

Liquid metals (LM) have shown a very broad development prospect over the past decades. This review article focuses on the latest research dedicated to liquid metal materials and their applications in five significant areas: stretchable conductive composite, intelligent sensing electronic skin, catalysis, 3D printing material, and driving machines. The fabrication, specific properties and application of stretchable liquid metal-polymer composites that can be used as self-healing materials have been summarized. Liquid metal deposition printing technology, liquid phase 3D printing, suspension 3D printing technology, micro-contact printing technology, and in vivo 3D printing

molding technology have also been reviewed. Furthermore, the application of liquid metal catalyst in aldehyde reaction, photocatalysis, and electrocatalysis have been discussed. We have shown that electricity, magnetism, sound, light and heat could stimulate the movement of liquid metal. Through this comprehensive overview of the latest research, the main practical application, development, and mechanism of liquid metal were summarized and described. The future development of liquid metal technology was prospected, thus providing a strong basic research support for the further development of LM materials and their applications.

1. Introduction

Liquid metals are metal alloy or elemental metal that are liquid at room temperature. In nature, the pure traditional metals that are liquid at normal temperature are mainly mercury (Hg), gallium (Ga) and cesium (Cs), with melting points of -38.87°C , 29.8°C and 28.65°C , respectively.

Given the scarcity of pure liquid metals, liquid alloys are generally used in practice. Room temperature liquid metal are generally composed of Gallium-based metal or Gallium-Indium eutectic metal. These substances have the dual characteristics of the liquid fluid and metallic compounds. They have a fluidity and compliance of liquid fluid, and the extensibility and conductivity of metallic compound. At the same time, Gallium-based metal has a fluidity like liquid at room temperature, low melting point, low viscosity, non-volatile, non-toxic, and not easy to react with other substances. Its electric conductivity is strong, and reaches 107 S m^{-1} . It also has a high boiling point up to 2000°C , and a melting point below 300°C . These alloys predominantly contain post transition and zinc group metals.

With its unique physical and chemical properties, liquid metal has good properties in the production of many functional materials. Over the past decade, LM (Liquid metal) was studied as an ideal material for a tensile conductor, flexible sensor, and skin,^[1] 3D printing, catalysts, micro-driven machine, and could also be applied in various fields.^[2]

Up to now, the application of liquid metal has penetrated into many fields of natural science and engineering technology.

For instance, the tensile liquid metal-polymer composite has broad and bright prospects in medical devices, energy devices, and electronic devices. The properties of composite materials still could be improved greatly. On the other hand, Liquid metal electronic skin^[3] has become a kind of wearable and intelligent flexible electronic skin. It was drawn on a special carrier to make an electronic skin. Then the electronic skin was covered with other devices to increase the additional performance. The liquid metal circuit could also be directly drawn on the human skin to monitor the human health. Furthermore, liquid metal 3D printer could realize the automatic and direct printing of electronic devices at room temperature. It has broken the limitation of high surface tension of liquid metal. Liquid metal catalysts were also studied in order to improve the efficiency of energy utilization, and complete the energy supply and security system. An evolutionary algorithm was used to solve the optimization problem of micro-driven liquid metal machine in the field of micro-driven machine.

The application of liquid metal is becoming more and more widespread. Due to its unique properties, LM breaks the limitation of traditional technology, and promotes the formation and development of new industrial system. Therefore, it is urgent to develop the application and recent progress of liquid metal materials. In this minireview, the applications of liquid metals in five fields have been developed and discussed. Many works in the field of LM materials were screened and classified. Some representative works were selected from different research directions. Through these representative works, the progress, and challenges on specific LM research could be systematically understanding. Finally, the current problem, possible solution, and future development direction of LM were also summarized.

2. Stretchable Liquid Metal-Polymer Composites

The foundation of a soft electronic circuit is the flexible conductor. The materials with high thermal conductivity are usually rigid, and incompatible with the elastic, soft and mechanical materials. Because micron-scale structures rarely have electricity, robustness, long-term stability, and reliable mechanical properties in large areas. Manufacturing flexible

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wiring network to distribute and carry the current in soft circuits was an ongoing challenge. In the past decade, a combination of materials and manufacturing technology have been proposed to design of scalable conductors. In terms of the stretchable capability of the material, effective structural design could make the metal film adapt to more complex mechanical scene. After the structure of nanomaterial has been optimized, composites withstand greater deformation could be obtained. This part mainly introduced the stretchable composites, which were formed by liquid metal and polymer composites.

2.1. Fabrication of Liquid Metal-Polymer Composites

Tensile liquid metal composites were usually composed of liquid metal and other materials. The tensile liquid metal-polymer composite has attracted much attention at present. These liquid metal composites have several important properties, such as: electrical conductivity,^[4] thermal conductivity,^[5] extensibility,^[6] and magnetism. In this part, several preparation methods of liquid metal-polymer composites were introduced. Using liquid metal, polyurethane sponge (PUS), polymethacrylate (PMA), polydimethylsiloxane (PDMS), carbon nanotubes, silicone resin, polyester sponge, silicone rubber, styrene-butadiene-styrene block copolymer (SBS) rubber, gadolinium fluid, metal particles and other materials, liquid metal-polymer composites of different properties were manufactured.

By vacuumizing the liquid metal (Galinstan) into porous PUS, and encapsulating it with PDMS, the PDMS-PUS-LM composites with high tensile strength (1.11 MPa) and high electrical conductivity ($1.87 \times 10^6 \text{ S m}^{-1}$) were obtained.^[7] At the same time, one-dimensional nanostructures, such as carbon nanotubes and metal nano-coatings, were embedded into the flexible products or composite elastomers to obtain materials with both high conductivity and tensile property.^[8] PDMS and liquid metal alloy were mixed with silicone resin, then the mixture was cooled and solidified to obtain the elastic composite. It could greatly improve the thermal response, scalability, and efficiency of thermal equipment (Figure 1A).^[9]

High conductivity elastic composites with tensile properties could be formed by filling liquid metal into polyester sponge and then combining with silicone rubber. Styrene-butadiene-styrene (SBS) rubber fiber was used to adsorbing the silver precursor, and then convert them into silver nanoparticles in the fiber felt. Therefore, silver nanoparticles could penetrate the

fiber, and formed a 150 mm cushion with 100% strain and higher volume conductivity ($s \approx 2200 \text{ S cm}^{-1}$).^[10]

A new liquid metal composite material for manufacturing ideal 3D printing was also proposed in 2018.^[11] By using modification technology, the uncoated metal particles were mixed into liquid metal by ultrasonic wave, which permanently and quantitatively changed the rheological properties, and improved the viscosity and elasticity of the mixture. The final product was a highly structured and printable film. It could be directly writing on a surface of a rough substrate, such as conductor and textured material.^[12]

