EDL and surface-charge redistribution along the surface of the liquid metal droplet, thus, is induced and altered as shown in Figure 2.4 (d).[21]

**Figure 2.4.** (a) The electric-field-induced transformations of liquid metal objects in water, from the original flattened state 1 to intermediate states 2 and 3 and finally to a sphere 4. (b) Planar locomotion of a liquid metal sphere induced by an electric field. (c) Scheme of electric field induced planar locomotion.[20] (Reproduced with permission from ref. 20, copyright 2014, John Wiley and Sons.) (d) Working mechanism of the liquid metal enabled pump. Schematic of the experimental setup, Schematic of the Galinstan droplet surface charge distribution when placed in the droplet chamber filled with NaOH solution. Schematic of the Galinstan droplet surface charge distribution when an electric field is applied between the graphite electrodes. (e) Sequential snapshots for the pumping effect of a Galinstan droplet. (f) Formation of vortices along the droplet surface coloured by velocity magnitude of the flow.[21] (Reproduced with permission from ref. 21, copyright 2014, National Academy of Sciences.)
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The voltage drop across the EDL is less at the downstream (left) hemisphere, according to the Lippmann’s equation, a higher surface tension is generated at left. The imbalance of the surface tension $\gamma$ induces a pressure difference exists continuously along the surface of the Galinstan droplet as long as the electric field is applied, resulting a flow motion which is explained by continuous electrowetting (an electrical analogue to the Marangoni effect). Meanwhile, a thin layer of gallium oxide is electrochemically formed on the downstream hemisphere of the droplet, reducing the surface tension on this side, halts the motion effect. So if apply an alternating voltage to avoid the formation of the oxide layer on the Galinstan surface, continuous pumping could be achieved as demonstrated in Figure 2.4 (e). The similar modulations have been applied for different systems, such as soft actuator,\textsuperscript{[22-23]} delivery,\textsuperscript{[24]} but nearly all the operation environments are neutral or alkali. It was demonstrated that the Galinstan droplets in acidic solutions weakly affected by electrowetting effect, since the medium surrounding the metal should be insulating for the accumulation of charges.

Although there is no direct contact between electrode and liquid metal, the intrinsic interactions between the liquid metal and substrate also have influence on the electrowetting effect. For example, comparing with being placed on a glass substrate, liquid metal can exhibit a lot of peculiar behaviours when contracts with the graphite surface, as shown in Figure 2.5 (a). A thin oxide layer could be formed due to the potential elevation and electrochemical interaction between liquid metal and graphite in the NaOH electrolyte, resulting the decrease of surface tension of liquid metal and the shape transformation from the original rounded droplet to a dull, flat puddle.\textsuperscript{[25]} By confining areas with such active substrate, stable shapes including triangle and rectangle could be easily achieved (Figure 2.5 (b)). These conductive substrates which have electrochemical interaction with liquid metal can affect the surface-charge redistribution and potential difference across the formed EDL. When placing two electrodes with voltage at the two sides of liquid metal to trigger the continuous electrowetting, different from the smooth and quick movement of liquid metal on the glass surface, the liquid metal puddle on graphite wriggles slowly in various configurations like a worm. Moreover, as shown in Figure 2.5 (c), with an applied voltage of 10 V, the liquid metal puddle can even climb towards the cathode along a 10° graphite lop.
Figure 2.5. (a) The transformation of the liquid metal droplet on glass (left) and on a graphite substrate (right) in NaOH; (b) two typical shapes of liquid metal manipulated by glass slides including triangle and rectangle; (c) the upslope locomotion of the liquid metal on graphite under an electric field.\(^\text{(25)}\) (Reproduced with permission from ref. 25, copyright 2016, John Wiley and Sons.) (d) Time lapsed top and side view images of p-type CuO coated liquid metal when a voltage of 25 V was applied across the electrodes; and zoom-in top view images of the liquid metal marble during actuation at 4 s and 12 s; the characteristic potential distribution and the nanoparticle cluster formation during the electrochemical actuation of a p-type coated liquid metal.\(^\text{(26)}\) (Reproduced with permission from ref. 26, copyright 2014, AIP Publishing.)
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The complexity and diversity of the electrochemical induced actuation system would be further enhanced by integrating the liquid metal with semiconducting nanoparticles. The liquid metal marbles which represent liquid metal droplets coated with nanoparticles, as a typical example, offer an extra dimension for affecting the bipolar electrochemically induced actuation.\textsuperscript{[26-28]} Under the influence of electric field, these particles may readily migrate along the surface of liquid metals, altering the capacitive behaviour and interfacial tension in a highly asymmetric fashion.\textsuperscript{[29]} Figure 2.5 (d) presents the time lapse images of the actuation of one type liquid metal marble (p-type CuO coated galinstan) under electric stimulus. Significant morphology changes were observed and varied with the applied voltage. After the nanoparticle cluster dislodged from the tail of liquid metal, the direction of liquid metal marble motion abruptly reverses, and swiftly accelerating towards the other side.\textsuperscript{[26]} The liquid metal-semiconductor junction is expected to conduct at a particular point on the channel. The p-type particles significantly alter the actuation behaviour and morphology of the liquid metal marbles during their transition from insulating to semiconducting state. It is different with the actuating behaviours of the n-type WO\textsubscript{3} coated liquid metal marble,\textsuperscript{[27]} suggests huge opportunities to build smart actuators that can respond differently to the same stimulus, even for precise and selective electronic controllable soft robots.

2.2.3. Chemical and biochemical induced manipulation

As an amphoteric compound, the highly sensitive amphoteric oxide layer offers the possibility of regulating the interface tension between the metal and surroundings outside by simply localized chemical reaction, without the help of electric or electrochemical stimulus. Benefited from liquid and soft characters, thus, liquid metals are able to withstand significant bending, stretching, and deformation via chemically creating competition between various forces.

The recent developed self-actuation of liquid metals that can convert the energy from spontaneously chemical reaction into mechanical activity, resulting autonomous movement of liquid metals droplets.\textsuperscript{[30-31]} It was demonstrated that liquid metal objects are able to self-actuate with a small Al flake as fuels (Figure 2.6). As shown in Figure 2.6 (b), during the autonomous movement, hydrogen bubbles continually arise from the chemical dissolution of Al in NaOH, and lateral motion is evoked on the surface of the liquid metal due to convective flow. The actual self-propulsion mechanism of the fuelled liquid metal motor is the force from the bubble recoil with an acceleration of
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Bubble release and the imbalance of surface tension caused by the bipolar electrochemical reaction, synergistically propelling the liquid metal droplet to move autonomously and overcoming the resistance from surroundings. Furthermore, with the assistance of a metal wire covered by Al granules, self-powered liquid metal-based oscillator confined in the specified direction can be successfully fabricated. This type of metal-fuelled liquid metal-based actuators represent excellent candidates for use in the fabrication of future soft and self-powered biomimetic robots.

Figure 2.6. (a) Motion behavior of a self-fuelled liquid metal motor in a circular channel. (b) Schematic mechanism of the liquid metal motor running: hydrogen continually bubbles from the Al flake-propelled locomotion of the liquid metal, various forces then affect the velocity of the liquid metal droplet, and the lateral motion of the liquid metal motor heads opposite to the direction of the bubble departure. (Reproduced with permission from ref. 31, copyright 2015, John Wiley and Sons.)

Metals that alloyed with liquid metal including Al, Cu, Ag are not the only fuels for actuation, biomolecules have been also displayed the ability to trigger external manipulation for biotechnological applications by the localized molecular recognition and enzymatic reactions in physiological environments. Besides these chemical or bio-chemical reaction driving actuations, another exciting breakthrough was directly breaking the charge symmetry that exists on the surface of
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A liquid metal via the modification of the liquid electrolyte surrounding (pH stimuli) to generate a differential pressure.\textsuperscript{[38]} In details, the pH of the electrolytes in the channel is adjusted by adding basic or acidic electrolyte, and the ionic concentration of the electrolyte are modified through the addition of salts. As shown in Figure 2.7, the highly controlled pH imbalance between the two opposing hemispheres of the liquid metal droplet and the ionic concentration gradients across the surface of the droplet could result deformation and Marangoni flow dynamics, respectively. The kinetic energy from these two dynamic propulsion allowed the liquid metal droplets continuously deforming and propelling without the need for an external electric potential (Figure 2.7 (b)). The self-propelling liquid metal droplet only controlled with the fluid surrounding, makes a significant advancement towards truly autonomous soft systems.

![Figure 2.7](image)

**Figure 2.7.** (a) Top view schematic of the liquid metal droplet, the arrangement of ions form an electrical double layer on the surface. (b) The liquid metal droplet propels from acid side to basic reservoir. (c) Schematic of the deformation ratio measurements for $D_1/D_2$ assessment. ‘Black square’ indicates experiments with deformation dominating the dynamics and Marangoni flow dominant experiments are represented by ‘red circles’. (d) Demonstration of Marangoni flow and sequential snap shots shows a micro particle transferring from NaOH to HCl. (e) Selected enlarged images showing droplet deformation towards NaOH, while Marangoni flow (in red arrows) direction is towards HCl.$^{[38]}$ (Reproduced with permission from ref. 38, published by Springer Nature under the Creative Commons CC BY License.)

In addition to designing self-propelling actuator, the shape of the liquid metal was able to be manipulated through adjusting the interfacial tension which induced by the modification of the
chemical surroundings,\textsuperscript{[39-45]} which would be useful for flexible electronics such as switches, reconfigurable antennas. As shown in Figure 2.8 (a) – (e), only in alkaline solution, hydrogen peroxide and the graphite substrates can act synergistically to oxidize the upper and lower surfaces of the liquid metal in the meantime.\textsuperscript{[40]} The induced surface tension gradient on the surface of the liquid metal causes the Marangoni effect, leading to the quick spread and fractal of the liquid metal with remarkable morphologies.

**Figure 2.8.** (a) Hydrogen peroxide-induced deformation of liquid metal immersed in an alkaline solution on a glass plate and a side view of the contact angle in this case. (b) Deformation of liquid metal immersed in acidic electrolyte on the graphite with the addition of $\text{H}_2\text{O}_2$ and a side view of the contact angle in this case. (c) Fractal phenomenon of liquid metal immersed in alkaline solution on graphite plate and its contact angle on the same condition. (d) Schematic diagram of electron transfer between graphite surface and liquid metal. (e) The bubbles were produced in the liquid metal immersed in the acidic electrolyte.\textsuperscript{[40]} (Reproduced with permission from ref. 40, copyright 2018, Elsevier.) (f) Schematic illustration of the liquid metal fractal by adding acid in CuSO\textsubscript{4} solution. (g) Diagram of Cu–Ga galvanic cell and the direction of surface convection of the bulk liquid metal.\textsuperscript{[41]} (Reproduced with permission from ref. 41, copyright 2018, American Chemical Society.)

In acid surroundings, displayed in Figure 2.8 (f)-(g), the shape shifting and fractal phenomenon could also be achieved by adding $\text{Cu}^{2+}$ ion to trigger the displacement reaction occurred in the surface of liquid metal and induce unbalanced interface tension.\textsuperscript{[41]} The influences of different electrolyte environments, including acidic, alkaline, and neutral aqueous on the oxidation formation of liquid
metal droplets surface have also quantified to better understand and control the on-demand mobility of liquid metal droplet as well as the environmentally responsibility.\textsuperscript{[39]}

**Figure 2.9.** (a) Schematic of the transformable liquid metal nanodroplets drug delivery system, including the preparation, delivering process, targeted cancer therapy and acid-triggered fusion and degradation process. Chemical structures of MUA-CD and m-HA. (b) The EGaIn sample before and after ultrasonically dispersing and loading. (c) TEM images of the liquid metal delivers after different time at pH ~ 5.0.\textsuperscript{[46]} (Reproduced with permission from ref. 46, published by Springer Nature under the Creative Commons CC BY License.)
The regulation on the oxidation layer of liquid metal not only helps building soft motions, but also can be used for switch that can separate or expose the metal core from the outside. Gu and co-workers reported a liquid metal transformable nanocarriers, as shown in Figure 2.9, which is a core-shell nanostructure with liquid-phase gallium-indium alloy as core and thiolated polymer as shell. This structure can be easily synthesized by ultrasonication and tailored through ligand-mediated self-assembly. After accumulating in tumor site through binding tumor-target ligand, due to the oxide layer of the liquid metal nanostructure dissolving in mild acidic environment, the drug-loaded nanocarriers with initial average diameter of about 100 nm fuse to large nanoaggregates and decompose in 72 h. The endocytosis and fuse process of the liquid metal nanocarriers in the cells were confirmed and observed by TEM imaging, as shown in Figure 2.9 (c). The biochemical environment induced fusible and degradable behaviour provides a new strategy for smart drug delivery and tissue engineering.

### 2.2.4. Mechanical force induced response

As an ideal combination of fluidic and metallic properties, the Ga-based liquid metal shows huge potential for electronics that are soft, flexible, stretchable, and even reconfigurable. Smart materials are defined to be able to form part of a smart structural system sense its environment and respond to that external stimulus via an active control mechanism. Taking the advantage of deformability and intrinsic high electric conductivity, the functional behavior of liquid metal constructed electronics could be altered by applying mechanical force, such as the frequency shifting of the liquid metal antenna in response to the pressure induced conductive shape changing. Moreover, liquid metal flexible electrics that can sense touch, pressure, and strain can be established through the mechanical-stimulus responsive change in resistance or capacitance.

