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Preparation and application of gallium-based conductive materials in the very recent years

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Gallium and its alloys are a group of metallic materials with low-melting points at or around room temperature. Apart from the good electrical conductivity, the unique liquid state endows those metals with excellent compliance and self-healing capacity, which present great value in the development of flexible and stretchable electronics. Constrained by the high surface tension and low viscosity, however, liquid metals cannot be applied to some common microelectronics manufacturing technologies such as micro-electro mechanics in the preceding years, which impedes their mass production in electronic devices. To address these issues and broaden the applications of liquid metals in electronics devices, numerous efforts have been taken and great progress has been made especially in the very recent years. This review summaries the recent development of liquid metal-based conductive materials from the aspects of preparation or modification methods and their accommodative fabrication techniques in flexible electronic applications. Further outlook including expectations and challenges of liquid metal-based conductive materials are also presented.

liquid metal, conductive materials, fabrication techniques, flexible electronics

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1 Introduction

Flexible electronics is an advanced technology in the development of electronics in recent years, which have great prospects in the fields such as electrical information [1–4], energy [5], medical [6–9] and national defense [10]. One of the key components in the flexible electronics is the interconnect material, which should maintain conductive when subjected to certain degree of mechanical deformation including bending, folding, stretching or distortion. Several categories of materials have been applied including thinning bulk metal materials, metallic or carbon nanomaterials, organic and inorganic materials [4,11,12]. Among those materials, the room temperature liquid metals (LM) based on gallium and its alloys, such as eutectic-gallium-indium (EGaIn) and galinstan (GaInSn), present unique advantages in developing flexible and even highly stretchable electronics (Figure 1(a)). The melting point of gallium is around 29.8°C and its alloys usually have even lower melting points. The superb fluidity at room temperature together with the basic metallic characteristics including high electrical conductivity, make liquid metals highly desirable candidates as flexible conductor. Moreover, compared with other low melting point metals such as Hg, Rb, Cs or Fr, gallium-based alloys are less toxic, non-volatile and non-radioactive [9].

Previously, researchers have attempted to apply LM directly to the manufacture of electronic devices via some methods like perfusion or direct printing or writing. However, the high surface tension, the low viscosity and the non-stick to various surfaces limits liquid metals in fabricating more sophisticated electronic circuits with higher resolution on more universal substrates. To overcome these challenges,

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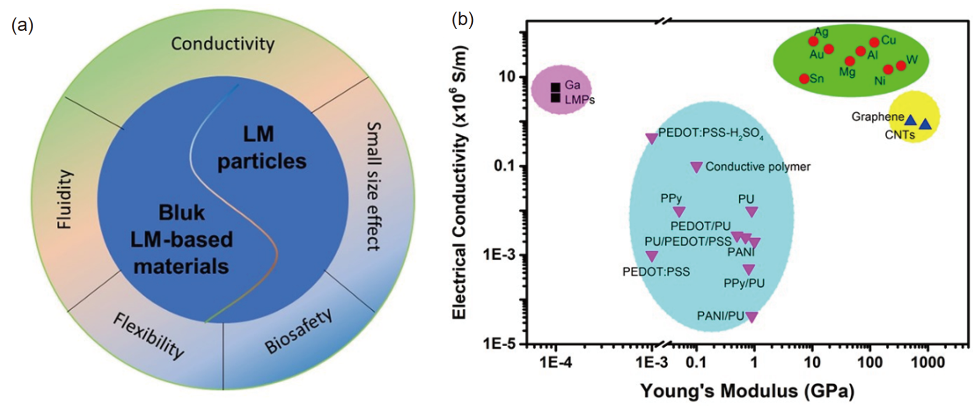

Figure 1 (Color online) (a) The properties of liquid metal materials. (b) Comparison of electrical conductivity and Young's modulus of conductive materials. Each background area indicates a set of materials as follows: Ga-based LM (purple), traditional metals (green), carbon material (yellow), and conductive polymer (blue).