2.2. Properties of Liquid Metal-Polymer Composites

Several reactions between liquid metal and polymer for the formation of functional composites have been developed. Compared with the original liquid metal, the tensile property, electrical conductivity, shielding property, self-healing property, and thermal stability of the liquid metal-polymer composites could be greatly improved:

- (1) Improvement on dielectric constant: EGaln alloy and uncured liquid silicone or polyurethane were mixed at a volume load of 0%–50% (LM). Then a material with a special conductive elastic property was formed.^[13] Compared with the material adding 10–30% volume of inorganic filler, this kind of material could increase the dielectric constant to more than 400%. It could be stretched to several times of its original length (Figure 1B).
- (2) Improvement on thermal conductivity: Electrical insulation composite materials were used to overcome the limitation of poor electrical conductivity of flexible composite materials. These composite materials could show metallic thermal conductivity. They have elastic compliance like biological soft tissue, and the ability to withstand extreme deformation.^[14,15]
- (3) Self-healing performance: PDMS (polydimethylsiloxane) and EGaln were used as raw materials to prepared LM-TO elastomers in 2018. Then the PDMS prepolymer was mixed with EGaln to form an emulsion. Finally, the dispersed suspension of the EGaln droplets was formed in the silicone rubber matrix.^[16] The gallium based LM alloy embedded in silicone rubber elastomer could be used to create a circuit interconnection with a function of self-healing. Its conductivity could reach $1.37 \times 10^3 \text{ S cm}^{-1}$. (Figure 1C)



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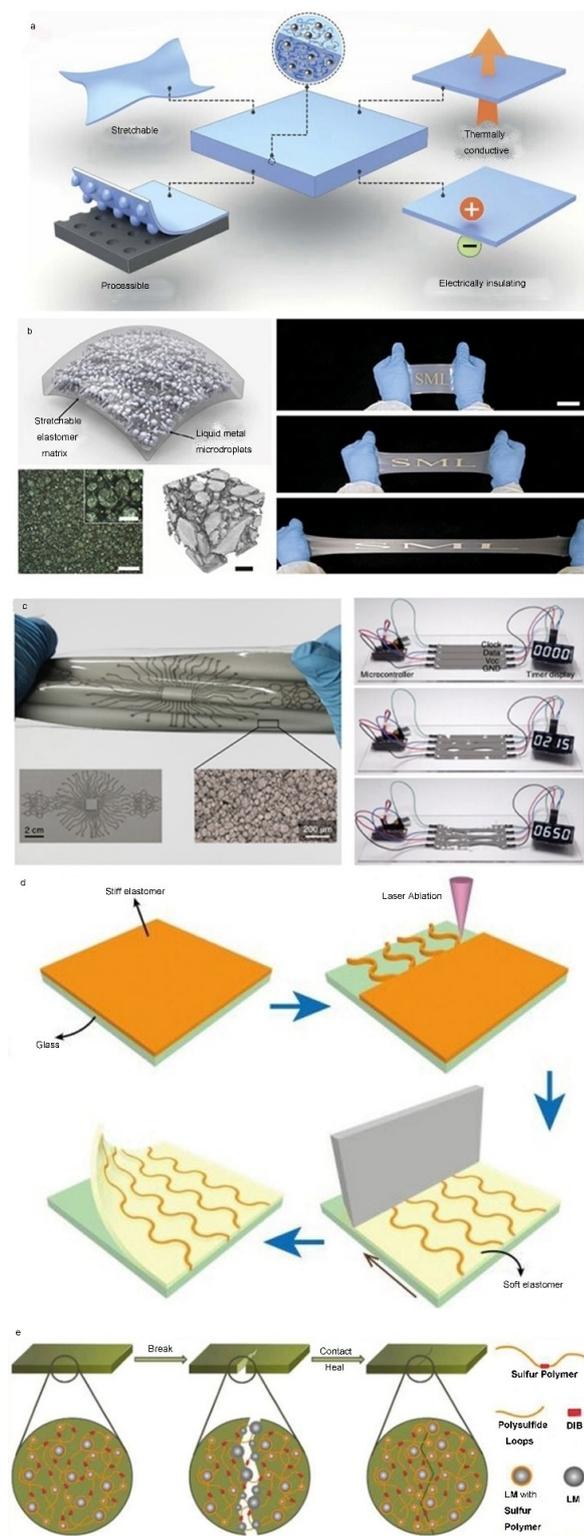


Figure 1. (A) Schematic diagram of liquid metal alloy droplets embedded in elastomer composite materials; (B) Liquid metal droplets were dispersed in a flexible stretchable elastomer matrix to form LMEE materials; (C) Self-healing stretchable and twisted liquid metal elastomer composites; (D) Liquid metal composites were prepared by laser ablation; (E) Liquid metal composite material with self-healing function.

- (4) Improvement on tensile property: A composite with different shapes was prepared in 2019, by mixed the liquid metal (75.5% gallium and 24.5% indium) with uncured silicone rubber, then treated the uncured elastomer with liquid ethanol. This material has a very high tensile property (700%).^[17] LM composite expand and deform freely under heating conditions, which plays an important role in the free phase transition of the composite.
- (5) Improvement on shielding performance: At a low temperature, porous anisotropic gallium matrix composite was mixed with PDMS to achieve reliable shielding performance in 2020.^[18] By adjusting the direction of the incident electromagnetic wave, the porous structure and anisotropy of conductivity of this composite enable it to change the reflection coefficient from 40% to 85%.
- (6) Improvement on thermal stability: A kind of high scalability optical fiber with excellent conductivity was also manufactured in 2020, which was composed of three layers: the super-elastic core (polyurethane (PU) fiber), the intermediate adhesive layer (polymethacrylate (PMA)), and the outer layer (EGaln).^[19] These LMs could maintain stable thermal stability at a temperature close to 250 °C. When the tensile strain reached 500%, the conductivity could reach above 10^3 S cm^{-1} , which was better than the conductivity of existing tensile conductive fibers.

Various polymer materials and inorganic materials could be matched with liquid metal and compound by means of modification. Considering the published papers, liquid metal-polymer composite was still in its infancy. The phase diagram, molecular dynamics, and mathematical modeling are used to predict, and the suitable extensible liquid metal polymer composites are selected through experiments.

2.3. The Application of Liquid Metal Composites in Scalable Circuits

On condition that liquid metal nanoparticles were embedded into the elastomer matrix, these LMs would become conductive bodies under pressure.^[20] Soft circuit board and adjustable antenna were fabricated by using thin mechanically adsorbed films, and micro-fluidic traces of EGaln nanoparticles.^[21] EGaln particle films casted in PDMS remain insulated, until mechanical sintering combines them to become conductive. Finally, the critical pressure of mechanical sintering was changed by adjusting the thickness and substrate of micro-fluidic devices, and the antenna with arbitrary frequency was drawn.