Figure 2.10 (a) and (b) show two typical demonstrations that detect the mechanical force, and output the electronic signal by measuring the correlating changes in resistance arising from the deformation due to the compression of liquid metal encased in elastomer. These sensors, depends on the choice of channel geometry and elastomer, can display high tunable sensitivity and detecting range from finger touching to running over by a car wheel. Building capacitors based on liquid metal with dielectric materials is another choice to realize the mechanical responding, either in self or mutual capacitive modes. Figure 2.10 (c) present a simple but effective stretchable capacitive
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sensors of torsion, strain, and touch by using double helix liquid metal fibres. The capacitance between the two liquid metal filled fibres can be predictably changed by the geometry shifting in response to twisting or elongating the fibres. Besides in the field of sensor, the liquid metal-based smart system also showed the potential to harvest mechanical energy and convert to electric power. For instance, a constructed liquid-metal-based triboelectric nanogenerator,[56] which allows a total contact between the metal and the dielectric, generate high power in response to the vibration, illustrating as high as 70.6% instantaneous energy conversion efficiency.

Figure 2.10. Soft smart sensors using liquid metal. (a) Soft skin sensor based on liquid metal in elastomeric microchannel, which changes resistance when deformed due to changes in geometry of the metal.[49] (Reproduced with permission from ref. 49, copyright 2012, IEEE.) (b) Schematic of S-shaped liquid metal based microfluidic tactile sensor which changes the contact resistance when applied pressure.[50] (Reproduced with permission from ref. 50, copyright 2016, American Chemical Society.) (c) Liquid metal based torsion sensor which changes capacitance between the intertwined liquid metal filled fibres when changes the geometry by twisting.[51] (Reproduced with permission from ref. 51, copyright 2017, John Wiley and Sons.)
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It is believed that a more smart behaviour of liquid metal in response to the mechanical stimuli should be the self-healing liquid metal conductors. Several examples of self-healing circuits have been easily realized by filling the bulk Ga-based liquid metal into the polymer made microchannels.\(^{59-60}\) The Ga-based liquid metal is very sensitive to the oxygen, when the microchannel are cut, the filled liquid metal neither leaks out from nor retreats into the microchannel by forming an oxides protective layer. Once the damaged parts were re-contacted, the liquid metal could merge together by breaking the thin oxides layers, and form a continuous conductive path.

![Figure 2.11](image)

**Figure 2.11.** (a) Micro-CT data with schematic superimposed image of liquid metal releasing into the crack plane from the microcapsules; the following schematic shows the crack damage breaks the conductive pathway, but soon restoring the electron transport by simultaneously rupturing the capsules to fill liquid metal to the area of damage.\(^{57}\) (Reproduced with permission from ref. 57, copyright 2011, John Wiley and Sons.) (b) Examples of the as-prepared stretchable liquid metal-elastomer are still electrically conductive after inducing severe mechanical damage; (c) the schematic illustration of the self-healing mechanism in response to different damage mitigation strategies.\(^{58}\) (Reproduced with permission from ref. 58, copyright 2018, Springer Nature.)

As an advanced smart self-healing conductor, an autonomously electrically self-healing composite has been achieved by constructing liquid metal-based microcapsules with a polymeric urea–formaldehyde shell wall. In response to the cut damage on the circuit (Figure 2.11 (a)), the embedded
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microcapsules nearby were also broken, the liquid metal fluid core released from the microcapsules into the damaged area restoring the electric conductive path.\textsuperscript{[57]} This self-healing design involve the incorporation of healing agents directly into the damaged areas, which lacks repeated restoration ability of conductive failure. Through building a novel material architecture composed of liquid metal droplets suspended in a soft elastomer, another autonomously electrically self-healing composites exhibited uncompromising resilience to repeatable mechanical damage.\textsuperscript{[58]} With a particular distribution of liquid metal droplets in the soft elastomers, when local mechanical damage applied, the liquid droplets units would rupture and re-route new electrical connections with the neighbour droplets without interruption (Figure 2.11 (b), (c)). This smart self-healing response offers huge potentials for power and data transmission that can instantaneously repairs itself even under extreme continually mechanical damage.

2.2.5. Magnetic field induced characters

![Image](image.png)

**Figure 2.12.** (a) Locomotion of liquid metal droplets under the rotated magnetic field, in comparison to the moving style of the solid metal spheres; the schematic mechanism of the forces induced on liquid metal in the system is also demonstrated.\textsuperscript{[62]} (Reproduced with permission from ref. 62, copyright 2018, ROYAL SOCIETY OF CHEMISTRY.) (b) Alternating-magnetic-field induced manipulation of liquid metal blobs.\textsuperscript{[63]} (Reproduced with permission from ref. 63, published by Cell Press under the CC BY-NC-ND License.)
Magnetic field can be applied to materials remotely, which avoids the introduction of potentially invasive wires or electrodes. It is a noninvasive stimulus exhibiting very low interaction with nonmagnetic materials, and have ability of penetrating through most materials including bio-materials. The magneto-active smart materials show great potential applications for microfluidics, bioengineering, and healthcare. Although the Ga-based liquid metals show almost unresponsive to a permanent magnetic field at room temperature, as conductive fluids, they are still able to be driven by a Lorentz force.\textsuperscript{[61]} As shown in Figure 2.12 (a), the EGaIn liquid metal droplet were actuated by moving a permanent magnet under the droplet in an aqueous solution, the self-rotation and circular motion were both observed. The force and torque, as the results of the interaction between the induced eddy current and rotating magnetic field, drives the liquid metal droplets moving towards the travelling direction of the magnet.\textsuperscript{[62]}

![Figure 2.12](image1.png)

**Figure 2.12.** (a) The photographs of EGaIn containing different amount of Fe with and without an applied magnetic field; (b) shear stress response of EGaIn containing ~40% Fe particles to a magnetic field.\textsuperscript{[64]} (Reproduced with permission from ref. 64, copyright 2017, American Physical Society.) (c) Schematic of the magnetocaloric refrigeration process based on the developed magnetic liquid metal.\textsuperscript{[65]} (Reproduced with permission from ref. 65, copyright 2017, American Chemical Society.)
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Furthermore, by applying an external alternating magnetic field to an EGaIn liquid metal, various physical phenomena including exothermic behavior, controlled locomotion, electromagnetic levitation, and shape transformations of liquid metal were observed.\textsuperscript{[63]} As shown in Figure 2.12 (b), a droplet of liquid metal positioning above the centre of a magnetic coil, instantly exhibited a “stand-up” shape when applying a $250 \text{ A} \cdot \text{m}^{-1}$, $245 \text{ kHz}$ alternating magnetic field. This deformation behavior was reversible with turning on or off of the alternating magnetic field. The eddy currents induced by the alternating magnetic field in the liquid metal, according to the Lenz’s law, off a sufficient repulsive force for the liquid metal to overcome gravity.

As another common strategy to achieve manipulations by the magneto-stimulus, physical coating of ferromagnetic materials on the surface of liquid metals to form liquid metal marbles have been used to offer the magnetic field responsive ability.\textsuperscript{[66-69]} The introduction of magneto-stimulus responsive properties allows them to change the motions and shapes by the application of the magnetic materials as a force mediator under the magnetic field. Dispersing ferromagnetic materials, even the permanent particles into the liquid phase is another synthesis route to magneto-responsive liquid metal marbles.\textsuperscript{[64-65, 70-72]} A typical example that mixing the Fe particles with EGaIn liquid metal, forming a biphasic colloidal suspension, was shown in Figure 2.13 (a). In the presence of a magnetic field, these inside colloidal magnetic particles align along the magnetic field, provide deformability of these liquid metal marbles, also leading to an increased viscosity (Figure 2.13 (b)) in comparison to the condition without applied magnetic field.\textsuperscript{[64]} Most of ferromagnetic particles have low solubility in Ga-based liquid metal, but even a relative low concentration may result good magneto-induced application. The developed ferro-fluid containing Gd nanoparticle (Figure 2.13 (c)) has displayed spontaneous magnetization and a large magnetocaloric effect. This biphasic liquid metal-based ferro-fluid presents promise for applications in future fluidic magnetocaloric devices, which can absorb heat when exposed to a negative magnetic field strength gradient, and release heat in a positive gradient mode.\textsuperscript{[65]}

2.2.6. Light-induced responsive properties

Light, as an electromagnetic radiation, can also be applied to materials remotely. In addition, the use of light offers unique advantages in tuning the external stimulus, including regulation of light intensity and frequency, as well as fine-tuned control of irradiation direction, position, area and duration. Generally speaking, for metals, light will either be re-emitted or reflected when the
electromagnetic energy encounters the conduction band electrons, depending on the frequency of the incident light. The plasma frequency, namely the frequency of oscillation of an electron cloud, for the Ga-based liquid metal lies in the energy range that are comparable to UV light.\textsuperscript{[2, 73-74]} Therefore, the response of Ga-based liquid metal for the light in the visible and infrared region is reflection, behaviours like a mirror. When the photons with wavelengths shorter than UV light penetrating through the Ga-based liquid metal, localised surface plasmon resonances may happened as a result of the interaction between the free electrons and the light.\textsuperscript{[75]} It is attractive to design plasmonics devices based on these soft liquid metals, and well-defined plasmon resonance extinction peaks have been demonstrated with the film covered by the nanoparticles smaller than 100 nm.\textsuperscript{[76-77]} Strategies involving particles size adjustment,\textsuperscript{[78-79]} coupling nanoparticles\textsuperscript{[80]} and surface oxide thickness control\textsuperscript{[81]} have been utilised to successfully manipulate resonance frequency, even shift the resonance peak from UV region towards the visible region.

\textbf{Figure 2.14.} (a) Shape transformation of liquid metal in aqueous solutions. The morphology transferred from nanospheres to nanorods, due to the localized chemical reaction triggered by the light irradiation.\textsuperscript{[82]} (Reproduced with permission from ref. 82, copyright 2017, American Chemical Society.) (b) Schematic of the formation of polymeric encapsulating liquid metal particles under 254 nm ultraviolet irradiation; (c) visible and thermographic images of a liquid metal droplet before and after irradiation with a 785 nm laser, as well as the thermal response of the liquid metal solution; (d) thermal expansion of laser-driven liquid metal droplet in air and solution.\textsuperscript{[83]} (Reproduced with permission from ref. 83, published by Springer Nature under the Creative Commons CC BY License.)

The light irradiation generated heat or thermal effect is another common stimulus-responsive result, also can be applied to manipulate Ga-based liquid metal. It has been demonstrated that EGaIn-
based nanodroplets show a great morphological transformation in response to a simple light irradiation to the aqueous dispersion (Fig. 2.14 (a)). Actually, the light applied on the surface of liquid metal in the aqueous solution triggered a localized chemical reaction that the Ga-based nanospheres convert to high aspect ratio Ga oxide nanorods.[82] Taking advantage of the photochemistry strategy, more complex liquid metal-based functional materials could be obtained. With the irradiation of UV light, a photo-polymerization reaction could happened at the surface of the EGaIn droplet, forming a liquid metal-based nanocapsules with high water dispersibility (Figure 2.14 (b)). In response to the NIR laser irradiation, as shown in Figure 2.14 (c) and (d), the synthesised nanocapsules further generated thermal energy and reactive oxygen species, resulting in the destruction of the capsule structure. Using these photo-stimulus responsive properties, applications including remotely controlled drug releasing, optical manipulation of a microfluidic blood vessel, and spatiotemporal-targeted marking in organs and in a living mouse have been demonstrated based on liquid metal droplets.[83]

Figure 2.15. (a) Schematic illustration of Mg-EGaIn in vivo cancer photo-thermal therapy; (b) the thermal response of 2 g EGaIn and 2 g Mg-EGaIn after irradiation with an 808 nm NIR laser.[84] (Reproduced with permission from ref. 84, copyright 2018, John Wiley and Sons.) (c) Schematic of light-induced motion of a WO₃-coated galinstan droplet.[85] (Reproduced with permission from ref. 85, copyright 2013, AIP Publishing.)
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Constructing hybrids of Ga-based liquid metals with other functional materials can further enhance the photo-induced effect. For example, the addition of Mg in the EGaIn liquid metal resulted in a 61.5% increase in photo-thermal conversion in comparison to that of the pure EGaIn liquid metal, displaying efficient photo-thermal therapy of skin tumor (Figure 2.15 (a), (b)). The formation of a new intermetallic phase Mg$_2$Ga$_5$ in the liquid metal marbles was believed to enhance the photo-thermal effect.[84] Photo-induced locomotion can be also realized by combining the photo-active semiconductors with liquid metals. As shown in Figure 2.15 (c), the liquid metal marbles coated with WO$_3$ nanoparticles could exhibit photocatalytic properties in response to the light irradiation with a wavelength smaller than 460 nm. As a result of photocatalytic reaction in the H$_2$O$_2$ solution, oxygen bubbles generated at the localized area from the decomposition of H$_2$O$_2$, leading a rolling force to actuate the liquid metal marble towards to the opposite side of bubbles evolution.

2.3. Summary

In this chapter, we reviewed and discussed representative manipulations of Ga-based liquid metals and the applications of these stimulus-responsive properties. Continuous and vigorous development in this area can be expected and exciting results yielding many innovations should be anticipated. Despite increasing advances on the development and applications of liquid metals that have been made in the past decade, there are still research gaps aplenty in this field. As an emerging smart material, the discoveries of new possible stimulus-responsive properties in the liquid metal system are still insufficient, especially in response to the thermal, magnetic field and light stimuli. Furthermore, the fine manipulation of liquid metal by an applied stimulus is still full of challenges, and the integration of different stimulus-responsive modes and the construction of highly intelligent smart systems are still lacking.