numerous attempts have been made including physical or chemical modification of bulk LM-based material and manufacturing based on LM particles or preparation of particle-based composite materials, which can be applied for various electronic fabrication techniques and facilitate broad applications. As a whole, LM-based conductive materials can be applied in many fields, such as flexible conductor [13–16], printing [2,17], architectonics [18], biomedical [19–21] and so on [22–24]. As the LM-based materials developed rapidly in the most recent years, this paper is dedicated to introducing the very recent advances of LM-based conductive materials and their accommodative fabrication techniques. In this review, we introduce the preparation and application of LM-based conductive materials in bulk and particulate-based materials. Moreover, in order to achieve a variety of different functionalities, LM-based conductive composite materials have been paid more and more attention. In this article, the development of LM-based conductive materials and flexible electronic devices will be summarized, and the challenges in flexible electronics are also discussed at the end.

2 Bulk gallium-based materials

With excellent electrical conductivity (around 2×10^6–7×10^6 S/m, one order less than commonly used conductor like Cu and Ag) [13,14], pure gallium and its alloys such as EGaIn and GaInSn are generally Newtonian fluids with enormous surface tension (about 600 mN/m, which is ten times of water) [9]. Thus, LM usually appears sphere and cannot be easily shaped with fine resolution. When in the presence of oxygen, it is easily oxidized with a thin oxide layer at several nanometers [9,25], which can act as surfactant to great reduce the surface tension of LM. The surface oxide can stick to surface of some materials like polyvinyl chloride (PVC), which benefits for the LM printing. Dense surface oxides (usually several nanometers) will prevent the continued oxidation of LM in static or solid state. However, during the process of movement and deformation, the old oxide layer ruptures and forms more surface oxides, which may impair the conductivity to a certain extent. To improve the performance of LM as flexible conductor and further broaden their applications, bulk gallium-based materials are generally developed. With the excellent conductivity of LM, the mainly preparation of LM-based materials as well as their applications are elaborated as follows.

2.1 Pure gallium and its alloys as extensible conductor

As it is known that, flexible conductor should have excellent extensibility and high electrical conductivity. To intuitively show the advantages of LM used in flexible devices, comparison of electrical conductivity and Young's modulus of conductive materials has been shown in Figure 1(b). It can be seen that traditional metals have high electrical conductivity while with high Young's modulus. And conductive polymers have low Young's modulus and with low conductivity. Based on the intrinsic characteristics, such as conductivity and fluidity, gallium-based liquid metal can be directly applied as flexible conductors in many studies [10,26–31]. To utilize this fluid conductor in flexible electronics, several fabrication techniques have been developed.

In the early years around 2015, the LM are usually shaped by perfused into predesigned channels or space to form patterns with certain functions including antenna, pressure and strain sensors, typically as shown in Figure 2(a) [15,32,33]. Briefly, at first the elastomer, such as poly(dimethylsiloxane) (PDMS), and ecoflex or polyurethane (PU), are shaped by the mold or lithograph. Then LM is squeezed or casted into the channel using syringe needle. Lastly the elastomer should be used to encapsulate the device to be