In order to establish a continuous channel with high conductivity, a severe mechanical pressure was needed to destroy liquid metal micro/nano-droplets in the soft polymer matrix, which would seriously damage the integrity of the composite. This problem could be solved by adding a small amount of non-functional graphene flakes into the composite materials. Even if the loading of graphene was very low ($\approx 0.6 \text{ wt}\%$), a high conductivity could also be obtained.^[22]

A scalable circuit was proposed by using liquid metal to selectively infiltrate metal patterns in 2015.^[23] Galinstan alloy

was treated with hydrochloric acid on different substrates, the I–V characteristic curve showed that this scalable circuit still has good electrical and mechanical properties, even after 6000 times of twisting (180°) and stretching (60%). Compared with the previous method, the accuracy of manufacture of the LED integrated circuit has been significantly improved.

A method of using uniformly dispersed platinum to modify carbon nanotubes was developed in 2019. Then the carbon nanotubes were added into liquid metal matrix, and the liquid metal-based scalable interconnection composite materials were prepared. These materials would be required for flexible three-dimensional interconnection devices with high-resolution.^[24]

2.4. Application of Liquid Metal Composites to Self-Healing Processes

A unique composite material with mechanical and electrical repair effect was formed by using nickel sheet and EGaln particles in the carboxylated polyurethane matrix. This material has complete flexibility, self-healing, and energy storage.^[25] When the composite material was damaged, it could repair itself through the instantaneous connection mechanism of liquid metal droplets. It could also form a circuit with self-healing and shape reconfigurability. (Figure 1E) The deformation ability of liquid metal droplets could prevent the propagating of cracks in the elastomer, resulted a high integrated and extensible elastomer.

Besides, the complexation reaction of Ga with TFSI ligands was a reversible faraday reaction. The new conductor has excellent ductility, self-healing, conductivity, and electrochemical stability. This conductor could maintain its original capacity at 200% tension without performance degradation. It has a charge-discharge cycle of 600, and a tensile release cycle of 1000, which were higher than most elastic and self-healing batteries.

2.5. Application of Liquid Metal Composites to Electronic Components

The reliable electromechanical connection between liquid metal, integrated circuit chips, and other microelectronics could provide the basis of the fabrication of multi-functional and scalable electronic components. Liquid metal particles were atomized by ultrasonic to make the deformable conductor appear in the form of interconnects and contacts. Polyvinyl alcohol (PVA) substrate was spun and cast on a glass substrate. By the scraper coating process, the shell with a thickness of 500 μm was prepared. The serpentine and island structures were eliminated by laser, and a layer of soft silicone rubber was added on its surface. The sacrificial layer was dissolved in warm water, and the composite material excited from the surface was released from the glass matrix.^[26] (Figure 1D)

Through the research on the electromechanical interface between component pins and LM interconnects, by using hydrochloric acid steam to treat LM lead angle could overcome

some shortcomings. The connection between electrical component pins and LM leads were robust. By combining this interface technology with the dual-phase LM circuit structure, a novel fully functional scalable circuit composed of EGaln and microelectronics could be obtained.

3. Flexible Liquid Metal Intelligent Electronic Skin

Electronic skin has a simple structure, a variety of functions, and is flexible and stretchable. It has advantages of flexibility, stretchability, shock resistance, high efficiency, low-cost manufacturing, and a wide application prospect in wearable or implantable fields. It could be designed and processed into any shape, and cover the surface of the equipment like clothes.

Electronic skin could make robots anthropomorphic and intelligent. It could make intelligent artificial limbs, skin grafting, and even effectively treat cancer in the medical field. E-skins (electronic skin) are already capable of providing augmented performance over their organic counterpart, both in superior spatial resolution and thermal sensitivity. They could be further improved through the incorporation of additional functionalities (e.g., chemical, and biological sensing) and desired properties (e.g., biodegradability and self-powering).

Liquid metal makes it possible for electronic skin to be thin, flexible and extensible. Liquid metal could attach to many carriers and would not lose the performance of electronic skin because of instability. It could integrate with various carriers or devices with certain functions to form a new type of equipment with conductivity. Liquid metal electronic skin also has a non-negligible contribution in the field of intelligent robots. It could not only help robots obtain real-time environmental information, but also give them mechanical flexibility.

To enhance the conductivity, wettability, and adhesiveness, various materials such as copper, nickel, and iron particles were mixed into the liquid metal. The researchers found that copper particle was more conductive than liquid metal, and could enhance the conductivity of the liquid metal. Because of the good forming ability of Cu–EGaln, when it was printed or sprayed on the carrier by instrument, this material was not easy to flow away, and could form a fixed pattern.

In addition to Cu–EGaln, Ni–EGaln was made by mixing a large number of nickel (Ni) particles with EGaln. The fluidity and surface tension of Ni–LM could be reduced. A layer of gallium oxide was also coated on the surface of Ni–EGaln, which could adhere to the surface of many common materials, and greatly expanded the application range of electronic tattoo. The research team has successfully developed an electronic tattoo of Ni–EGaln (Figure 2A).^[27] The wettability and adhesion of Ni–EGaln to polymethacrylate (PMA) adhesive was significantly enhanced. (Figure 2C, D)

The liquid metal also exhibited significant adhesion selectivity on different substrates, including Polydimethylsiloxane (PDMS), paper, and polymethacrylate (PMA) glue. PDMS has the characteristics of stable chemical properties, high transparency,