2.4. References


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3. Experimental Procedure

3.1. Chemicals and Materials

The chemicals and materials used in this work are listed in Table 3.1.

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<th>Purity (%)</th>
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<td>Sigma-Aldrich</td>
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<tr>
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<td></td>
<td>75⁺</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>

Table 3.1. Chemicals and materials used in this work.

3.2. Materials Preparation

The preparation methods used in this work mainly include the co-melting method for the preparation of alloys and ultrasonication method for the preparation of nanomaterials.

3.2.1. Co-melting Method

All the ingot of Ga-based alloys were prepared from high purity elements by co-melting under protective Ar atmosphere. To minimize the oxidation of the pure metals, all the metals were weighted in specific mass ratio under Ar protection. To avoid the loss of Ga, In and Sn, and also protect the metals from any reactions with quartz ampoules, sealed graphite crucibles were used. Stoichiometric
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Amounts of Ga, In and Sn were loaded in the graphite crucibles inside of quartz ampoules, and then sealed under a pressure less than $10^{-6}$ Torr. The ampoules were slowly heated up to 1123 K, cooled down to 923 K at 1 K/min and then annealed for 12 hours. To keep the alloy preparation consistency, the temperatures for melting and annealing and their durations were maintained the same for all the co-melting process. Galinstan bulk samples were prepared by co-melting Ga, In, and Sn in the weight ratio: 68% Ga, 22% In, and 10% Sn.

3.2.2. Ultrasonication Method

Ultrasonication produces a cavitation phenomenon in the fluid medium. When the acoustic power inputs are sufficiently high, the sound waves transmitted in the liquid could create alternating compression and rarefaction cycles. Microbubbles or voids are then created in the liquid, and grow bigger. When the bubbles attain a volume at which they can no longer absorb energy, they collapse during the compression phase, resulting violent shock waves passing through the medium. This shock waves equivalent to several hundred, even thousand localized atmospheres pressure, which may abducts material from the workpiece surface. The cavitation mechanism in ultrasonication horn system is illustrated in Fig. 3.1.

![Ultrasonication process](image)

**Figure 3.1** Schematic diagram of the ultrasonication process in the aqueous solution.\(^{[1]}\) (Reproduced with permission from ref. 1, copyright 2018, Springer Nature.)
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All the ultrasonication processes applied here were carried out by the use of a probe-type ultrasonic homogenizer, which has a high localized power input intensity and great localized cavitation effect. During this sonication, the liquid metal bulk stabilized by the oxidation layer was easily fractured under the oscillating shear force, and small droplets successively separated from the bulk matrix in a spherical shape, due to the high surface energy of the freshly exposed oxide-free surface. For typical galinstan nanodroplets preparation, 2 g galinstan was added into 200 mL ethanol solution containing 1 mg thiol. Then, ultrasonication was performed using a conical tip sonicator (Sonics VCX 750 ultrasonic processor, with a 19 mm diameter high-gain solid probe) in this solution. The power of the ultrasonication was directly controlled by the instrument as 40% of the maximum power (750 W), the amplitude of the sonicator was adjusted to 80%, and the sonication proceeded for 60 min. The temperature of the sample during ultrasonication was controlled by using a cold water bath at about 20 °C. After sonication, the slurry was further washed by neat ethanol several times, followed by mild centrifugation to remove the excess thiol, and then the samples were suspended and stored in neat ethanol for further use.

3.3. Characterization Techniques

3.3.1. Scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX) analysis

SEM employ electron beams to visually observe, or get information from, an area of interest which is completely different way from that of the naked eye or even normal optical microscopy. As shown in Figure 3.2, the main signals detected are the backscattered electrons that can produce images with contrast that carries information on the differences in atomic number, and secondary electrons that can give topographic information and generate a grayscale image of the sample at very high magnifications. Besides, also as the products of electron beam-matter interaction, transmitted electrons can describe the sample’s inner structure and crystallography; and cathodoluminescence signal can give information on the electronic structure and the chemical composition.
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Figure 3.2 Schematic diagram of the electron-matter interaction depicting its different products.

Another type of signal that is widely used in SEM is X-rays. The EDX provides elemental identification and quantitative compositional information. It is based on the detection of characteristic X-rays emitted of an element as a result of the de-excitation of core electron holes created by a high energy electron beam. As the electron beam from the SEM itself strikes the specimen surface, the electrons within the atoms of this area of interest are elevated to an excited state. When the electrons in these atoms then return to their ground state, a characteristic X-ray is emitted. These x-rays are then gathered by the X-ray detector and converted into “useful” information. An energy measuring x-ray detector with a thin, low mass element window associated with the SEM system, as a result, enables EDX for all elements from carbon on up in atomic mass. In combination with the second electron image, an EDX analysis or even a mapping for the interest are of the given specimen can be adjusted simply based on the magnification at which the specimen is being observed, identifying the type of elements that exist in a sample.

In this work, the morphology and chemical composition of various liquid metal bulk and nanodroplets were analyzed by the field emission SEM and EDX (JSM-7500FA, JEOL, Tokyo, Japan; JEOL JSM-6490LV microscope coupled with an Oxford instruments X-maxN 80mm² SDD energy dispersive spectrometer) in UOW.
3.3.2. Atomic Force Microscopy (AFM)

The AFM is comprised of a cantilever-tip assembly that raster scans across the sample surface using a piezoelectric tube controlled by a computer. The cantilever tip tapers to a very sharp point, typically less than 10nm radius of curvature. The deflection of the cantilever is monitored using an optical detection system in the form of a laser that reflects off the back of the cantilever and onto a four quadrant photodiode. A feedback loop maintains a constant tip-sample force. There are basically three operation modes of AFM classified by the way of tip motion, which can be divided in contact mode, where a constant cantilever deflection is maintained, or in tapping mode where the cantilever is oscillated near resonance and constant amplitude is maintained, or non-contact mode. Figure 3.4 Classifies the AFM working principle and modes. With the help of different tips, the AFM enable us to study the mechanical and electric properties of an individual liquid metal nanodroplet by the force spectroscopy and electric current measurements.

![Schematic drawing of the work principle and working modes of AFM.](image)

**Figure 3.4** Schematic drawing of the work principle and working modes of AFM.
3.3.3. X-ray Powder Diffraction (XRD)

XRD is a rapid analytical technique for identification and investigation of crystalline materials and provide information of phases and crystal structures. The fundamental principle of XRD as well as the Bragg equation are illustrated in Figure 3.5. The atoms in crystalline materials are arranged periodically. The incident X-ray beam shining on the crystalline sample would be scattered by the periodic array of atoms with long-range order. For the different planes of the periodic array in the material, the resulting diffracted X-rays travels via different optical path lengths. This path length depends on the incident angle of beam and the distance between the periodic planes, which can be summarized in the Bragg Equation shown in the Figure 3.4. Based on the equation, constructive interference occurs only if the path difference ($2d \cdot \sin \theta$) is a multiple of the used X-ray wavelength. The angles that related to the constructive interference can be measured, then, utilizing the value of the wavelength already known and the Bragg equation, the distance between the lattice planes of the material was determined. In this work, the possible crystalline information of the liquid metal and its hybrids were determined by a powder X-ray diffractometer consists of an X-ray source (MMA, GBC Scientific Equipment).

![Figure 3.5] Fundamental principles of XRD.
3.4. Mechanical, Electric and Magnetic Measurements

3.4.1. Rheological measurement

Rheology is the study of flow and deformation of materials under applied forces which is routinely measured using a rheometer. The measurement of liquid metal’s rheological properties could help to understand the deformations, viscosity and viscoelasticity properties of liquid metal, and these properties may also vary depending upon the external conditions applied, such as stress, strain, timescale, temperature and magnetic field. There are two modes, rotational and oscillatory mode, for any type or combination of rheological tests. Here, the oscillatory mode were chosen, to determine not only the viscous but also the elastic properties of a material. During rheological tests in oscillation, a sample is exposed to a continuous sinusoidal excitation of either a deformation or a shear stress. Depending on the type of excitation, the material will respond with a stress or a deformation. Oscillatory measurement techniques are ideal to quantify the amount of viscosity and elasticity hidden in a material’s structure, so it is a preferred method for investigating the storage behavior and shelf life stability of complex materials, which is suitable for the investigations of liquid metal and its hybrids.

In our work, the Rheological properties of samples without and with magnetic field applied were carried out by a commercial rheometer (Physica MCR301, Anton Paar Co., Austria) equipped with a magneto-controllable accessory MRD180, as shown in Figure 3.6.
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Figure 3.6 Instrument schematic diagram for the measurements of fluid viscosity as a function of magnetic field. The main parts contain a rheometer MCR 301 of parallel disc and a magnetic control cell.[3] (Reproduced with permission from ref. 3, copyright 2017, IOP Publishing.)

3.4.2. Mechanical Compression Test

The compression test is a method for determining the behavior of materials under a compressive load. Compression tests are conducted by loading the test specimen between two plates, and then applying a force to the specimen by moving the crossheads together. During the test, the specimen is compressed, and deformation versus the applied load is recorded. The compression test is used to determine elastic limit, proportional limit, yield point, yield strength, and (for some materials) compressive strength. In this work, the mechanical properties of samples were tested by the MTS Universal Test Systems.

3.4.3. Physical Property Measurement System (PPMS)

The PPMS is an automated low-temperature and magnet system for the measurement of material properties like specific heat, magnetic AC and DC susceptibility and both electrical and thermal
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transport. In this work, the resistivity and magnetic properties of liquid metal and its hybrids are the study content, so the DC Resistivity option and Vibrating Sample Magnetometer (VSM) option were the two mode that chosen during the measurement. The DC Resistivity option is used for making basic DC resistance measurements by applying a current and measuring the resulting voltage. Four point resistance measurement setup were performed in this work. The Resistivity option can report DC excitation based resistance as well as resistivity, conductance, and conductivity. The VSM option transforms the PPMS into a sensitive DC magnetometer for fast magnetic data acquisition of the sample. The sensitivity of the VSM detection coils is not significantly affected by large magnetic fields, which facilitate sensitive measurements up to the maximum field available from the magnet in the system. The basic measurement is accomplished by oscillating the sample near a detection coil and synchronously detecting the voltage induced. By using a compact gradiometer pickup coil configuration, a relatively large oscillation amplitude and a frequency of 40 Hz, the system is able to resolve magnetization changes of less than $10^{-6}$ emu with 1 sec averaging. In this work, the electrical and magnetic properties of samples were tested by the PPMS DynaCool equipped with resistivity assessment and VSM assessment.

![Digital photo of Physical Property Measurement System, and schematic diagram for sample chamber.](image)

**Figure 3.7** Digital photo of Physical Property Measurement System, and schematic diagram for sample chamber.

### 3.5. References


Chapter 3: Experimental Procedure

Chapter 4

4. Preparation of liquid metal nanodroplets for mechanical-active printing electronics

4.1. Introduction

The next-generation micro/nano electronic devices are expected to be lighter, smaller, more flexible, faster, and more energy-efficient, as well as being able to meet the requirements of recent innovations in new microsystem technologies such as micro/nano integrated circuits, lab-on-a-chip biosensors, etc.\cite{1-4} Although intrinsically rigid and stiff materials, such as Cu,\cite{5} Au,\cite{6} and even Si,\cite{7} have the ability to be rendered flexible by making them thin enough, then constructing devices that maintain the function after folding or crumpling.\cite{8-9} Moreover, by fabricating these sufficiently thin rigid materials in strategic geometries, the fabricated devices can be rendered stretchable.\cite{1} However, the stretchability and deformability of these devices are still very limited and highly depended on the design of circuits, which is far away from 100 % soft electronics required in the next-generation micro/nano electronic devices.\cite{10} It is expected to remove this limitation by using the intrinsically soft materials, but often failed to meet the requirement of good electronic performance. Recently, the re-emergence of room temperature liquid metals presents a forgotten exciting paradigm for an ideal combination of metallic and soft properties.\cite{6}

As metals that are liquid at room temperature, Ga-based LMs have an extremely high deformation capability in the in-plane direction, in addition to out-of-plane flexibility at room temperature.\cite{11-13} These unique characteristics allow the Ga-based LMs to retain electrical connections after being stretched, compressed, and/or bent in different configurations.\cite{14-15} Taking advantage of their flexibility and tractability, numerous applications, including reversibly deformable and mechanically tunable fluidic antennas, three-dimensional stretchable conductors, large-scale flexible strain sensors, and wearable tactile interfaces, have been successfully developed in recent progress on the development of Ga-based LMs.\cite{6, 16}

However, when making the micro/nano- electronics based on such fluid metal, the high surface tension and the spontaneously formed oxide skin make the bulk Ga-based LMs be challenging to
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reach patterning precision.\textsuperscript{[17]} To overcome the limitations posed by high surface tension, here we demonstrate the creation of LM nanoparticle inks by sonication liquid bulk sample in a thiol solution. Each LM particle in the ink was protected by the oxide layer, which can be broken by external pressure. A continues and conductive thin film with defined micro- or nano-size can be obtained by applying localized pressure on the LM particles. These LM dispersions exhibit excellent wettability to metallic, oxide, and polymer surfaces. By using these dispersions as inks, stretchable and flexible electronic devices have been fabricated and demonstrated on polydimethylsiloxane (PDMS) and polyethylene terephthalate (PET) plastic substrate by direct printing and laser etching.