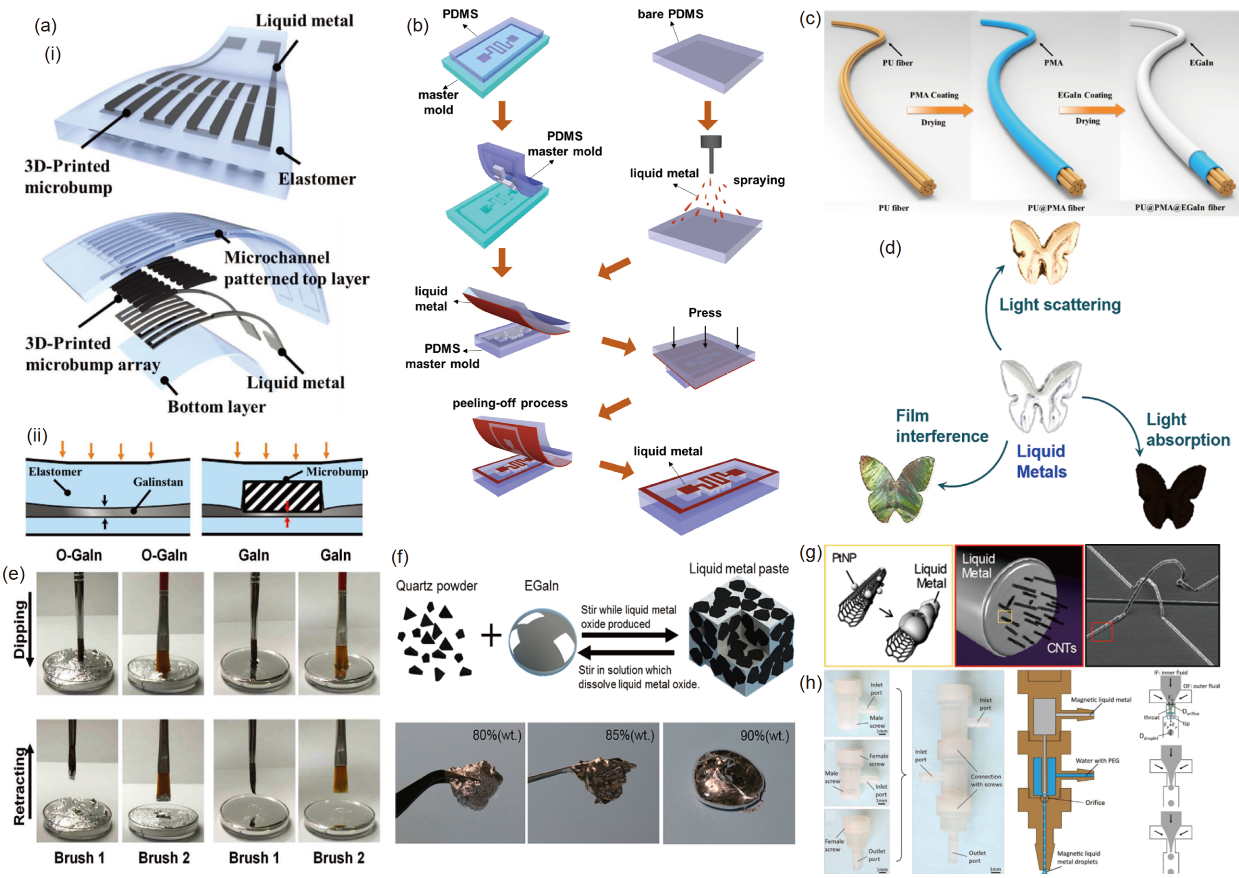

Figure 2 (Color online) (a) (i) Schematic view of the proposed 3D-printed rigid microbump-integrated liquid metal-based pressure sensor (3D-BLiPS). (ii) Effect of the microbump on pressure sensitivity. Reproduced with permission from ref. [6]. Copyright 2019, WILEY-VCH. (b) Schematic illustration of the LM transfer process. Reproduced with permission from ref. [26]. Copyright 2020, Elsevier. (c) Schematic illustration showing the fabrication process of the PPE fiber. Reproduced with permission from ref. [40]. Copyright 2020, American Chemical Society. (d) Coloration of liquid-metal soft robots: from silver-white to iridescent. Reproduced with permission from ref. [38]. Copyright 2018, American Chemical Society. (e) Dip-in test with two types of brushes dipped into and retracted from O-GaIn and GaIn. Reproduced with permission from ref. [3]. Copyright 2019, WILEY-VCH. (f) Schematic illustration of the reversible preparation process of GIS and optical photographs of GIS with different EGaIn content. Reproduced with permission from ref. [46]. Copyright 2020, American Chemical Society. (g) 3D printing of CNT/LM composites. Reproduced with permission from ref. [52]. Copyright 2019, American Chemical Society. (h) Images of coaxial microfluidic devices. Schematic formation process for producing magnetic liquid metal droplets (MLMDs). Reproduced with permission from ref. [53]. Copyright 2020, Springer Nature.