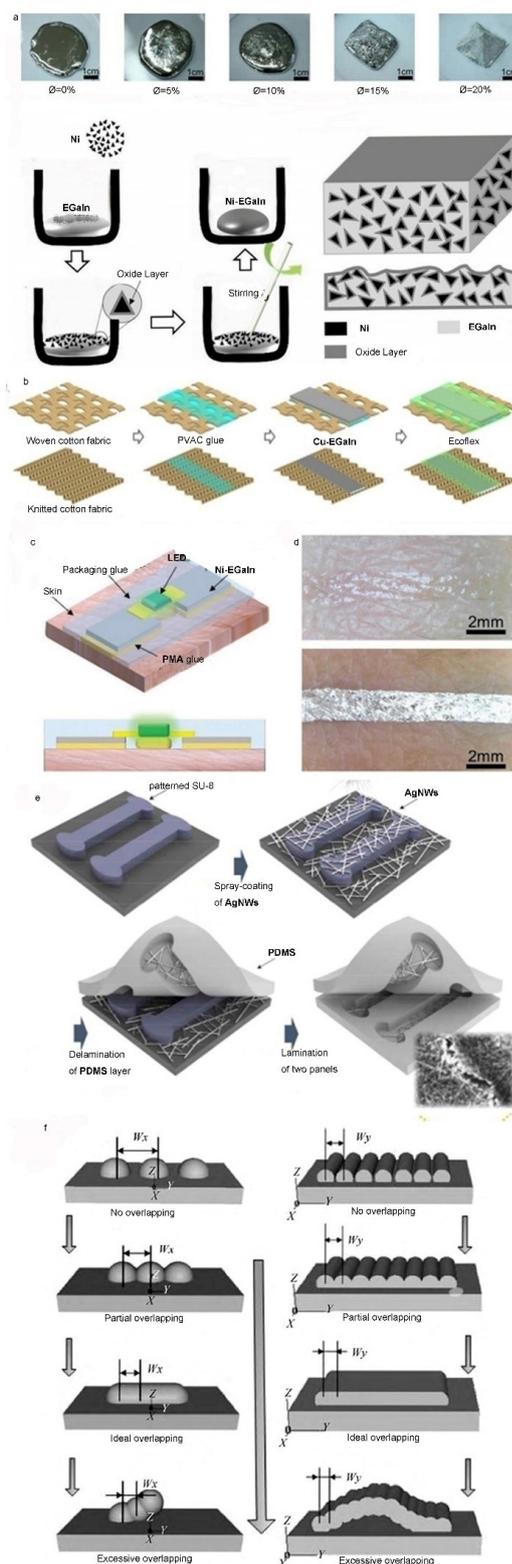


Figure 2. (A) Cu–EGaln with different proportions and fabrication process of Ni–EGaln; (B) Preparation of Cu–EGaln electronic skin on fabric by PVAC adhesive; (C) Ni–EGaln based ultraconformable electronic tattoo; (D) Optical photos of PMA (polymethacrylate) on skin and Ni–EGaln on PMA; (E) Crack-enhanced microfluidic stretchable e-skin; (F) Metal droplet stacking forming technology.

and variable mechanical properties. Due to its good performance and commercial usability, it has been widely used. The PDMS could help liquid metal being able to print or spray the on the substrate, and producing clear, stable, and efficient graphics.^[28–29] (Figure 2B)

In a microfluidic channel, Ag NW was uniformly sprayed on the lens wafer as an electrode of the capacitive sensor. Then liquid PDMS was dropped onto the wafer. Finally, the PDMS adhesive was thermally cured, and then it was separated slightly. The surface of PDMS was smooth and flat, but microcracks were uniformly generated in the whole area of Ag NW. By injecting liquid metal into the cracks, soft electronic components with high electrical conductivity and tensile property could be finally fabricated.^[30] (Figure 2E) by improving the wettability and adhesion of liquid metal on the substrate, the substrate could be modified, and improving the sensing efficiency.

4. Printing Technology of Liquid Metals

At present, cleaning, and other process in traditional machining method (such as lithography and etching) are complex, and time-consuming. While existing metal 3D printing technology is much simpler, however, there are still some printing problems, such as high temperature, too much energy consumption, too high maintenance cost of equipment, and too big difference of melting point between metal and non-metal materials.

The emergence of liquid metal ink material could realize the rapid manufacture of various functional circuits in a low cost and energy saving way. Using liquid metal with low melting point as forming material, based on existing metal 3D printing, it not only breaks through the limitation of material in shape and temperature, but also could use the mixed printing method of metal and non-metal as functional materials at room temperature. It is helpful to promote the development of intelligent production and flexible manufacturing field. Nowadays, the 3D printing technology of liquid metal was still under continuous research. 3D printing of liquid metal mainly included liquid metal melt deposition printing technology, liquid phase 3D printing, suspension 3D printing, microcontact printing technology, and in vivo 3D printing molding technology, these technologies were presented and discussed in this part.

A kind of metal droplet stacking molding technology was proposed in 1993, which achieved the molding effect by discrete superposition.^[31] Based on the way of inkjet printing, uniform metal droplets were generated, and the movement of the nozzle and 3D substrate was controlled. So that, the metal droplets could be accurately and orderly deposited in the designated position and realized fusion and solidification step by step. The points were stacked layer by layer, resulting in complex 3D graphics. (Figure 2F)

4.1. Melt Deposition Printing Technology

Melt deposition printing was one of the basic 3D printing methods. By depositing the melt ink layer by layer and solidifying it on the substrate. This method could print the object from bottom to top.

A low melting deposition type printing was proposed.^[32] Gallium Indium alloy was used as ink material (melting point 52 °C). A desktop 3D printer was used to directly carry out 3D printing at room temperature. Under the heating of the resistance wire, the low melting point metal in the stainless-steel barrel was completely melted. The air pressure pump was used to apply constant pressure on the metal, so that the liquid metal could be continuously extruded from the printing nozzle. The height and printing speed were adjusted in the process of movement. Liquid metal was continuously deposited, stacked, solidified, and bonded layer by layer, finally forming a three-dimensional structure. (Figure 3A)

Low melting-point metal was directly molded by 3D printing into 3D structures, which has advantages in mechanical property and electrical conductivity. It could provide technical guidance for other complex 3D printing technologies. On this basis, the non-metal printing process could be developed in the future, to realize the integrated molding and packaging of the

three-dimensional circuit and provide electronic circuits and implantable biomedical treatment.

4.2. Liquid Phase 3D Printing Technology

A liquid-phase 3D printing method was proposed, which could rapidly manufacture metal object.^[33] The principle was to deposit and form metal in liquid cooling fluid, which could be water, ethanol, acid, or alkaline electrolyte. The metal forming method was the pneumatic melting deposition method. The liquid phase printing experimental device was shown in figure 3B, which was composed of a syringe, printing nozzle, nitrogen tank, and solenoid valve. When the printing nozzle was immersed in liquid cooling fluid, the process of droplet formation was observed by using a high-speed camera. When the injection speed of liquid metal was lower than the critical value, a single liquid drop would be formed at the needle head. While when the injection speed was higher than the critical value, a metal jet would be formed at the needle.^[34]

The liquid 3D printing method could print metal particles, rods, cones, and cylinder structures. Compared with other cooling materials, the cooling fluid has higher thermal conductivity and melting point. Thus, it could achieve rapid metal