4.2. Experimental Section

4.2.1. Preparation of Galinstan Bulk and Nanodroplets

Galinstan bulk samples were prepared by the co-melting methods with the weight ratio: 68\% Ga, 22\% In, and 10\% Sn. And related galinstan droplets are prepared by ultrasonication methods.

4.2.2. Characterization

Field emission scanning electron microscope (FE-SEM) observations were performed using a JEOL JSM-7500FA microscope. Samples for FE-SEM characterization were prepared by depositing galinstan suspension onto Si wafers. The diameters of the as-prepared nanoparticles were obtained by counting more than 200 particles in several SEM images for each sample, using the Image J free software. Transmission electron microscope (TEM) images, selected area electron diffraction (SAED) patterns, high-angle annular dark field (HAADF) images, and EDX spectra were obtained using a JEOL ARM-200F and a Tecnal G2 F20 operating at 200 kV with an EDX solid-state X-ray detector.

4.2.3. AFM Measurements

The force–displacement measurements were performed in air using a JPK Nanowizard AFM. 28-nm diameter silicon based tips with frequency of 70 kHz and spring constant of 2 N·m\textsuperscript{−1} were used to apply a 36 nN force on an individual galinstan nanodroplet for the force spectra. The I–V curves before and after breaking the galinstan nanodroplets with the tip were also collected by using the c-AFM. Both force and conductive analysis was performed in contact mode.
4.2.4. Fabrication of Micro-patterns or Electronics

The inkjet ink used for printing was a 200 mg/10 mL galinstan nanodroplets suspension in ethanol. The patterns were directly printed on a flexible plastic substrate (PET). For the patterns and electrodes prepared by laser lithography, a uniform thin film of the galinstan nanodroplets ethanol suspension was first deposited on PDMS elastomer. Then, a fiber laser cutter system (Universal PLS6MW Multi-Wavelength Laser Platform, 1.06 μm, 30 watts, spot size of ≈25 μm) was used to etch the unwanted components and achieve the desired pattern and electrode. For galinstan thin-film etching, the laser power was set at 23%, the scan speed was fixed at 10% and image quality level was set as “Quality”. The mechanical sintering route to make the conductive paths for micro-patterns or electrodes was conducted using a writing utensil to press the top surface of the plastic and PDMS. The resistance of these electrodes after the mechanical sintering process and continuous bending process was recorded by a multimeter.

4.3. Results and Discussion

![Figure 4.1. Schematic illustration of the preparation route for galinstan nanodroplets. Before ultrasonication, the galinstan bulk sample presents as millimeter sized droplets. After ultrasonication in the ethanolic solution of thiol, the millimeter droplets are separated into nanometer sized droplets.](image)
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The galinstan bulk alloy used here is a low-viscosity liquid at RT, with a composition of Ga, In, and Sn in different weight ratios. Galinstan normally presents as millimeter-size droplets when dropped on a substrate under gravity. These oval-shaped droplets can remain mechanically stabilized by intrinsic passivation due to the formation of a thin gallium oxide skin in air. Nevertheless, the skin obstructs direct printing of the Ga-based LMs in 3D or 2D structures with defined size. For facilitating the printing of micro/nanoelectronics, the galinstan nanodroplets were obtained here via a simple ultrasonication process in the presence of thiols. In the typical synthesis, as shown in Figure 4.1, a certain amount of galinstan bulk was first dropped into an ethanolic solution of thiol. Then, probe sonication was applied to introduce cavitation in the solution, leading to local extremes of pressure and temperature for ultrashort life-spans.

Figure 4.2. (a) From left to right: galinstan bulk in ethanol solvent before probe sonication, galinstan ethanol suspension after the probe sonication, galinstan acetone suspension after the probe sonication and re-dispersion in acetone after centrifugation, and galinstan aqueous suspension after the probe sonication and re-dispersion in water after centrifugation. (b), (c) FE-SEM image of galinstan
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nanodroplets prepared by 40% power ultrasonication at 20 °C for 60 min. (d) Size distribution of galinstan nanodroplets. The mean diameter is ≈110 nm.

During this sonication, the liquid galinstan bulk stabilized by the oxidation layer was easily fractured under the oscillating shear force, and small LM droplets successively separated from the bulk matrix in a spherical shape, due to the high surface energy of the freshly exposed oxide-free surface.\textsuperscript{[18]} In the meantime, thiolated ligands, which can easily and strongly bind to soft elements, readily assembled onto the surface of the new-born small galinstan droplets, competing with the re-oxidation process, which also took place at the interface.\textsuperscript{[19]} Finally, spherical galinstan nanodroplets (TEM image in Figure 4.1) formed under continuous ultrasonication and remained mechanically stabilized because the protection from the thiolate-ligand self-assembly and rapid oxidation on the surface. After the ultrasonication and removal of excess thiols by washing with ethanol, grey slurry was obtained and re-dispersed in different solvents, which all remained suspended up to several weeks (Figure 4.2 (a)). The FE-SEM microscope image in Figure 4.2 (b) and (c) also confirms that a large quantity of uniform spherical galinstan nanodroplets was successfully synthesized by the ultrasonication process. By counting more than 200 particles in several SEM images for the as-prepared sample with the assistance of Image J free software, the particle size distribution of the samples (Figure 4.2 (d)) obtained after a 60 min sonication indicates an average diameter of about 110 nm.
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Figure 4.3. TEM and scanning TEM (STEM) characterization of galinstan nanodroplets at room temperature: (a) Representative TEM image of galinstan nanodroplets. (b) HRTEM image demonstrates the core–shell structure of galinstan nanodroplets; the black core is the liquid metal (galinstan alloy), and the lighter part is the coating shell; two layers of shell can be observed: the inner coating (gallium oxide) is ≈3 nm thick, and the organic matter layer is ≈3 nm; the inset is the corresponding SAED pattern. (c) A typical STEM image of galinstan nanodroplets, as along with element mapping of the same galinstan nanodroplets. From left to right, the images show galinstan nanodroplets mapped for C (yellow), O (magenta), Ga (red), In (green), and Sn (blue).

TEM together with EDX elemental mapping of particles taken from the as-prepared galinstan (65% Ga, 24% In, 11% Sn by weight) suspension revealed the microstructure and constitution of the galinstan nanodroplets after ultrasonication. As seen in Figure 4.3 (a), (b), smooth core–shell-like spherical NDs are uniformly packed together and two concentric layers are evenly coated on the core. Despite the slight size disparity among the different NDs, the inner and outer shells of these particles are all ≈3 nm thick and ≈2 nm thick, respectively. Both the shells and the core are entirely amorphous, which is similar to the case of the galinstan bulk sample at RT. The low magnification HAADF scanning TEM (STEM) images which are sensitive to atomic number, as well as the element mapping of the sample (Figure 4.3 (c)) further verified that the amorphous nanodroplets present a homogenous
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distribution of elements and the element compositions of these nanodroplets were the same as for the bulk.

**Figure 4.4.** (a) EDX spectrum and analysis (inset) of the galinstan (65% Ga, 24 % In, 11% Sn by weight) nanodroplets at room temperature; the weight ratio Ga:In:Sn of these nanoparticles is 31.47:11.54:5.44, almost the same as for the original bulk sample; the signals of C and O correspond to the Ga oxide and organic coating; the Cu element is from the TEM grid. (b) HAADF-STEM image combined with different phase identifications of the galinstan nanodroplets at room temperature; based on the element mapping in Figure 3.3 (c): Phase 1 shows the eutectic alloy phase containing Ga/In/Sn, Phase 2 shows the Ga oxide shell of the droplets, and Phase 3 shows the outer organic matter layer of these droplets.

As proposed in the schematic illustration of the synthetic process and confirmed by the EDX quantitative analysis (Figure 4.4 (a)), Ga, In, and Sn appear to be evenly dispersed in the core of the ND in the same weight proportions as in the galinstan bulk sample. Oxygen and Ga are present in the inner shell and carbon is only present on the outer surface of the spherical nanodroplet. As shown in Figure 4.4 (b), the element mapping results confirmed that Ga is easily passivated to form an oxidation layer when the nano-sized galinstan drops are separated from the galinstan matrix and
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exposed in an oxygen-rich environment. At the same time, an organic coating containing carbon surrounds the gallium oxide during the thiolated ligand self-assembly process in the ethanol solution.

The two layers covered the surface of galinstan nanodroplets, as a result of the competition between thiolated ligand self-assembly and the oxidation process. They acted as protective shells for the newborn galinstan nanodroplets, which ensure that these nanosized droplets are mechanically stabilized against coalescence in a neutral solution or in the atmosphere. Akin to noninfiltration liquid droplets, these non-crystallized galinstan nanodroplets exhibit good elasticity and can deform under the pressure of other particles (Figure 4.2 (a)), due to the liquid characteristic of the core and the protection of the hetero-phase shells. Besides the structure and morphology of the galinstan nanodroplets, mechanical information of these soft liquid particles with protective shell are essential for better handling these galinstan nanodroplets towards soft electronics. Characterization of LM nanoparticles with AFM is a simple and effective tool to study the surface properties of individual particles, but has been rarely reported.

Figure 4.5. (a) AFM topographical image and (b) 3D morphological reconstruction of an as-prepared galinstan nanodroplet on a silicon wafer.

Figure 4.5 shows a typical AFM topographical image and 3D morphological reconstruction of the nanodroplets sample, which is similar to SEM observation. Figure 4.5 (b) shows that the selected isolated liquid metal nanoparticle has a lateral size of 100 nm. The mechanical properties was investigated by contact mode AFM, the response of individual nanodroplet to the localized force
applied was quantified by in-situ breaking an individual galinstan nanodroplet (≈100 nm in diameter) under external force by an AFM force–displacement measurement, as demonstrated in Figure 4.6.

Figure 4.6. Force–displacement curve obtained for one individual galinstan nanodroplet; the red line tracks the approach process between the AFM tip and the particle, while the blue line tracks the retraction of the AFM tip from the particle; the inset presents the I–V curves before and after the galinstan nanodroplet is broken by the applied external pressure.

First, the AFM tip was made to approach the individual galinstan nanodroplet until negative force feedback was observed (indicating attraction between the tip and the nanodroplet surface due to van der Waals attraction). The tip was then lowered to touch the nanodroplet surface by further reducing the tip-sample distance. After that, a gradually increasing force was applied to the surface through the tip, which led to the compressive deformation of the nanodroplet, as reflected by the linear force–displacement behavior. When the applied force was greater than ≈50 nN, breakthrough of the galinstan nanodroplet occurred, as evidenced by the kink that appears in the force–displacement curve. In the retraction process (shown by the blue curve), the force curve does not overlap with the curve.
corresponding to the approaching force curve (in red). This is attributed to the adhesion between the tip and the liquid core of the nanodroplet, as well as the great surface tension of galinstan. The I–V curves before and after the breaking of the galinstan nanodroplet by external pressure were also measured by using the AFM conductive mode (c-AFM). Excellent electrical conductivity was achieved in the individual nanodroplet after the shell breaking, indicating that nano-sized galinstan droplets also retain the same high electrical conductivity as the bulk form.

![Image of galinstan bulk and SEM of galinstan nanodroplet](image)

**Figure 4.7.** (a) Digital image of galinstan bulk and SEM of galinstan nanodroplet. (b) – (d) Schematic and digital images of the electronics prepared by different routes including directly writing, inject printing and laser engraving, based on the droplets. (e) The image shows a flexible micro-coil and micro-gapped interdigitated electrode prepared by laser lithography from an galinstan nanodroplets film assembled on PDMS; (d) the resistance stability of the micro-coil on PDMS after mechanical sintering is demonstrated over a hundred rounds of bending and folding.

By using these dispersions as inks, any defined patterns can be fabricated and demonstrated on the varying substrates by direct hand writing, inject printing and laser engraving (Figure 4.7 (b)-(d)). Generally, printed flexible devices suffer from low conductivity because of the poor in-plane electrical connections between nanodroplets with insulating/semiconducting shell structures. Unlike the conventional solid metallic or conductive polymer nanodroplets, which need various complicated sintering methods to improve their conductivity in printed devices, the in-plane electrical conductivity of galinstan nanodroplets films can be enhanced by a facile “mechanical sintering” method.\[20-21\] In
other words, the insulating shells of the galinstan nanodroplets can be easily broken as the response to the external force stimulus and thus, the electrical connections can be significantly improved by merging individual nanodroplets together. A highly conductive path (Figure 4.7 (b)) could be easily obtained by simply directly writing with these galinstan nanodroplets dispersions with relative high concentration, due to a local pressure simultaneously applying on these nanodroplets during the writing process. This illustrates that the mechanical sintering process is easily conducted to realize the coalescence of galinstan nanodroplets, and hence, that the electrical conductivity of the galinstan-nanodroplet-based flexible circuits can be greatly improved.

4.4. Conclusion

In this work, we reported preparation and characterization of galinstan liquid metal nanodroplets with average particle sizes of ≈110 nm synthesized by using sonication and thiol self-assembly. A systematic characterization of the microstructure, crystallization, phase, phase components, and mechanical properties was carried out on the as-prepared galinstan nanodroplets. In additional to common characterization with SEM and TEM, AFM characterization was firstly conducted to provide more information on the mechanical force-stimulus responsive properties of liquid metal nanoparticles. The galinstan nanodroplets with a liquid-phase core and solid shell structure can be merged together in response to the local pressure applied, forming a desirable conductive path to active the printed electronics. This work provide deep understanding on the mechanical stimulus response of individual LM particles, and shows LM nanodroplets promising candidates for developing practical micro-/nano-sized stretchable electronic devices.