applied in the subsequent applications. For example, recent study applied EGaIn with high electrical conductivity (3.4×10^6 S/m) in electronic skin with the perfusion method [34,35]. However, the melting point of EGaIn is 16°C, which limited its usage in lower temperature. With lower melting point [9,24], $Ga_{68.5}In_{21.5}Sn_{10}$ was injected into the micro-channel forming soft pressure sensor using multi-nozzle fused deposition modeling (FDM) process. As shown in Figure 2(a), the sensor combined four layers (bottom layer, GaInSn, rigid microbump array, microchannel patterned top layer). Verified by experiments, the sensor showed high sensitivity under pressure (0.158 kPa^{-1}), excellent robustness and repeatability (10000 cycles) of multidirectional stretching or bending and low resistance (1.6 Ω) [6]. To enhance the elasticity and mechanical properties, Ning et al. [36] infiltrated LM (GaInSn) into polyurethane sponge (PUS) and followed by encapsulation with PDMS to prepare a stretchable conductor. The prepared PDMS/PUS/LM composite showed excellent electrical conductivity (10^4 S/cm) and electrical conductivity stability under various mechanical deformations, which is higher than the other composites currently. However, the difference between using the PUS or not and the interaction between PDMS and PUS should be explored to know more about the advantage than without PUS. Furthermore, to prepare human-friendly electronics, the electromagnetic interference (EMI) shielding properties of the three-dimensional (3D) LM network were investigated by Bin Yao et al. [13]. The 3D LM network was fabricated by encapsulating LM into lithographically fabricated (PDMS) nanonetworks, which showed an unprecedented frequency (2.65–40 GHz), which is relevant to 5 G technology than the current EMI shielding materials (8.2–12.4 GHz) [37]. It proved that the feasibility and harmlessness of LM-base flexible devices used in human body.

Additionally, the spraying method is another way to prepare LM bulk materials. Commercial $Ga_{68.5}In_{21.5}Sn_{10}$ was used for fabricating the LM film on PDMS mold [26]. As it can be seen in Figure 2(b), on the one side the mold substrate should be prepared, and on the other side LM was sputtered to transfer plate at high speed. Then LM membrane was transferred to the prepared mold. The thickness of the sprayed LM was 10–20 μm [26], which is thinner than that by perfusion method. That is to say, the resolution of this method is higher than perfusion method. And the electrical conductivity is 1.93×10^6 S/m and can be utilized as an electrode in the triboelectric nanogenerator (TENG). The preparation process is simple and flexible for application, but it is difficult to control the uniformity and reusability, and outflowing of liquid metal may occurred during the transfer process.

Beyond using pure LM, more and more researchers pay attention to fabricating LM composites used in flexible electronics to broaden the LM-based flexible materials. Totally, other rigid metal particles and polymers are often combined with LM to form the functional materials. On one hand, to maintain or even to enhance the conductivity, other metals (like Cu/Ag/Fe/Al) are applied [38,39]. For example, Hou et al. [38] fabricated colorful LM composites (Figure 2(d), from silver-white to iridescent) through adding aluminum and anodic oxidation, which could be applied in preparing colorful soft robots and flexible electronics. Combined with Ag, Sohn and Chu [39] used silver nanowires (AgNWs) and EGaIn to fabricate a self-healing conductor used for e-skin. The connection between AgNWs and EGaIn showed high mechanical flexibility and stability under applied stress condition. Due to the excellent conductivity and antibacterial activity, Ag is a promising additive for skin electronics and biomedical engineering. The composite conductive materials mixed with Ag are more combined with liquid metal particles, which are reviewed in more detail in the next section. On the other hand, to improve the stretchability and maintain the conductivity of LM, polymers (like PU/fibroin/polyvinyl alcohol) are used to form the functional composites. Recently, a stretchable EGaIn fiber was fabricated. Simply, EGaIn, as an outer layer, was brushed on the core fiber (polyurethane, PU) directively. And to enhance the connection, polymethacrylate (PMA) was used as an intermediate modified layer. The obtained PU@PMA@EGaIn (PPE) fiber (Figure 2(c)) demonstrates excellent conductivity (10^5 S/cm) when it was stretched up to 500% strain [40].