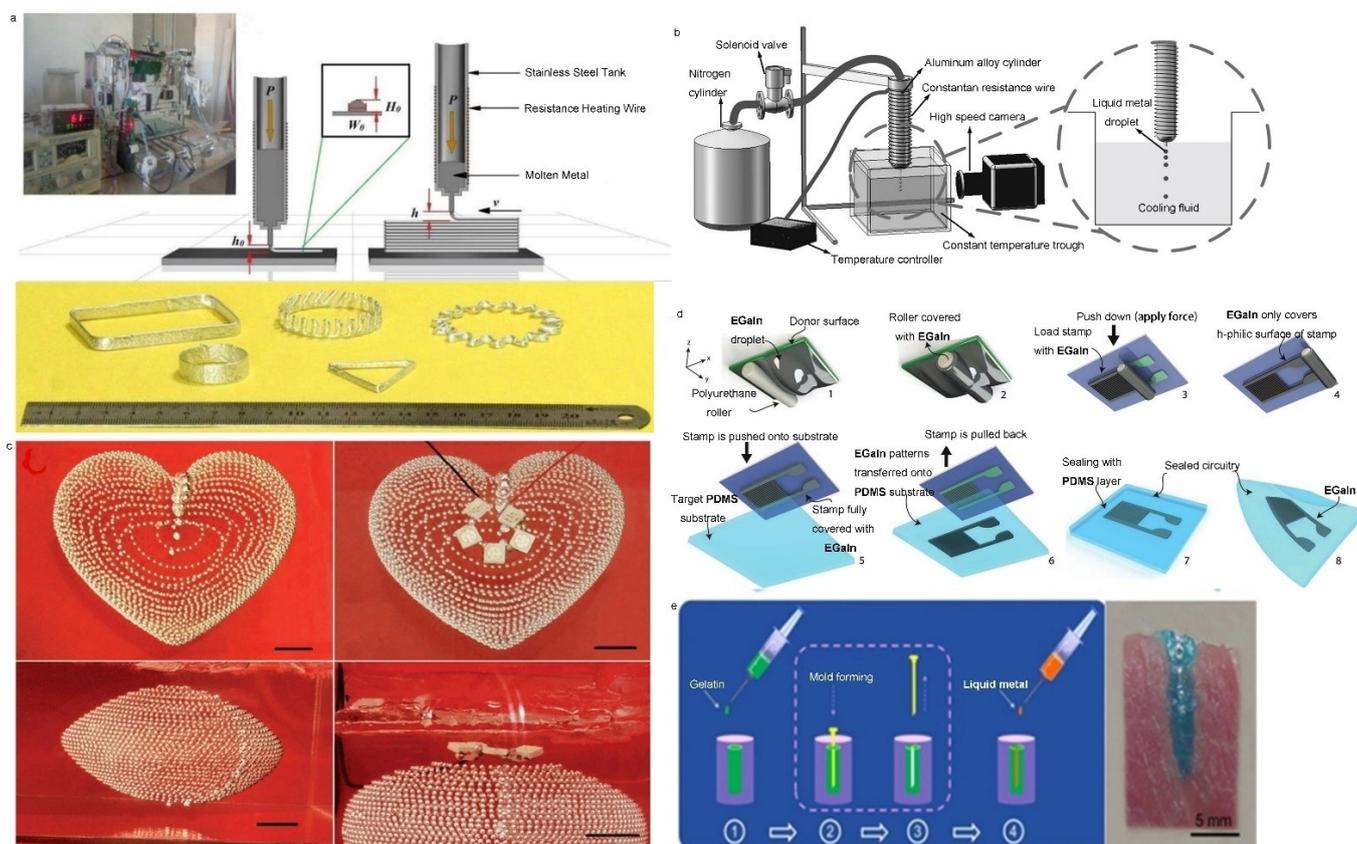


Figure 3. (A) The picture of Liquid metal melt deposition printing system, and the printed 3D forming structure; (B) Experimental device of liquid metal liquid phase 3D printing technology; (C) A liquid metal electronic circuit suspended in a gel; (D) The printing process of liquid metal micro-contact printing technology; (E) Liquid metal printing bioelectrodes in biological tissues.

deposition, and the oxidation problem of metal ink could be effectively avoided.

4.3. Suspension 3D Printing Technology

A liquid metal suspension 3D printing technology was proposed. With self-recovered hydrogel as supporting material, the liquid metal with a three-dimensional structure was fabricated by suspension printing.^[35] The forming principle of suspension printing was shown in figure 3C. It used self-recovery hydrogel as supporting material, making use of the dynamic and freely convertible characteristics of the gel between the fluid and solid-state. In the gel environment, the printing nozzle could reciprocate according to the predetermined forming path, continuously extrude liquid metal material, and use gel material to support and fix. The liquid metal was piled up layer by layer, to obtain a three-dimensional forming structure with complex shapes.

As shown in figure 3C, the three-dimensional structure of liquid metal printing molding was installed, and the circuit was connected. Utilizing suspension printing, liquid metal material played a significant role in the manufacturing of medical electrode and functional electronic device.

4.4. Micro-Contact Printing Technology

The micro-contact printing technology has the advantages of softness, scalability, high resolution, and high extensibility.^[36] This method could be used to produce liquid metal circuits with a line width as small as 15 μm .

In the preparation process, photolithography was used to make the stamps reusable, and improve the resolution. As shown in figure 3D, a method for manufacturing flexible and scalable liquid metal electronic products was demonstrated. For the process of microcontact printing manufacturing, polydimethylsiloxane (PDMS) was prepared by elastic preparation. In order to solve the problem of poor impact pressure and reproducibility, high-precision automatic micro-actuator was designed and manufactured. The electrical property of the fabricated circuit was also tested. The results show that the method was universal in manufacturing liquid metal-based circuits.

4.5. 3D Printing Technology for Implantable Biomedical Electronic Devices

Implantable biomedical electronic devices in vivo 3D printing molding technology was a kind of medical electronic device manufacturing method, which directly injected into the target tissues in vivo.^[37] The molding process was shown in figure 3E.

Firstly, the biocompatible packaging material LM was injected into the biological tissue to form a specific structure. Then, a tool was used to insert and pull out the solidified packaging area to form the electrode area. Finally, the

conductive metal ink, insulating ink, and the matching micro/nanoscale devices were successively injected to form the target electronic device.

Figure 3E showed an injection-molded bioelectrode in pork tissue. Due to the high compliance, conformal, minimally invasive, and low-cost characteristics, the flexible devices fabricated by this in vivo 3D printing technology shows a good application prospects and has an important significance in the field of implantable biomedical electronic technology.

After the combination of liquid metal and 3D printing technology, the rapid prototyping of electronic circuit functional devices, the automatic manufacturing, and packaging of terminal products have been realized. The whole production process has the advantages of fast, green, and low cost. The traditional electronic circuit manufacturing rules have been changed, and a revolutionary development path has been provided for the modern electronic industry.

5. Liquid Metal Catalysts

The catalysis of catalyst could save energy consumption, reduce production cost, reduce, and restore environmental pollution problems. However, the development status of catalysts was still in the solid phase. Compared with traditional catalysts, liquid metal catalysts have become a new research direction due to their characteristics such as uncertainty, isotropy of the surface, good fluidity, and larger contact area than the solid state. The catalyst research based on liquid metal will be a new driving force to promote the development of catalyst. In this section, liquid metal catalysts with different compositions were summarized. Liquid metals were mainly used to catalyze the growth of graphene, catalytic hydrogen production, aldehyde reaction, photocatalysis, and electrocatalysis. The working mechanism and reason of the catalyst obtained from the experimental results were briefly described.