4.5. References


Chapter 5: Ga-based liquid-metal nanodroplets for low-temperature-active superconductive electronics

5. Ga-based liquid-metal nanodroplets for low-temperature-active superconductive electronics

5.1. Introduction

The next-generation micro/nano electronic devices are expected to be lighter, smaller, more flexible, faster, and more energy-efficient, as well as being able to meet the requirements of recent innovations in new microsystem technologies such as micro/nano integrated circuits, lab-on-a-chip biosensors, etc.\cite{1,2} Superconductors are regarded as one of the most promising candidates for next-generation advanced electronic devices, because their zero electrical resistance and high current density are great advantages for achieving energy saving and ultrahigh-speed processing.\cite{3} Furthermore, nanoscale superconductors, which are featured by high current transport density with no loss and strong quantum-size oscillations effect below their critical temperature ($T_c$), have attracted considerable attentions for building high-speed micro-/nano-electronic devices, including rapid responding biosensor, quantum computer and micro Nuclear Magnetic Resonance (NMR) device.\cite{4-8} In despite of some recent progress on developing nano-sized superconducting electronics by nanolithography techniques, including atomic superconductor thin film and Josephson-junction-devices, can be fabricated on laminated films consisting of a superconductor layer and a buffer layer by nanolithography techniques, the processing complexity and high manufacture cost limit these superconducting micro/nanodevices in certain areas but not practical in more extensive applications.\cite{9-12}

Moreover, the intrinsic brittleness of these superconducting nanodevices does not allow any deformations, e.g. stretching or bending, which make them impossible to be incorporated in flexible electronics.\cite{13} Among all the superconductors, Ga and Hg are exceptional which were expected to be used for superconducting micro/nano devices because their RT fluidity benefits device processing and offers the devices RT-flexibility.\cite{14-16} However, either low $T_c$ (1.08 K for Ga) less than liquid helium temperature (4.2 K, the lowest temperature for practical application) or toxicity (Hg) of these two RT LMs significantly limits their potential usage. To date, it is still a great challenge to develop superconductors that have comprehensive properties of non-toxicity, higher $T_c$, RT-
Chapter 5: Ga-based liquid-metal nanodroplets for low-temperature-active superconductive electronics

fluidity/tractability, and good wettability, which are highly demanded for the development of flexible superconducting micro/nano electronics.

In this work, we developed a series of Ga-based liquid metals and corresponding nanodroplets, which can be used to fabricate flexible superconducting micro/nanoelectronics by direct printing. These Ga-based LMs demonstrate a great potential for building flexible micro/nano electronics, owing to the RT fluidity, low resistivity, low viscosity, and tractability of LMs.\textsuperscript{17-20} More importantly, the intrinsic passivation of Ga results in high surface tension for the Ga-based LMs, which ensures that LM nanodroplets can keep excellent mechanical and electronic properties of their bulk even when they are dispersed into solutions as the inks. By varying component proportions of Ga, In, and Sn in Ga-based alloys, we have successfully modulated superconducting $T_c$ as high as 6.6 K. The related nanodroplets have also been prepared by an ultrasonication approach. These nanodroplets retain their bulk superconducting properties and can be dispersed and stored in various solvents, including ethanol, acetone, and water. By using these dispersions as inks, stretchable and flexible superconductive devices, including micro-size superconducting coils, electric circuits, and superconducting electrodes, have been fabricated and demonstrated on substrate by direct hand writing, inject printing and laser engraving.

5.2. Experimental Section

5.2.1. Material synthesis

Ga-In-Sn alloy bulk samples with various component proportions were prepared by co-melting Ga, In, and Sn in the appropriate weight ratio. And related galinstan droplets are prepared by ultrasonication methods.

5.2.2. Characterizations

The products, LM nanodroplets were analysed by FESEM (JEOL-7500A) equipped with the Oxford EDX detector. The in situ temperature dependence TEM analysis was performed with a JEOL ARM-200F and a Tecnal G2 F20 operating at 200 kV with an EDAX solid-state X-ray detector. A TEM Cu grid with nanodroplets was loaded into a liquid nitrogen cooling holder from JEOL. Temperature control of the specimen was achieved through a metallic rod connecting the specimen
holder to the liquid nitrogen dewar, which contains an electric heater for heating and adjusting the temperature. The TEM images and SAED patterns were collected every 10 °C from RT using a JEOL ARM-200F operated at 200 kV. The HAADF images were collected using a 50 mrad inner collection angle and a 180 mrad outer collection angle. The STEM–EDX spectrum was acquired by a NORAN SDD with ≈1 sr collection angle, at −150 °C.

5.2.3. Fabrication of electronics

Conductive electrodes was directly hand wrote down at the paper by a brush pen. The inkjet ink used for printing was a 200 mg/10 mL LM nanodroplets suspension in ethanol. The patterns were directly printed on a flexible plastic substrate (PET). For the patterns and electrodes prepared by laser lithography, a uniform thin film of the LM nanodroplets ethanol suspension was first deposited on PDMS elastomer. Then, the laser was applied to create the designed pattern and electrode. A final mechanical sinter process was conducted for the inkjet and laser printing route.

5.2.4. Superconductivity and Magnetization Measurements

Resistivity was measured using PPMS with a standard four-probe method. Samples 2 mm × 5 mm × 0.1 mm in size were prepared for the resistivity measurement. DC magnetization and the magnetic relaxation measurements were performed using the vibrating sample magnetometer option of the PPMS.

5.3. Results and Discussion

In the previous work, Ga-based liquid metal bulk has been divided into nanodroplets via a simple ultrasonication process in the presence of thiols. After the nanosizing process, the uniform ethanol dispersion of nanodroplets enables easy fabrication of fine microcircuits and functional devices by inkjet printing, laser lithography, and even handwriting. As demonstrated in Figure 5.1, different RT-flexible devices on PET and PDMS substrates, including planar coils and electrode arrays, were fabricated by inkjet printing and/or laser lithography. The LMs (galinstan) flexible electric circuits on PDMS can retain high in-plane conductivity after a hundred rounds of bending and folding (Figure 5.1 (d)). However, the structure evolution and the electric behaviours in response to the temperature changing have been rarely revealed.
Chapter 5: Ga-based liquid-metal nanodroplets for low-temperature-active superconductive electronics

Figure 5.1. (a) and (b) are digital images of sintered flexible circles printed with the galinstan nanodroplet based inkjet and of the good electrical conductivity measured by a multimeter (inset image). (c) The image shows a flexible micro-coil and micro-gapped interdigitated electrode prepared by laser lithography from an galinstan nanodroplets film assembled on PDMS; (d) the resistance stability of the microcoil on PDMS after mechanical sintering is demonstrated over a hundred rounds of bending and folding.

Nanomaterials exhibit exotic physical properties, in contrast to their bulk forms, due to the size effect. Generally, the melting points of metals are depressed in nanomaterials.\(^\text{21-23}\) Determination of the crystallization behavior of galinstan nanodroplets is therefore critical for processing micro/nanodevices. In situ temperature-dependent TEM was applied here in order to determine the melting point and to investigate the crystallization process for the as-prepared galinstan nanodroplets. As shown in Figure 5.2 (a), snapshot TEM images and selected area electron diffraction (SAED) patterns of galinstan nanodroplets were recorded every 10 °C (10 K) from RT to liquid nitrogen temperature (77 K). The crystallization of EGaInSn occurs at −80 °C (193 K), as the corresponding SAED pattern shows well-defined diffraction spots. While the spots in the pattern were clear, they
Chapter 5: Ga-based liquid-metal nanodroplets for low-temperature-active superconductive electronics

appeared and disappeared in a time frame of seconds, which is due to spontaneous amorphization and recrystallization at this temperature.

![Figure 5.2. TEM images at different temperatures of galinstan nanodroplets. (a) TEM images (top) and the corresponding SAED patterns (bottom) of galinstan nanodroplets at representative temperatures: from left to right, 10 °C (283 K), −70 °C (203 K), −80 °C (193 K), −140 °C (133 K), and −150 °C (123 K). (b) STEM image of galinstan nanodroplets, as along with element mapping of the same galinstan nanodroplets at −150 °C (123 K): from left to right, the images show galinstan nanodroplets and mappings for C (yellow), O (Magenta), Ga (red), In (green), and Sn (blue).](image_url)

Interestingly, the galinstan nanodroplets undergo a phase separation accompanied by crystallization. It is clearly demonstrated in HRTEM images that a small part of each individual nanodroplet has separated out from the amorphous matrix. Detail information of the SAED pattern at −80 °C (193 K) shown in Figure 5.3 (a), indicate that these separated parts appeared at −80 °C only consist of crystalized In and Sn. With further cooling, displayed in Figure 5.3 (b), the crystallized Ga appeared at the temperature of −140 °C (133 K). Moreover, the SAED pattern of the nanodroplets was retained and did not change any more with further decreasing temperature, indicating the fully crystalline state of all the galinstan nanodroplets. The HAADF image and element mapping of these
nanodroplets at −150 °C (123 K) (Figure 5.2 (b)) further confirmed the phase separation during this cooling process.

**Figure 5.3.** SAED patterns of galinstan nanodroplets at (a) −80 °C and (b) −150 °C. The diffraction spots in the SAED pattern at −80 °C can be indexed to In and Sn, and no Ga related diffraction spots can be observed in this SAED pattern, indicating that In and Sn have started separating out and becoming crystalline, while Ga is still in a liquid amorphous phase at this temperature. When the temperature is reduced to −150 °C, Ga related diffraction spots appear, implying the crystalline nature of Ga and the full crystallization of the whole particle.

These results imply that the melting point or the fully crystalline point from liquid to solid of the as-prepared galinstan nanodroplets was ≈−140 °C (133 K, defined as $T^*$), which is depressed by almost 150 °C (150 K) compared with the bulk EGaInSn (=10 °C, 283 K). Another interesting result should be noted is, as shown in phase mapping of these nanodroplets at −150 °C (Figure 5.4), that the original liquid galinstan nanodroplets at RT separated into two phases at this low temperature. According to the element mapping results, these two phases are Ga phase and InSn alloy phase, indicating the In and Sn are still alloying together and embedded in the solid Ga matrix.

**Figure 5.4.** HAADF-STEM image combined with different phase identifications of the galinstan nanodroplets at -150 °C (123 K). Based on the element mapping in Figure 2(e), besides the Ga oxide shell phase and the outer organic matter layer (Phase 3 and Phase 4), the initial single phase of the core in the particle at RT is now divided into two phases. These two phases, Phase 1 and Phase 2, are related to Ga metal and InSn alloy respectively.
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Having demonstrated the good electrical conductivity of the microelectronics printed by the as-prepared galinstan nanodroplets, the superconductivity of the alloy at low temperature is now first revealed in this work. The transition temperature of the Ga-In-Sn alloy can be modulated by varying the ratio of its component elements, as shown in Table 5.1 and Figure 5.5. Based on evaluating both the onset $T_c$ and the offset $T_c$, the sample with the highest $T_c$ among all the samples was Ga$_{30}$In$_{47}$Sn$_{23}$ (30% Ga, 47% In, 23% Sn by weight), the $T_c$ of which reaches as high as 6.6 K, which is much higher than those of the individual components (1.08 K for Ga, 3.41 K for In, and 3.73 K for Sn).$^{[24-25]}$

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_c^{onset}$ (K)</th>
<th>$T_c^{offset}$ (K)</th>
<th>$H_{c2}(0)$ (T)</th>
<th>$\xi$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga$<em>{65}$In$</em>{24}$Sn$_{11}$</td>
<td>6.63</td>
<td>4.33</td>
<td>0.83</td>
<td>19.9</td>
</tr>
<tr>
<td>Ga$<em>{90}$In$</em>{7}$Sn$_{3}$</td>
<td>6.63</td>
<td>4.14</td>
<td>0.44</td>
<td>27.3</td>
</tr>
<tr>
<td>Ga$<em>{30}$In$</em>{47}$Sn$_{23}$</td>
<td>6.63</td>
<td>5.66</td>
<td>0.85</td>
<td>19.7</td>
</tr>
<tr>
<td>Ga$<em>{10}$In$</em>{61}$Sn$_{29}$</td>
<td>6.55</td>
<td>3.85</td>
<td>1.34</td>
<td>15.7</td>
</tr>
<tr>
<td>Ga$<em>{0}$In$</em>{68}$Sn$_{32}$</td>
<td>6.55</td>
<td>5.32</td>
<td>0.93</td>
<td>18.8</td>
</tr>
</tbody>
</table>

Table 5.1. Summary of the onset $T_c$ and offset $T_c$, as well as the upper critical field at 0 K and the coherence length, of the Ga-In-Sn alloy samples (2 mm × 5 mm × 1 mm) with different component proportions.