2.2 Modified liquid metal-based materials by changing the rheological and any other properties

Nowadays, printing technology has been spread in many fields, including aerospace [41], soft circuit [42], bioengineering [8,9], construction [18], and water treatment [43]. LM can also be applied in printing technology for flexible electronics fabrication. Totally, the liquid metal printing method should overcome the challenges caused by low viscosity, high surface tension and density of the LM ink. Through changing the rheological and any other property of LM, LM-based composites have been prepared to benefit for printing (Figure 2(e–h)). Generally, combined with LM in printing, other rigid metals [44,45] and inorganics [20,46,47] are usually used. Thus the composites can be fixed by direct writing, printing, roller-assisted or spraying-assisted screen printing. With these methods, a serial of flexible electronic components or functional circuits are developed including flexible conductor, electrodes and even embolic agents [2]. Recent studies further developed the diverse properties of LM suitable for printing. Among that, Guo et al. [45] prepared Fe-GaIn conductive ink with conductivity (1.53×10^6 S/m), forming multifunctional flexible electronics. Colorful LM-based hybrid materials used in printing electronics have also been reported in the previous work [48]. These materials combined GaIn and other metals and usually own high conductivity. However, the connection between them is not stable and the composites appear granuliform [49–51], which will affect the printing resolution and precision.

To reinforce the connection, non-metal materials are applied to form composite materials. Recently, through changing the rheological property, a recoverable LM paste (Ga-In-SiO_2, GIS) was prepared through mixing EGaIn and nonmetallic SiO_2 (quartz) particles (Figure 2(f)). It is proved that GIS has excellent conductivity (13 Ω/m) and printable properties [46]. While during the recovery process, acid or alkali solution was used, which is still not so safe. As known that the rheological properties change with surface tension, and surface tension change with the formation of surface oxide layer, which affecting LM stick to some substrate materials such as PVC, cloth, and paper [30,46,47]. For example, to reduce the surface tension, directly, Ou et al. [27] wrote partially oxidized liquid metals (POLMs) on cloth material, filling POLMs into fiber networks to form wearable, stretchable, and flexible electrically conductive elements. The result demonstrated that the electrical resistance of the prepared heating element is highly reliable (1.7 Ω) and endurable after 1000 cycles of deforming. Similarly, as illustrated in Figure 2(e) [20], to get better tumor treatment results under an alternating magnetic field (AMF), oxidized GaIn mixture (O-GaIn) was developed and printed, used as e-skin by Wang et al. [3]. And due to LM's favorable magnetothermal effects, it was used not only as e-skin but also the *in vivo* experiments on tumor bearing mice constructed as conformable bioelectrodes exhibited good effect on tumor therapy under AMF exposure. Even though it was a relatively complete experiment about this mixture, it was assumed that the conductivity and applicability should be enhanced by combining any other composites in the further work. Considering the conductivity of carbon and its derivatives, combined the advantages of LM with that of carbon nanotubes (CNT), Park et al. [52] introduced LM-based composites (CNT/LM) by uniformly dispersing Pt-decorated CNT in a LM matrix to be used as stretchable interconnection materials (Figure 2(g)). After well mixed, the CNT/LM composites can be 3D printed directly through a nozzle, getting high resolutions (5 μm), free-standing, wire-like 3D structures. Simultaneously, the printed composites owned high conductivity (3×10^6 S/m) and current density (3.5×10^{10} A/m^2), comparable to conventional metal interconnections (10^{10} A/m^2). Based on this, more applied research should be done toward next-generation electronics, such as graphene or carbon compounds. Additionally, no matter for wearable or implantable devices and so on, these LM composites, which are usually used in the uniaxial printing process, need additional encapsulation after printing LM to prevent the leakage of liquid metal. To avoid extra encapsulation, different materials should be mixed at the same time during printing. In this context, the coaxial printing method has been developed. As shown in Figure 2 (h), GaInSn was mixed with Fe/Ni, and then was printed from inner nozzle, with poly(ethylene glycol) (PEG) extruded from outer nozzle [53]. Through coaxial printing, LM could be modified by PEG without separate operation. By coaxial printing, LM and other hydrogels could be combined to form LM-hydrogel wire, which can be used in flexible devices. Owning to the good biocompatibility and stretch ability, the hydrogel based flexible electronic can be a direction for future research. However, due to the good fluidity and low viscosity, it is still an issue to transfer LM onto needed substate easily after printing. From another perspective, inspired by Ag as the laser-assisted direct ink to write planar and 3D metal architectures [54], LM could be transformed to fit for laser printing and reconfiguration.