5.1. Catalysed Dehydrogenation of Organic Compounds

Peter Wasserscheid et al. have reported a liquid metal catalyst for butane dehydrogenation, which is a Gallium and Palladium liquid mixture supported in porous glass.^[38] The catalyst was very stable, not easy to coking, and has a remarkable catalytic performance. The supported liquid metal catalyst has a very strong dynamic property. Its catalytic effect was not carried out on the surface of nanoparticles, but on the metal atoms which distributed on the surface of liquid metal catalyst.^[39]

It also found that the addition of liquid Gallium to the aluminum supported rhodium catalyst had an efficient effect on the activity and selectivity of the catalyst. They found that when the loaded Ga–Rh alloy was in liquid state, rhodium induced propane dehydrogenation activity increased. Because the surface of the liquid metal catalyst was highly dynamic, if propane was supplied from the gas phase, rhodium only periodically appeared at the interface, and the time of being trapped there became longer. In the catalytic process, there was a synergistic

mode between Gallium and Rhodium. Propane was activated at the rhodium atom, and then the remaining propyl group was transferred to the surface of gallium, and the two separated hydrides were recombined to hydrogen at the rhodium atom point.^[40] (Figure 4A)

At the same time, Yuta Nishikawa et al. found that Indium supported on silica (In/SiO_2) could catalyze the dehydrogenation of methane at high temperatures. Other useful products could also be obtained.^[41] They used X-ray diffraction and scanning electron microscopy to characterize the supported Indium catalyst under working conditions, and the obtained catalyst was in liquid state. (Figure 4B)

Recently, four types of liquid alloys (Ga-In-Sn-Bi) were increased by Liu Jing et al. By aluminum water decomposition, they also studied the effect of this type of liquid metal alloy on hydrogen production.^[42] The results showed that the reaction rate of activated aluminum with water was stable, and the hydrogen production rate was as high as 92%, which was superior to the previous binary and ternary alloys.

5.2. Supported Liquid Metal Rhodium Catalyst for Aldehyde Reactions

The supported rhodium liquid metal catalyst has unprecedented activity and high selectivity for olefin aldehyde reaction.^[43] By adding Rh into GaInSn alloy in a certain mass ratio, Rh(0.1%)LM was obtained, which was reused in the aldehyde reaction of styrene. The catalyst could be reused for at least five times without obvious mass loss. After releasing CO/H_2 gas, Rh(1) was formed in situ, which could be reduced to metal Rh (0) by free electrons. The supported Rh-liquid metal catalyst could be recovered without deactivation. (Figure 4C)

5.3. Photocatalysis

Mohamad B. G. et al. studied the growth of MnO_2 monolayers on the liquid metal alloy. It was found that the oxide formed on the surface of liquid metal would fall off by itself, which resulted in the continuous formation of ultra-thin metal oxide sheets. Under the condition of mechanical stirring, the separation of gallium oxide sheets was promoted. The porous shell was formed around the solid indium core. This core-shell nanostructure material was composed of hydrated manganese dioxide and gallium oxide sheet. (Figure 4D) Ultrasound was

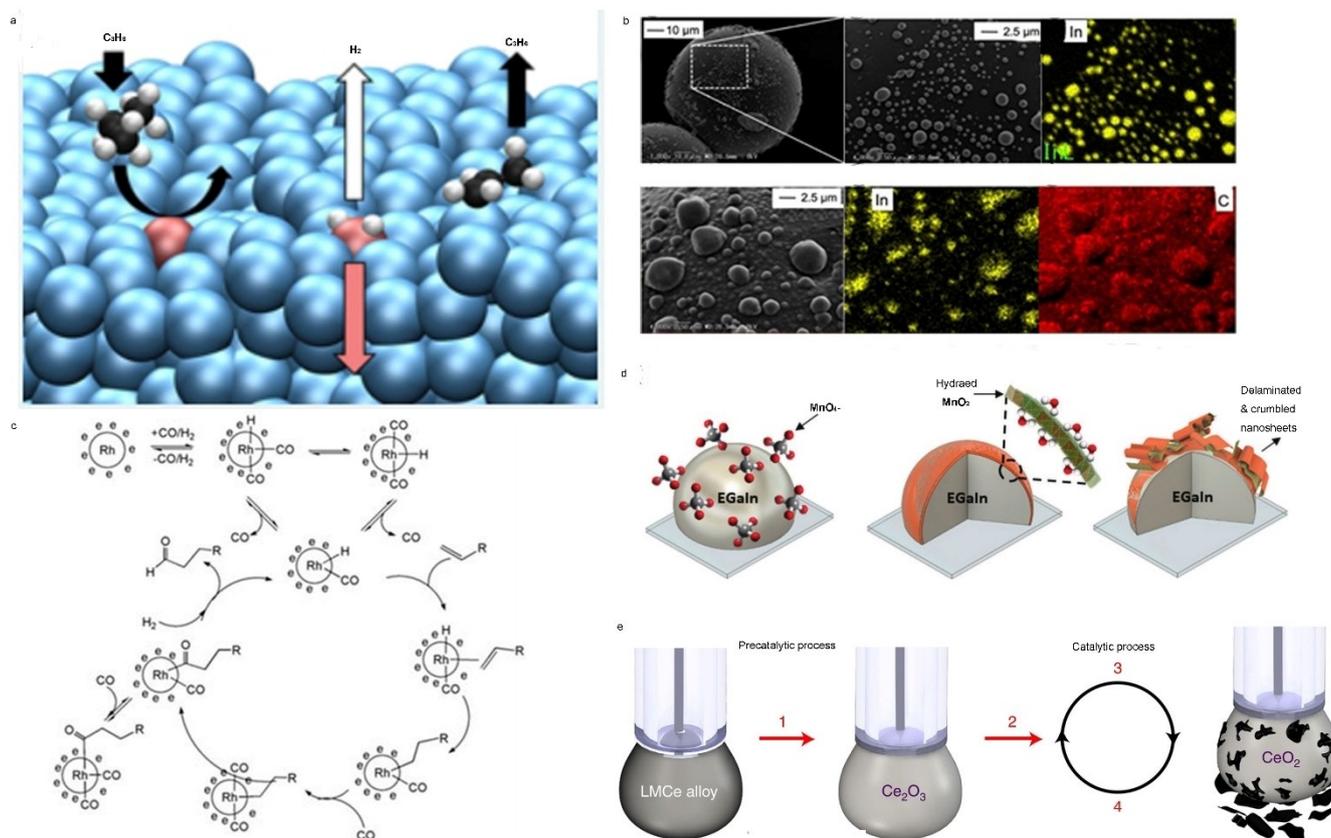


Figure 4. (A) Dehydrogenation of propane catalyzed by aluminum supported gallium rhodium liquid metal alloy; (B) SEM and EDS of indium loaded on silica before and after reaction; (C) Mechanism of supported liquid metal rhodium catalyst for olefin aldehyde reaction; (D) Schematic diagram of formation of hydrated manganese dioxide on the surface of gallium indium alloy liquid metal; (E) Schematic diagram of electrocatalytic reduction of carbon dioxide by liquid metal containing cerium.

used to move the Gallium part of the liquid alloy to the surface, leaving a solid indium core. The obtained core-shell structure material has been used in the photocatalytic degradation of Congo red. Compared with MnO_2 sheet material or other composite materials, it has a high degradation efficiency.