$T_c^{onset}$ and $T_c^{offset}$ are determined by the criterion of 90% $R_n$ and 10% $R_n$, respectively, where $R_n$ is the normal state resistance at 8 K. The upper critical field $H_{c2}$ is deduced by the criterion of 90% $R_n$ as a function of temperature. The zero-temperature upper critical field $H_{c2}(0)$ could be obtained by the Werthamer–Helfand–Hohenberg (WHH) formula:

$$H_{c2}(0) = -0.693T_c \frac{dH_{c2}}{dT}_{T=T_c}$$

The coherence length $\xi$ could be calculated by the formula:

$$\xi = \sqrt{\frac{\phi_0}{2\pi H_{c2}}}$$

Where $\phi_0$ is the magnetic flux quantum.
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Figure 5.5. (a) Temperature dependence of the resistance between 2 K and 8 K for different Ga-In-Sn alloys with various component proportions, normalized by the resistance at 300 K. (b-f) Normalized temperature dependence of the resistance between 2 K and 8 K for the different alloys under different magnetic fields: (b) Ga$_{10}$In$_{61}$Sn$_{29}$, (c) Ga$_{17}$In$_{60}$Sn$_{23}$, (d) Ga$_{30}$In$_{47}$Sn$_{23}$, (e) Ga$_{65}$In$_{11}$Sn$_{24}$, (f) Ga$_{90}$In$_{7}$Sn$_{3}$.

The two-step behavior of Ga$_{10}$In$_{61}$Sn$_{29}$ in superconducting transition region is a clear signal for the inhomogeneous distribution of superconducting regions with different \( T_c \). The first transition at around 6.5 K corresponds to the \( T_c \) of InSn alloy, and the second one occurring at around 4 K is related to \( T_c \) of individual Sn or In. With the increment of applied magnetic field, both of the two transition
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temperature shift to low value. The lower $T_c$ shifts to the value less than 2 K when the field is increased up to 0.2 T, overstepping the range of our transport measurements. Thus, the step in lower temperature seems to vanish at high magnetic fields in Figure 5.5 (c). Only one superconducting transition at around 6.5 K could be observed in Figure 5.5 (d). The step-like transition at high field is related to the broadening of the resistivity transition. This broadening at high magnetic field is a direct evidence of thermal fluctuation in a vortex system due to the inhomogeneous distribution of Ga and InSn alloy. There is an anomalous tail effect on the resistivity transition in Figure 5.5 (e) and 5.5 (f), which could be attributed to the inhomogeneous distribution of InSn alloy and Ga particles in low temperature. InSn alloy enters into the superconducting state when the temperature just below 6.5 K. While Ga or possible In and Sn is still metal due to low $T_c$ (1.08 K for Ga, 3.41 K for In, and 3.73 K for Sn). The coexistence of superconducting phase and metallic phases could produce the superconductor-metal-superconductor junction. This kind of junction displays different properties depending on the distance between adjacent superconductors. When the distance is within the coherence length $\xi$, this junction behaves as Josephson junction, providing a superconducting channel to the current. If the distance is much larger than the value of $\xi$, the resistance of this junction will be nonzero. The inhomogeneous distribution of of Ga and InSn alloy leads to presence of the junctions with different superconducting $T_c$. Thus, the resistivity cannot reach zero quickly with the decrement of temperature, forming a tail effect on the resistivity transition.

The transition temperature of the Ga-In-Sn alloy is above the liquefaction point of helium, promoting this alloy’s practical application. Thus, the Ga$_{30}$In$_{47}$Sn$_{23}$ in the forms of bulk alloy and nanodroplets was chosen to study the superconducting properties. Figure 5.6 displays a comparative study of the temperature dependence of the resistivity ($\rho$–$T$) between the bulk sample and the nanodroplets-based printed circuit, which show similar metallic behavior above 6.6 K. It was found that the conductivities of the bulk and nanodroplet liquid metal samples show a slight difference at room temperature but almost the same below $T_c$. It should note that there is a jump in $\rho$–$T$ curves at around 225 K for both bulk and nanodroplet samples. Considering that the value of 225 K is close to phase separation and crystallization temperature observed in TEM characterizations, the origin of this jump is most likely attributed to effect of the transition from amorphous matrix to crystallized samples in this system. In this case, the scattering for charge carriers is significantly depressed due to the
formation of long-range ordered phonon vibration, leading to cliffy increase in conductivity, i.e., an obvious dip in temperature dependent resistivity.

\[ \text{Figure 5.6. Temperature dependence of the resistivity (\(\rho-T\) curves) between 2 and 300 K for the bulk sample (2 mm x 5 mm x 0.2 mm) and a printed nanodroplets pattern (2 mm x 5 mm x 0.1 mm) after mechanical sintering; inset: enlargement of the \(\rho-T\) curves between 2 and 8 K. The superconducting transition temperatures } T_c \text{ of these two samples are both around 6.6 K.} \]

The inset of Figure 5.6 shows an enlarged view of the \(\rho-T\) curve at low temperature, ranging from 2 to 8 K, where the two samples demonstrate the same superconducting transition at the temperature of 6.6 K. The enhancement of the \(T_c\) compared to the individual components of the alloy is confirmed by the temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements at 50 Oe for the Ga\(_{30}\)In\(_{47}\)Sn\(_{23}\) bulk sample and the Ga\(_{30}\)In\(_{47}\)Sn\(_{23}\) nanodroplets sample, as shown in Figure 4b. Both the transport measurements and the magnetic measurements imply that the superconducting properties of Ga alloy have scarcely degenerated after nano-crystallization. More importantly, as a flexible printed device, the Ga\(_{30}\)In\(_{47}\)Sn\(_{23}\)-nanodroplet-based printed circuit can be
deformed to be any shape in RT and retain the superconducting properties without any fading (Figure 5.7).

**Figure 5.7.** Temperature dependence of the resistance between 2 K and 100 K for a bended printed Ga$_{30}$In$_{47}$Sn$_{23}$ nanodroplets pattern after mechanical sintering; inset: enlargement of the temperature dependence of the resistance curve between 2 K and 8 K. The superconducting transition temperatures $T_c$ of this sample is also around 6.6 K.

It should be noted that the diameter of nanoparticles is crucial for retaining the superconductivity, since the coherence length ($\xi$) is also on the nanometer scale. In superconductivity, $\xi$ is the characteristic exponent of variation of the range of the superconducting order parameter, which is related to the Cooper pair size in the Bardeen–Cooper–Schrieffer theory. The superconducting order parameter could be strongly suppressed in the vicinity of a structural defect, such as a grain boundary in our case, with the effective size comparable to the coherence length $\xi$, leading to the destruction of the superconductivity. The nanodroplets here retain their superconducting properties under the condition that their diameter is at least twice as large as the superconducting coherence length $\xi$. Thus,
the diamagnetic signal of the nanodroplet sample is contributed by the magnetic moment residing in the nanodroplets under magnetic field.

Figure 5.8. ZFC and FC magnetization curves from 2 to 300 K of the nanodroplets under a magnetic field of 50 Oe. The inset schematic illustrations show that the nanodroplet would make the transition to crystalline from amorphous as the temperature decreases from RT (300 K) to $T^*$ (133 K, fully crystalline temperature point). The amorphous and then the crystalline nanodroplet remains paramagnetic when the temperature is above the $T_c$ (≈6.6 K), but the crystalline nanodroplet will change to diamagnetic when the temperature falls below $T_c$ (≈6.6 K) due to the Meissner effect in the superconducting liquid metal nanodroplet.

Along with the crystalline state at low temperature of the nanodroplet sample, three temperature regions were defined, as shown in the inset of Figure 5.8. When $T > T^*$ (fully crystalline temperature point), the three kinds of atoms (Ga, In, Sn) are in the amorphous state and magnetic field directly penetrates the nanodroplet without generating a magnetic moment. For the region $T_c < T < T^*$, the three kinds of atoms are arranged in an ordered structure, leading to crystalline nanodroplets. Nevertheless, there is still no magnetic moment, because the temperature is higher than $T_c$. The
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nanodroplets enter into the super-conducting state for \( T < T_c \), in which the perfect diamagnetism expels the field from the interior of the nanodroplets. Due to their rigidity and bad connectivity, high-temperature superconductors, such as \( \text{MgB}_2 \), pnictides, and cuprates, are extremely difficult to incorporate into flexible micro/nanodevices. The enhancement of \( T_c \) in the Ga-based liquid metal above the liquid helium critical point (4.2 K) paves the way for this flexible material to become a practical candidate for micro/nano-superconducting electronics. Moreover, their nontoxic nature allows Ga-based alloys and their nanodroplets to be practically and safely used for flexible, low-cost, and lightweight micro/nano-electronic devices, including, but not limited to, energy devices, micro-electromechanical systems, NMR, sensors, and display devices.

5.4. Conclusion

In summary, a series of Ga-In-Sn alloys and the corresponding nanosized droplets with different weight ratios of the component elements have been developed for realizing stretchable and printable superconductor microcircuits. The crystallization and phase separation of these nanodroplets take place as the temperature decreases from RT to liquid nitrogen temperature. Their applicability to inkjet printing, laser lithography, and handwriting to create different patterns is shown here to demonstrate their suitability for flexible superconducting microcircuits. Finally, the superconductive properties of such circuits based on the LM nanodroplets with different weight ratios are also analyzed. These discoveries provide strong prospects for the Ga-based liquid metal as promising candidates for developing practical stretchable superconducting micro/nanodevices. Moreover, this novel superconducting system has a huge potential to be extended with other metal, which offers a new platform for developing more application with superconductors.

5.5. References

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Chapter 6: A Liquid-Metal-Based Magnetoactive Slurry for Stimuli-Responsive Mechanically Adaptive Electrodes

6. A Liquid-Metal-Based Magnetoactive Slurry for Stimuli-Responsive Mechanically Adaptive Electrodes

6.1. Introduction

Bioelectronics, as a rapidly growing interdisciplinary research area, is opening up new opportunities for revolutionary medicine and advanced health care.[11-3] Biology is soft, elastic, and curved, so the electrode materials, as the main blocks for wearable and implantable bioelectronics devices, need to form intimate mechanical interfaces with biological tissue to enable applications.[4] Exciting advances have been made in the past several decades in developing soft and deformable electronics, including thin rigid conductors and inherently soft liquid metals or ionic hydrogels, for physical sensing, delivery of localized therapeutics, and restoration of damaged tissues.[5-7] Simply developing soft conductive matter is not the panacea for all the mechanical-mismatch induced challenges in bioelectronics, however, especially for implantable biosystems. Biological materials display highly diverse combinations of mechanical properties: for example, the cortical bone (Young’s modulus ~ 10 GPa) is rigid and brittle, the dura mater (Young’s modulus ~ 1 MPa) is tough, while the spinal cord and brain tissue (Young’s modulus ~ 100 Pa – 10 kPa) are soft and elastic.[8-9]

To match the mechanical features of the targeted specific area, directly designing integrated implants through integration of embedded electronics or pumps with tissue-matched elastomers has been achieved, such as the fabrication of an artificial electronic dura mater.[10] Nevertheless, given the possible trauma, local inflammation, and astroglial scarring around the implant, the mechanical coupling between the implant and the tissue is much more complex, especially for those implants with desirable functions, such as penetrating electrodes.[9, 11] The recently developed stimuli-responsive mechanically adaptive materials provide a new strategy to deal with multiscale, multifunction mismatches between the tissues and artificial implants, using polymer nanocomposites that can switch from a stiff and dry to a soft matrix 10-20 minutes after insertion into a physiological environment.[12-13] Their insulating nature, however, requires an integration of the polymers with metallic conductive components before use as the integrated implanted electrodes system.[14] Moreover, the controllability
of the stimulus-response time and subtle regulation of the mechanical properties are further expected to overcome the problems of more complex bio-environments, which are still big challenges for these chemo-responsive materials so far.

In this work, we developed liquid metal-based magnetoactive fluids or slurries (with slurry actually more appropriately to describe the densely packed liquid metal suspension feature of the samples, so LMMS is used as abbreviation for the as-prepared samples), formed by dispersing magnetic Fe particles in a Ga-based LM matrix. The stiffness and viscosity of the LMMS materials system designed here can be reversibly altered and subtly controlled within a very short time and over a wide range. In addition, unlike the non-conductive fluids (oil or other organics) used in traditional magnetoactive fluid, the room temperature LM matrix used here (galinstan) provides the best combination of conductivity and deformability. This unique feature along with its good biocompatibility gives Ga-based LM natural advantages, to be not only soft electronics wearable outside the body, but also show great potential for building implantable bioelectronics devices, including neural stimulation electrodes and nerve reconnection agents. With the advantages of being a good soft conductor and having mechanically stimulus-responsive properties, an implanted LMMS-based electrode was successfully engineered herein for a simulated bio-system. This electrode exhibits reversible stiffness changes upon exposure to an external magnetic field and a tunable electrochemical response to outside pressure when switching from stiff-mode, offering various functions including penetrating electrodes, soft implanted electrodes, and desirable electrically sensitive bio-electrodes. Our strategy and the proposed LMMS system pave the way to the efficient design and application of mechanically stimulus-responsive bio-electrodes with multi-functionality for different types of bio-systems and interfaces.

6.2. Experimental Section

6.2.1. Material synthesis

Ga-In-Sn eutectic alloy (galinstan, co-melted Ga, In, and Sn in the weight ratio 68% Ga, 22% In, and 10% Sn) was first added into a 1 M HCl acid ethanol solution, and the oxide layer was quickly removed. Then, Fe particles (size: 70 μm or 100 nm) in the appropriate molar ratio to Ga-In-Sn eutectic alloy were added into the solution, followed by mixing with a Digital Mixer. After all the Fe
particles were added in and completely incorporated in the Ga-In-Sn eutectic alloy, the final metallic colored product was washed with ethanol several times to remove the residual HCl and then vacuum dried at room temperature overnight. Several points should be noticed here. Fe particles were stored in the glove box, and the particular amount was weighed in the glove box when they were used. The Fe particles were taken out of the glove box for suspension in 100% ethanol, and then immediately added into the 1 HCl solution containing the LM with 100% ethanol as solvent. During the suspension of a large mole percentage of Fe in LM, the adding procedure should be divided into several repeated steps with only a small amount of Fe particles added at any one time. Adding a large amount of Fe particles at one time would leave more time for the Fe to react with the HCl, due to the contact area between the spherical LM and small particles with large surface area. Adding a small amount of Fe at one time (0.10 mole Fe for the LMMS-L samples and 0.01 mole for LMMS-S samples) could help the Fe to disperse in the LM more efficiently.