5.4. Electrocatalytic Reduction of Carbon Dioxide

In addition to the photocatalysis described above, electrocatalysis has recently been studied and it has been found that liquid metal catalysts can reduce carbon dioxide at room temperature, as well as obtained solid carbonaceous and graphitized products.^[44] This solid carbon-containing material was storable. (Figure 4E) They added cerium to Galinstan alloy, and put liquid metal alloy containing cerium into carbon dioxide saturated electrolyte. Under the electric catalysis, cerium oxide formed on the surface of liquid metal, which also reacted with carbon dioxide to form carbonaceous material and cerium dioxide. Cerium dioxide was reduced to cerium under the action of electric current. The reaction of carbon dioxide produced the above-mentioned products, which was also an important insight on this catalytic mechanism.

The use of liquid metal catalysts played an important role in improving the efficiency of chemical reactions, and has catalytic properties for many substances. One aspect of catalyst improvement and subsequent development was to develop a heterogeneous catalytic system. Based on the liquid metal, multi-element combined liquid metal and modified liquid metal provide new opportunities for future catalyst science and technology.

6. Liquid Metal Micro-Drive Machines

Liquid metals are widely used in various fields due to their excellent physical and chemical properties. Different from other materials, liquid metal has a good performance in conductivity, and heat conduction. Due to its stable physical and chemical properties, it is not volatile and has no toxicity. After liquid metal forms oxide layer, it is easy to be driven by external environment because of its surface tension. So liquid metal has a good application prospect in the field of micro driver. The liquid metal drive principle was described in detail in this section. Due to the unique physical and chemical properties of liquid metal, its motion could be stimulated in a variety of ways, such as electric, magnetic, chemical and optical drives, etc. The practical application of liquid metal under different driving principles was summarized.

6.1. Electrically Driven Liquid Metals

Due to the existence of surface tension of liquid metal, under the action of the external electric field, the surface tension would change with the distribution of surface charge. Then

change the force acting on the liquid metal, thus driving the liquid metal (Figure 5B).

Electrocapillary driving was realized by the electrocapillary phenomenon, which means that the surface tension of liquid metal changed with the change of electrode potential. When the voltage was applied on the electrode plate, an electric field force would be formed. Due to the existence of the electric field force, the liquid metal drops would be pulled down, and the contact angle would be changed. Based on dielectric wetting, the driving mechanism of continuous electric wetting was improved. External voltage was applied to both upper and lower ends of liquid metal, and continuous electric field force was formed through continuous voltage to guide liquid metal movement (Figure 5C).

Li et al. demonstrated a system called liquid metal pump. Under an appropriate electric field, a series of liquids were driven without mechanical moving parts. The pump contained liquid metal droplets, which induced liquid flow at high flow rates, but with extremely low power consumption.^[45]

6.2. Magnetically Driven Liquid Metals

The magnetic drive of liquid metal was mainly realized by modifying the liquid metal. The researchers used the magnetic elements to combine with liquid metal and form a metal bond. After the modification, the liquid metal was magnetic, and could be driven by the magnetic force in the field.^[46]

In recent researchers, someone proposed a corrosion-free and non-sticky, has the good elasticity and mechanical strength of the magnetic controlled liquid metal droplet. The obtained material consists of a liquid metal softcore coated with a mixture of ferronickel and polyethylene (PE). Besides, its functions include robot motor, controllable obstacle cleaner, and circuit flexible switch, which showed the potential application of LM in robot motion, manipulation, electronic circuit, and other fields (Figure 5A).

A method to control the movement of liquid metal droplets by a pure magnetic field without introducing ferromagnetic particles was proposed.^[47] The driving force came from the Lorentz force, which was generated by the eddy current from the relative motion of liquid metal droplet and magnetic field. By changing the size of the droplet, the concentration of NaOH solution, and the magnetic flux density, the velocity of the droplet could be easily adjusted. By electrochemical formation, and removal of a solid oxide layer on EGaIn surface to make sliding layer thinner, the driving of droplets could also be controlled. Combined with the unique properties of liquid metal droplet, it was possible to realize applications for soft robots, which could not be achieved by solid metal balls, and to assemble multifunctional MEMS and actuators (Figure 5D).

6.3. Liquid Metal Driven by Sound Field

In the sound field, the liquid metal absorbed and reflected the wave to obtain the radiation provided by the wave.^[48] Through