6.2.2. Characterizations

The structures of the samples were all investigated by XRD (GBC, MMA) using Cu Kα radiation. FE-SEM observations with EDX analysis were performed using a JEOL JSM-6490LV microscope coupled with an Oxford instruments X-maxN 80mm² SDD energy dispersive spectrometer. All maps were acquired using the Oxford Instruments AZtec software suite. Samples for SEM characterization were prepared by depositing the LMMS on Si wafers by the doctor blade technique. The topographical images of the samples were collected using secondary electrons as the high density of Ga, Sn and In film completely obscure backscatter signals from the Fe particles. To provide sufficient penetration though this film 30kV was used for mapping purposes. All EDX processed data was taken from the Fe maps. TEM images, SAED patterns, HAADF images and STEM-EDX spectra were obtained using a JEOL ARM-200F operating at 200 kV with an EDX solid-state X-ray detector.

6.2.3. Magnetic and Mechanical Measurements

DC magnetization and the magnetic relaxation measurements were performed using the VSM option of PPMS. The viscoelastic behaviour of the LMMS samples was studied by oscillatory tests by amplitude sweep and magneto-sweep experiments. A rotating parallel-plate rheometer (MCR 301, Anton Paar Companies, Germany) with a measurement system (PP-20, 20 mm plate, Anton Paar
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Companies, Germany) and a magnetic field strength control device were used to measure the rheological properties of the samples. The samples were placed on the bottom plate of the rheometer, and then the upper plate was lowered until there was a gap of 1 mm. The temperature used in the tests was set to match the room temperatures at 25 °C. The angular frequency used in all the tests was a constant 10 rad/s. The amplitude was varied from 0.1% to 60% with different currents applied to control the electromagnetic field strength from 0 A to 3.5 A. Compression testing was performed for up to 55% compressive strain at the speed of 0.3 mm/s, on a cylindrically-shaped LMMS structure (diameter ~ 6 mm, height ~ 10 mm). The Young’s modulus was established from the linear portion of the curve and calculated by the formula, $E = \frac{\sigma}{\varepsilon}$ Pa, where $E$ is Young’s modulus, $\sigma$ is the applied stress, and $\varepsilon$ is the strain.

6.2.4. Building and measurement of the implanted electrode

A cone mold with a bottom diameter of 3 mm was prepared, and the LMMS samples were inserted into the mold. Each sample in the cone-shaped mold was then cooled down to -30 °C to be solidified. After that, the cone shaped LMMS sample was taken out of the mold and covered by a protective layer of thin highly elastic silicone, to create the final electrode to be implanted. A flexible cranial window model based on transparent PDMS film was used as described previously [22-23] as a skull/dura mater-like substitute. A chitosan-based hydrogel was fabricated according to a previous report [24] as a bio-electrolyte model. This bio-electrolyte was then covered by the PDMS film as a complete bio-system, which could be used for penetration experiments and stress–electrical-response experiments. The electric properties were measured using a Bio-Logic Science Instruments VSP-300 multichannel potentiostat/galvanostat under ambient conditions, using the two-probe technique.

6.3. Results and Discussion

Due to their easy oxidation, the Ga-based LMs are easily passivated with a thin oxide layer that eliminates direct contact of the LMs with metals.[25-26] Although particles wrapped by an LM oxidation layer could achieve good particle dispersion and mixture with LM, the relatively heavily oxidized LM may result in a decrease in the conductivity.[27-29] In addition, the high interfacial tension between the oxidized metal particles and the liquid metal is also regarded as a barrier against the diffusion of metal oxide particles into LMs.[30] Therefore, as schematically shown in Figure 6.1,
diluted HCl solution under no-magnetic-based stirring is as an ideal experimental setting for the synthesis of LMMS. The LMMS was made by mixing commercial pure Fe particles into Ga-In-Sn eutectic alloy (galinstan), which is in the liquid state at room temperature.

Figure 6.1. Schematic illustration and photographs demonstrating the preparation of LMMS. The liquid galinstan becomes slurry-like and muddy after mixing with the Fe particles in the HCl solution. The viscosity of the LMMS sample clearly increases, and it can be molded into different shapes.

It was found that successfully suspending Fe particles in a Ga-based liquid metal matrix could only take place in acid surroundings, while the Fe particles still separated from the LM in neutral and alkaline solutions, which confirmed our understanding of the wettability considerations between LM and other metals. It should be noted that the successfully suspending Fe in neutral and alkaline solutions might be achieved by varying external electrochemical environment.[31] Based on this experimental procedure, a series of LMMS samples containing different amounts of Fe with different particle sizes (with the samples containing ~ 70 μm size Fe particles denoted as LMMS-L, and the samples containing ~ 100 nm size Fe particles denoted as LMMS-S) were prepared for further characterization, evaluation, and electrode engineering. The liquidity of galinstan was dramatically changed after the successfully addition of Fe particles. The as-prepared LMMS samples containing
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More than 5 mol% 100 nm Fe (LMMS-S5%) and more than 30 mol% 70 μm Fe (LMMS-L30%) could be easily molded into various shapes such as cubes (Figure 6.2).

**Figure 6.2.** Digital photograph of Ga-based liquid metal droplets containing 100 nm Fe and 70 μm Fe in various amounts. The results indicated that the maximum molar percentage that could be successfully suspended in the liquid metal was ~15% for 100 nm Fe, and ~50% for 70 μm Fe.

The surfaces of the as-prepared LMMS samples stored in the HCl solution still appeared shiny, but they became dull when exposed to air, indicating that all the Fe particles were suspended in the Ga-based liquid metal matrix, leaving the liquid metal as an outer layer that is very sensitive to oxygen. In addition, it was found that it is very difficult to evenly disperse more than 15 mol% 100 nm Fe and 50 mol% 70 μm Fe into the LM. This observation indicates that the maximum molar percentage of Fe that can successfully suspended in the liquid metal not only depends on the amount of Fe particles used, but is also highly related to the particle size (or surface area) of the Fe. As well as the significantly enhanced moldability of the LMMS in contrast to the pure LM, the mechanical properties of the as-designed LMMS samples herein could be precisely modulated by an external magnetic field. Taking the LMMS-L50% sample as an example, as shown in Figure 6.3, a cylinder composed of this material with a surface area of $1.13 \times 10^{-4} \text{ m}^2$ has the ability to support a weight of at least 50 g under an applied magnetic field from an permanent magnet (near field $\sim 0.2 \text{ T}$). When the magnet was removed, the stiffness of this LMMS-based cylinder suddenly disappeared, and the LMMS became a slurry with soft characteristics. Such a feature, where the apparent viscosity of the fluid greatly increases when subjected to a magnetic field, suggested that the LM was a good carrier fluid for designing and constructing magnetoactive fluid.
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Figure 6.3. Digital photograph for the stiffness of the LMMS sample could be further enhanced by applying an external magnetic field. The cylinder molded under the field from a permanent magnet shows no deformation with a 50 g weight on the top. The high cylinder toppled over immediately, however, after the magnet was removed.

The diffusion and dispersion of magnetic particles in fluid carriers are critical to determining the characteristics of magnetoactive fluids. Unlike the easy alloying process between Ga and Cu,[32] the phase diagram[33] shows that alloying between Fe and Ga barely takes place at room temperature, which means that the diffusion mechanism of Fe in Ga-based LM remains unclear. Several published reports have described the suspension of Fe in Ga-based liquid metal,[30, 34-35] but detailed morphological and structural characterization of the mechanism, especially on the microscale, has not been effectively revealed until now, which has hindered understanding of the process of embedding Fe.

XRD analysis was conducted on the LMMS-S sample and LMMS-L sample, as well as pure Fe particles and pure LM, to reveal the chemical composition after suspending Fe in LM. As shown in Figure 6.4 (a), the broad peak around 35°, which is contributed by the amorphous galinstan, was found in both the LMMS-S15% and LMMS-L50% samples after 1 day from their initial preparation, also agreeing with the pattern of pure LM, indicating that the liquid feature of the galinstan matrix was retained. The peaks related to pure Fe (JCPDS No. 05-0696) were observed in both the LMMS samples and the pure Fe sample, and the intensity of the peak (2θ ≈ 45°) was enhanced with the increased size of the Fe particles in the LMMS-L samples. The detection of the characteristic peaks for Fe indicates that the Fe particles suspended into the liquid metal matrix still maintained their
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separate identity after 1 day. It reflects that, distinct to Cu,\textsuperscript{[30]} the Fe did not quickly react with Ga and become incorporated in a Ga-Fe alloy at room temperature. The SEM and related energy dispersive EDX characterizations of LMMS-L50%, as shown in Figure 6.4 (b) – (c), displayed a rough surface and even distribution of Ga, In, Sn and Fe, without any obvious aggregation of Fe particles.

**Figure 6.4.** (a) XRD patterns of LMMS sample containing 15% 100 nm Fe particles (LMMS-S15%) and 50% 70 µm Fe particles (LMMS-L50%) after 1 d from the preparation, as well as the patterns of pure Fe and pure LM for reference. (b) – (d) SEM image of the surface of the LMMS-L50% sample, and related element mapping of Ga and Fe in the LMMS-L50%.

To reveal possible changes in the microstructure and constitution of the as-formed composites after Fe particles were dispersed in the liquid metal matrix, TEM analysis together with EDX elemental mapping was conducted on the LMMS samples containing small particles, as shown in Figure 6.5. The HAADF image, which is sensitive to atomic number, of a small fragment from the LMMS-S15% (Figure 6.5 (a)) presents a homogenous distribution of elements. Interestingly, however, the phase mapping of this fragment (Figure 6.5 (b)) shows that a small distinct phase was covered by a
big phase that matched and represents almost the whole fragment. The related element mapping of this fragment (Figure 6.5 (c) - (f)) further verified that the inner small phase belongs to nanoparticles containing Fe, while the outside phase belongs to the Ga-In-Sn alloy matrix.

**Figure 6.5.** Typical STEM image of a small piece from LMMS-S15% with phase mapping and element mapping of the same location. The inset in (a) is the corresponding SAED pattern of the selected area. (b) Combined phase mapping, with two possible phases represented on the same small piece. From (c) to (f), the images show the maps for Fe (yellow), Ga (red), In (blue), and Sn (green). (g) Line profile analysis of distribution of elements in LMMS-S15%.

It is worth noting that the element distribution of Ga also covers the inner small particle and can even be slightly higher in contrast than that of the outside area, along with the obviously reduced distribution of In and Sn in the same location as the inner particle confirmed by the line profile
analysis of the element distribution shown in Figure 6.5 (g). This indicates the possible alloying of Ga and Fe during the Fe particle suspension process in Ga-based liquid metal at room temperature. Moreover, well-defined diffraction spots and a highly diffusive ring pattern are both displayed in the SAED pattern (inset in Figure 6.5 (a)) taken from the area marked by the yellow circle, implying the co-existence of crystalline phase and amorphous phase. Combining these results with the phase mapping results and the XRD analysis, one can propose that the inner particle inside the amorphous outside matrix is mainly Fe surrounded by a certain amount of Fe-Ga based alloy.

![Figure 6.6](image)

**Figure 6.6.** SEM images of the surface of the LMMS-L50% sample, and related element mapping of Fe in the LMMS-L50%, (a) – (b) before and (c) – (d) after the application of magnetic field.

Magnetoactive or magnetorheological fluid is a term that usually refers to a carrier fluid with embedded microsized ferromagnetic particles. This smart fluid can respond immediately and dramatically to an applied magnetic field and features reversible change from a liquid to a semi-solid or solid.\(^{37}\) The phase change is attributed to the dipolar interactions introduced by the external magnetic force, which initiates the formation of a chain-like alignment inside the carrier fluid.\(^{38}\) Similar behaviours were also observed in the as-prepared LMMS samples, indicating LMs are also a
good and novel liquid carrier for developing magnetorheological fluid or slurry. As shown in the EDX mappings results of the thin LMMS film before and after applying a magnetic field (Figure 6.6), the randomly distributed Fe content was turned to a chain-like distribution along with the applied magnetic field orientation, while the other elements distribution remained uniform and random.

To investigate the viscoelastic behavior of the as-designed LMMS samples, oscillatory tests involving amplitude sweep and magneto-sweep were performed on the as-prepared samples. The storage modulus ($G'$) and loss modulus ($G''$) of the LMMS samples containing different molar fractions of Fe both increased with strengthening of the applied magnetic field. The variation in $G'$ and $G''$ presents a characteristic magnetorheological feature, which is due to the development of Fe particle-based chain structures inside these LMMS samples with increasing magnetic flux density. For better comparison of the elastic behavior of the Ga-based liquid metal with varying fractions of Fe suspended and typical LMMS-L samples with varying magnetic field, we plotted the variation of $G'$ with a constant low strain amplitude (0.2%) and a constant frequency ($f = 1.5$ Hz), as shown in Figure 6.7. The variation of complex viscosity is also included in the plots.

![Figure 6.7](image.png)

**Figure 6.7.** (a) Variation of storage modulus ($G'$) and complex viscosity for the LMMS samples containing different molar fractions of Fe. (b) Magnetic field dependence of $G'$ and complex viscosity at 0.2% strain amplitude for the sample containing an LMMS-L30%. The magnetization curves of pure LM, pure Fe, and LMMS-L30% are shown in the inset.

The pure galinstan show a very low complex viscosity, presenting a liquid character, which agrees with previous reports.[39] With no magnetic field applied, the storage modulus and complex viscosity both displayed significant enhancement with increasing molar fraction of Fe suspended in the galinstan (Figure 6.7 (a)), indicating the transition from liquid to solid. For the LMMS-L30% sample, as shown in Figure 6.7 (b), an increase by several orders of magnitude in the values of the
storage modulus and complex viscosity suggests the transition of the sample from liquid behavior to a quasi-gel, and finally to immobile solid-like behavior. The magnetic field for the saturation of these values was established to be 0.3 T, similar to the magnetic hysteresis curve of this sample displayed in the inset of Figure 6.6 (b). It should be noted that the elastic modulus of the LMMS-L30% sample designed here could be regulated from 5 kPa to more than 1 MPa. The mechanical adaptive response under magnetic stimulation was attributed to the particle arrangement, which gradually changed from random orientation to chain or column structures, and then rigid chains.

Figure 6.8. (a) Schematic illustration of the movement of Fe particles in LMMS samples with and without magnetic field applied. Chains of Fe particles are proposed to be formed under the alignment force of magnetic field, similar to the behavior of other magnetorheological fluids. (b) Variation of stress induced at different strains for the LMMS-L50% sample with and without magnetic field applied.

To further evaluate the mechanical behavior of the LMMS sample under saturated magnetic field, compression stress tests were conducted on cylindrically-shaped structures (diameter ~ 6 mm, height ~ 10 mm) composed of LMMS-L samples. Detailed information on the effects of loading pressure on the LMMS-based cylinder was acquired using a uniaxial quasi-static compression test at a crosshead speed of 0.3 mm/s up to a maximum strain of 55%. To present the maximum bearing stress capacity of the as-designed LMMS, LMMS-L50% was selected as the typical sample to demonstrate this. The loading stress – strain responses of LMMS-L50% with and without magnetic field are shown in Figure 6.8 (b). The curve measured without magnetic field features a simple J-shape, indicating that the material becomes stiffer at larger deformation and more difficult to press, but the slight increase in stress required during the deformation implies that the sample without magnetic field is still soft and
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easy to deform. In contrast, the S-shape curve acquired under applied magnetic field exhibits three definite regions, including linear elasticity, plateau, and densification, showing similar and typical compression behavior to mild steel, foam, or aerogels. [40-41]

As in the red curve shown in Figure 6.8 (b), the initial part shows a dramatic linear increase in the applied stress, which can be classified as the resilience region. In this region, the material possess the ability to return to its original form after the external force is removed, suggesting that the chain-like alignment inside the LM induced by the magnetic field (as shown in Figure 6.8 (a)) enables elastic deformation of the LMMS, which could not be broken in this region. As the strain and the force become greater, a plateau corresponding to the plasticity was observed, which means that the material would remain deformed without fracturing, even after the force is removed. A further increase in stress following the plateau indicates that the correlation between the stress and strain was caused by the densification. It should be noted that the point between the first straight line and the plateau, the yield point, represents an irreversible deformation that takes place during the compressive process, which means that the Fe chains formed in the LMMS sample have been broken. As calculated from the area under the yield point region, the Young’s modulus can be established to be 1.8 GPa, which is higher than for most biological components.

The compressive test and shear oscillatory tests on the LMMS-based sample indicate that there would be a reversible change when less than 10 % strain is applied, and the yield stress of the slurry can be controlled by varying the magnetic field intensity. To take advantage of the magnetic stimulus-responsive mechanically adaptive properties of the LMMS materials, the electrode for implantation was made by coating a thin PDMS protective layer over a LMMS sample with a needle-like shape. The assembled electrode initially showed a soft character and could not be inserted across the artificial bio-membrane to achieve contact with the inner bio-electrolyte (Figure 6.9 (a)). When a magnetic field was applied by a permanent magnet, the electrode immediately became rigid enough for penetration of the membrane during implantation (Figure 6.9 (b)). The electrode could be made to soften slowly by removing the magnet gradually, and it could return to stiff mode reversibly with and without applied magnetic field.
Figure 6.9. Demonstration of penetration of the LMMS-based electrode into the bio-electrolyte covered by an artificial bio-membrane: (a) without magnetic field applied and (b) with magnetic field applied. (c) The electrochemical current response to the LMMS electrode successfully inserted in and withdrawn from the electrolyte.

We further connected the electrode to an external electrical signal collection device and applied a stimulating voltage on the electrode relative to the bio-electrolyte to acquire the electrical response from the system. As shown in Figure 6.9 (c), a distinct current response was recorded when the electrode was successfully inserted into the bio-electrolyte, which can be attributed to the high conductivity of the LMMS. The stimulating current tended to be stable after 50 s, and after withdrawing the electrode, the current response disappeared. Three different places were chosen for repeating the insert and withdraw test, and the currents were successfully acquired during insertion and were found to show slightly differences due to changes in the bio-electrolyte surrounding the electrode.
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Figure 6.10. (a) Schematic illustration of the pressure on the implanted electrode from the tissue movement and external force. (b) The relationship between stress and applied magnetic field for the LMMS-based electrode. The relationship between the electric current response and the applied magnetic field also shows similar rising tendency as the observation for stress. Each plots for stress (upper left) and current response (lower right) versus strain are also shown in the insets in (b). (c) Schematic illustration of the test system based on the bio-electrolyte. The bio-electrolyte forms a dielectric layer between the inserted LMMS electrode and the contrast electrode, and the pressure would induce a change in the thickness of this dielectric layer.

Besides realizing the function of the penetrating electrode, the electric response to the pressure from the deformation and the movement of bio-system can also be tuned by varying the stiffness of the electrode with different external magnetic field intensity applied. As shown in the lower right corner inset in Figure 6.10 (b), the response current from the implanted electrode, induced by a constant 7.5 kPa stress, increases with the intensity of the applied magnetic field. The high conductivity of LMMS materials offers a rapid response and a stable electrical performance for this mechanically adaptive implanted electrode, whether it is in steady mode or stimulus-responsive.
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switching mode. The linear relation between the magnetic field intensity and the response current is similar to the relationship between the applied magnetic field intensity and the stiffness of the LMMS electrode, as demonstrated in Figure 6.10 (b). According to the model presented in Figure 6.10 (a) and (c), larger changes in the dielectric layer between the inserted electrode and the contrast electrode would be induced by applied compressive pressure on the soft bio-electrolyte near the stiff electrode with magnetic field applied. The results illustrate that the exchange of electrical signals between the as-designed LMMS electrodes and the bio-system can be controlled and tuned as desired by switching the mechanical properties via the magnetic stimulus response. These advantages would help to reduce the trauma and scars induced by the mechanical mismatch between implanted electrodes and different tissues, and establish stable and desirable electric communication between the inner bio-system and the outside, through the LMMS electrode.

6.4. Conclusions

In summary, the magnetically responsive LMMS materials designed here offer a new mechanically adaptive bio-electrode system to realize multi-functional implanted electrodes in bio-systems. The viscosity and stiffness of the electrode can be tuned to match different mechanical properties of tissues, which could significantly reduce the damage induced by implanted electrodes. The chains of iron particles formed in the LM matrix under magnetic field are regarded as the key factor enabling the change from softer fluid features to a stiff solid character. Based on the finding that the iron particles are partially alloyed with Ga-based liquid metal, other ferromagnetic particles or those with different morphology, such as nanowires featuring similar alloying possibilities, even when impossible in the phase diagram, are expected to successfully disperse in the LM to fill out the LMMS material family. Higher magnetic field-sensitive responses and long-range regulation of bio-electrodes suitable for more specific bio-issues are expected to be realized.

6.5. References

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Chapter 7: General Conclusions and Outlook

Chapter 7

7. General Conclusions and Outlook

7.1. General Conclusions

In this doctoral thesis work, the recent developments in the manipulations of Ga-based liquid metals and the applications of these stimulus-responsive properties were summarized. Considering the discoveries of new possible stimulus-responsive properties in the liquid metal system are still insufficient, three different approaches including mechanical-activated, temperature-induced and magneto-stimulated were explored to successfully build a variety of stimulus-responsive properties. These proposed and prepared Ga-based liquid metals and the hybrids displayed efficient external stimulus-response ability, which can be applied as smart electronics, such as mechanical sintering flexible electronics, printable low-temperature superconductive electronics, and magnetic-field active mechanically adaptive bio-electrodes.

To achieve the aim of building intrinsically flexible electronics in micro- or even nano-scale, the galinstan liquid metal nanodroplets with average particle sizes of ≈110 nm for the printing ink have been successfully synthesized by using sonication and thiol self-assembly route. As the response to the local pressure applied, these soft droplets with a liquid-phase core and solid shell structure can be merged together. Taking advantage of the mechanical-stimulus response ability, a conductive circuit with desirable shape and size could be printed and activated. Besides confirming the core-shell structure of the liquid metal nanodroplets by STEM, an in situ mechanical study on the process of breaking an individual liquid metal droplet has been also conducted with the assistance of the AFM system. The deep understanding on the mechanical force-stimulus responsive properties of liquid metal nanodroplets paves a way for developing practical micro-/nano-size stretchable electronic devices with liquid metals.

The electron transport and conductivity in the electronics are highly relative to the temperature. We found that Ga-based liquid metal galinstan would become superconductor in response to the temperature deceasing to certain value. A superconductive electronics are highly attractive for building high-speed micro-/nano-electronic devices, including rapid responding biosensor, quantum computer...
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and micro-NMR device. By using the as-prepared liquid metal-based nanoparticles as inks, superconductive devices, including microsize superconducting coils, electric circuits, and superconducting electrodes, have been fabricated and demonstrated on substrate by directly printing and laser engraving. Temperature-dependence TEM, transport measurements and magnetic measurements illustrated that the crystallization and phase separation of the as-prepared nanoparticles would take place as the temperature decreases, and be superconductive and diamagnetic with the temperature further decreasing. These discoveries provide strong prospects for the Ga-based liquid metal as promising candidates for developing practical stretchable superconducting micro/nanodevices.

In view of the magnetic field can be applied to materials remotely, the magneto-active smart materials show great potential applications for microfluidics, bioengineering, and healthcare. In the previous study, it was found that Ga-based liquid metals show almost unresponsive to a permanent magnetic field at room temperature. Then we constructed liquid metal-based magnetoactive slurries by dispersing magnetic Fe particles in a Ga-based liquid metal matrix. The stiffness and viscosity of this liquid metal-based hybrids can be reversibly altered and subtly controlled within a very short time and over a wide range by applying magnetic filed as stimulus. The chains of iron particles formed in the liquid metal matrix under magnetic field have been proved as the key factor enabling the change from softer fluid features to a stiff solid character. With the advantages of being a good soft conductor and having mechanically stimulus-responsive properties, we have also demonstrated an mechanically stimulus-responsive implanted electrode for a simulated bio-system.

Clearly, these demonstrated stimulus-responsive properties of the Ga-based liquid metals and their hybrids make the Ga-based liquid metals promising to meet the requirement of future smart soft-electronics and bio-systems.

7.2. Outlook

Materials featured by both metallic and fluidic character, that capable of responses to external stimuli no doubt represent one of the most exciting and emerging areas of scientific interest and possess huge potential for many unexplored applications. It is particularly important to develop a wide range of liquid metals or hybrids that can act as effective stimuli-responsive smart materials. Among
all above mentioned extend field induced manipulation or application of Ga-based liquid metal, magnetic field can be applied to materials remotely, exhibiting very low interaction with nonmagnetic materials, and have ability of penetrating through most materials including bio-materials. As for easily, precisely and remotely manipulating liquid metal-based materials and systems to meet the requirements of certain applications, the stimulus like thermal, magnetic field, and light would be ideal choices. However, building such smart system based on liquid metal still remain lots of challenges, including the design and synthesis of desirable-stimulus responsive integration, the mechanisms underlying the stimulus-response activities, the strategy for improving the efficiency of the whole system in the applications.

Another important extension of the research on liquid metal-based stimuli-responsive smart materials is exploring and developing multi-stimuli responsive liquid metals and hybrids. There are some considerations in this context. The development of multi-responsive liquid metal-based systems that can be actuated and be disrupted on demand by independent stimulus is also desirable and would enable advanced material application in future.

Generally, there is still a very long way to go in the development of such smart materials that are nearly as good as the one shown in the “Terminator” films, and in building such an intelligent shape-shifting robot that can operate with agility and accuracy. The aim of the research in this field is not to make the science fiction fact, but once similar achievements have been made, revolutionary advances in materials science, as well as ubiquitous applications relevant to electronics, optics, nanotechnology, and bio-medicine can be gained.
Appendix A: Publications


Appendix B: Conferences & Activities

Appendix C: Scholarships & Awards

Appendix C: Scholarships & Awards

1. 2015-2018: Faulty Scholarship & International Postgraduate Tuition Award, UOW.
2. 2016: ISEM 2016 Postgraduate Student Merit Award.