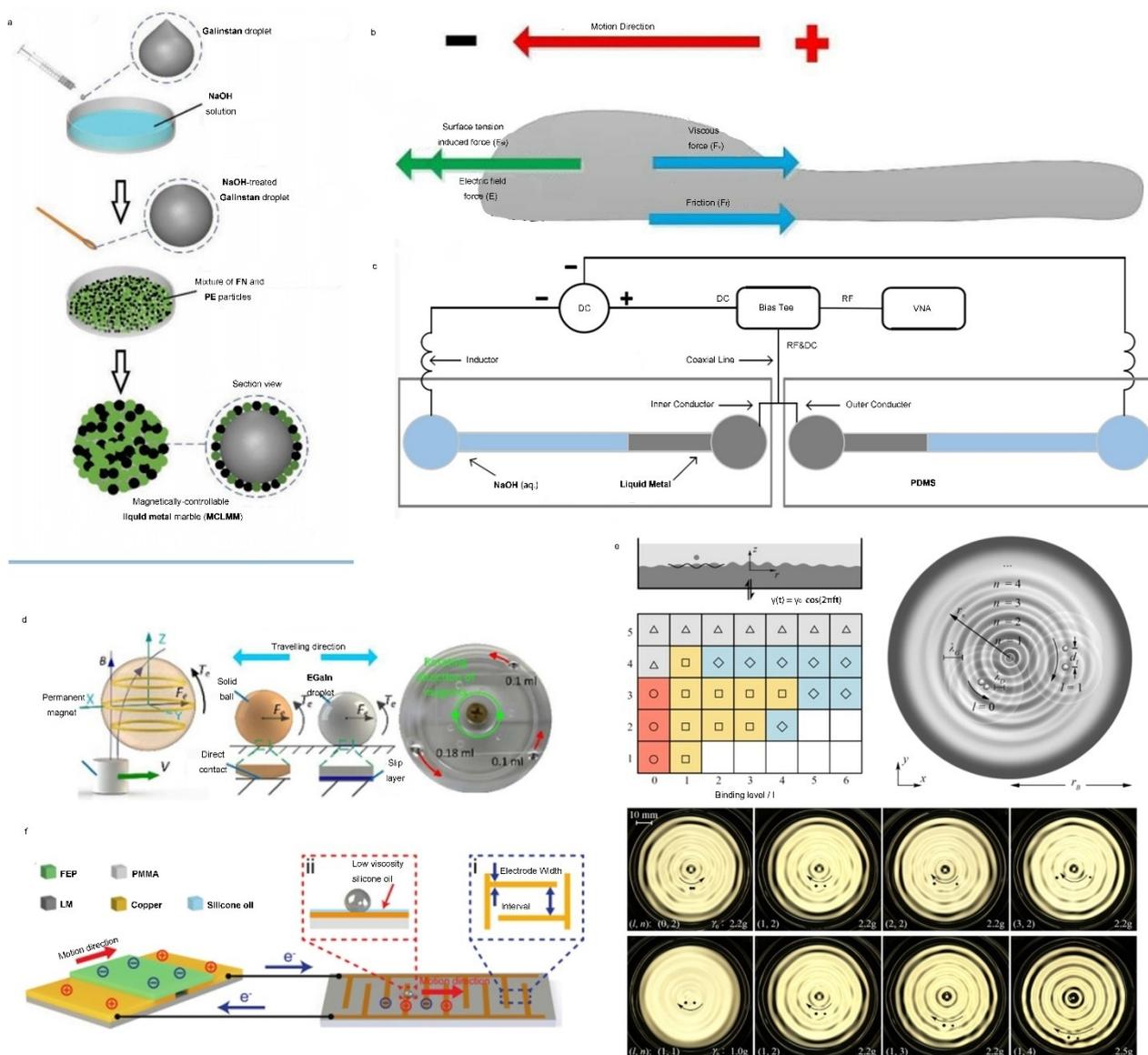


Figure 5. (A) Manufacturing schematic diagram of magnetically controllable liquid metal marble; (B) Force diagram of liquid metal in electric driving process; (C) Schematic diagram of liquid metal electrically driven antenna; (D) Magnetic driven liquid metal droplet motion; (E) Liquid metal driven by sound field; (F) Liquid metal drive based on friction effect.

the radiation force, the liquid metal could move in the sound field without contacting it. However, it should be noted that if the size of the liquid metal was far smaller than the wavelength, the liquid metal would not be affected by the radiation force.

Tang et al. revealed that the integrated guided wavefield was a clue to improve droplet guidance, thus extending the hydrodynamic particle-wave simulation to optical systems and other fields.^[49] Wang et al. used liquid metals as raw materials to prepare nanoparticles by ultrasonic crushing, and used nanoparticles as nanomotors to explore their motion behavior driven by sound field.^[50] It was found that the particle size of liquid metal nanoparticles prepared in the acoustic field could reach 40–100 nm. The single and group motion of liquid metal nanoparticles driven by sound field was studied. It was found that, the movement of single liquid metal nanoparticle was

relatively simple. The group liquid metal nanoparticles could realize aggregation and dispersion processes and could also move in a directional direction (Figure 5E).

6.4. Friction Driven Liquid Metals

Friction nano driven was based on the friction of electricity to converted mechanical energy into electrical energy. Then the liquid metal was driven by electrical energy. Bu et al. introduced a liquid metal actuator driven by a triboelectric effect, which was triboelectric nanogenerators (TENS), and precisely controlled the motion of LM.^[51] The Coulomb force and inertia effect of friction charge transferred in interdigital electrode,

drive LM to make a continuous linear and circular motion, respectively (Figure 5F).

7. Summary and Outlook

In this minireview, recent outstanding research on liquid metals and their use in tensile polymer composites, electronic skin, 3D printing, catalysis, and different driving systems in recent years were reviewed. The application and principle of liquid metal in different drive systems were summarized. The practical applications of liquid metals under different driving conditions were described.

Because the properties of polymer-composites still have great room for improvement, it has become an important development direction to develop stretchable liquid metal-polymer composites with excellent physical and chemical properties, and be able to carry out large-scale and low price. For example, liquid metals could be combined with other new polymer materials (2,5-Furandicarboxylic acid, 2-ureido-4[1H]-pyrimidinone et al.) to change their toughness, and self-healing properties. In other words, liquid metal-polymer composite materials have a broad and bright future in electronic devices, energy devices, and medical devices.

In the field of electronic skin, we could use liquid metal electronic skin to replace other electronic devices in the medical field, to achieve real-time and accurate body condition indication. In the future, wearable liquid metal sensing systems that continuously collect data from the human body will be studied. For example, liquid metal flexible skin with multiple sensing functions such as temperature, strain, humidity, light, magnetism and pressure could be further developed. Due to the current state of science and technology, we are still unable to produce a completely liquid metal electronic skin which functions as human skin. It is also a difficulty to be considered next.

The sustainable development of liquid metal catalyst in the future depends on the catalytic performance of the catalyst. Liquid metal has low melting point, large contact area, so it could be used as a popular material for the growth of two-dimensional (2D) or three-dimensional (3D) materials in the future. Liquid metal unit catalyst, multi catalyst, multi-phase catalyst, and other different multi-functional were the important direction of its development in the future. But the application of liquid metal in some fields is limited by its own characteristics. Therefore, in the future development, we should find ways to overcome its own characteristics. So that liquid metals could be used in more fields, such as gas sensitive materials.

The printing technology of liquid metal was still under continuous research. Although a lot of progress has been made in the early manufacturing of printing process equipment, material and software development, there are deficiencies in technology transformation, promotion, and industrialization. These problems will need to be solved quickly in the future. At the same time, more advanced printing methods could be developed in the future to prepare ultra-high precision liquid metal electronic devices, such as laser printing, micro-contact

printing, etc. Liquid metal printing technology will bring more development value in the manufacturing of flexible intelligent robots, electronic skin, and flexible power supply.

Liquid metal as a new intelligent driving material, shows a very broad development prospect. However, the application of liquid metal as actuator in the field of machinery was still in its infancy stage. Due to the limitation of the application of liquid metal, it could only be used in the solution environment, which limited the development of liquid metal as driver, and restricted the formation of more elaborate functional machine system. In the future for micro-drive machines, liquid metal could be used for drug delivery, microchannel delivery, and tiny robots.

It is helpful to fully understand the application and development of liquid metal, and lay a solid foundation for further development. The deformability and conductivity of liquid metals further bring imagination to the realization of deformable flexible machines, that could freely transform between different forms.

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Conflict of Interest

The authors declare no conflict of interest.

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