As flexible conductor, the high density of LM is also an issue. For instance, stack compression between layers caused by high density of LM will happen during the process of 3D printing, affecting the printing accuracy and artistry. For wearable and implantable devices, the comfortable and portable capabilities are limited due to the high density of LM. To make LM circuit more precise and smaller in size, low density LM composites are explored. Among that, Peng et al. [47] built a hybrid metallic foam (Figure 3(a)) through *in-situ* foaming of LM and PU. During the process, LM was combined with polymers, such as diphenyl-methane-diisocyanate (MDI) and dichloromethane (DCM). And different LM volume fractions showed different density, porous structure and properties. This metal foam has high electrical conductivity (3.9×10^4 S/m) and unique properties of low density (ρ<1 g/cm^3). And because of its structural characteristics, it exhibits excellent elasticity and mechanical stability, and can maintain its characteristics after 1000 compression cycles. This porous and conductive foam opens a window in broad fields, such as printing, flexible electronics, wearable sensors and soft robotics, which should be further researched. Certainly, the properties could be improved by the further or other combination. And recently, based on LM, Liu's group [55] has proposed a new conceptual material with lightweight, which can be as light as water. As shown in Figure 3(b), a heart-shape glass bubbles (GB)-EGaIn (10 mL) stood on a leaf. In the article, EGaIn and GB were mixed, with light density (2.010–0.448 g/cm^3), excellent conformability and electric conductivity. And its stiffness varies under temperature regulation. The research on lightweight LM provides a new way of thinking, and expands the applications of LM in underwater devices. Obviously, some issues, such as the reaction mechanism between GB and EGaIn, precise conditions to maintain conductivity and lightweight, practical application of the composite materials, and other potential composites, deserve to be further explored.

2.3 Wettability changing for broaden applications

It is reported that, the wetting behavior of LM has selective wetting [3,27] and reactive wetting [30,56] approaches for the generation of liquid metal patterns, which relates to the contact phenomenon between LM and substrates. Furthermore, apart from forming more multifunctional composites, the wettability of LM on various substrates can be altered by the external energies such as electricity, magnetic field, thermal energy, or different materials (mostly metals) (Figure 3(d)–(f)), which could lower the surface tension without changing the conductivity and hence expanding the application of LM (such as electrically driven, magnetic heat treatment, and soft robotics) [28,57,58]. Recently, Wang et al. [58] investigated the wettability change of EGaIn due to applying direct-current (DC) polarities on copper (Cu) substrate in the 0.5 mol/L NaOH solution (Figure 3(c)). It is proved that with the reduction in the oxidized surface of LM, the wetting is improved when the Cu substrate was connected to cathode. This phenomenon will be benefit for the application of Ga-based LM in microelectronic devices and intelligent switch and so on. Further problems such as the electricity environment should be optimized. And now the conducting solutions are usually hydrochloric acid, sodium hydroxide and sodium chloride, so that more conducting solutions should be used to explore the possibility. Without NaOH, Chen et al. [56] observed LM ($Ga_{67}In_{21}Sn_{12}$) could realize self-growing serpentine locomotion related to the unbalanced surface tension caused by copper ions (Cu^{2+}) (Figure 3(f)). Inspired by the phenomenon, different solutions or ions should be further researched to explore more interesting phenomenon and expand the application of LM in bionic multifunctional robots. Similarly, exploiting magnetic

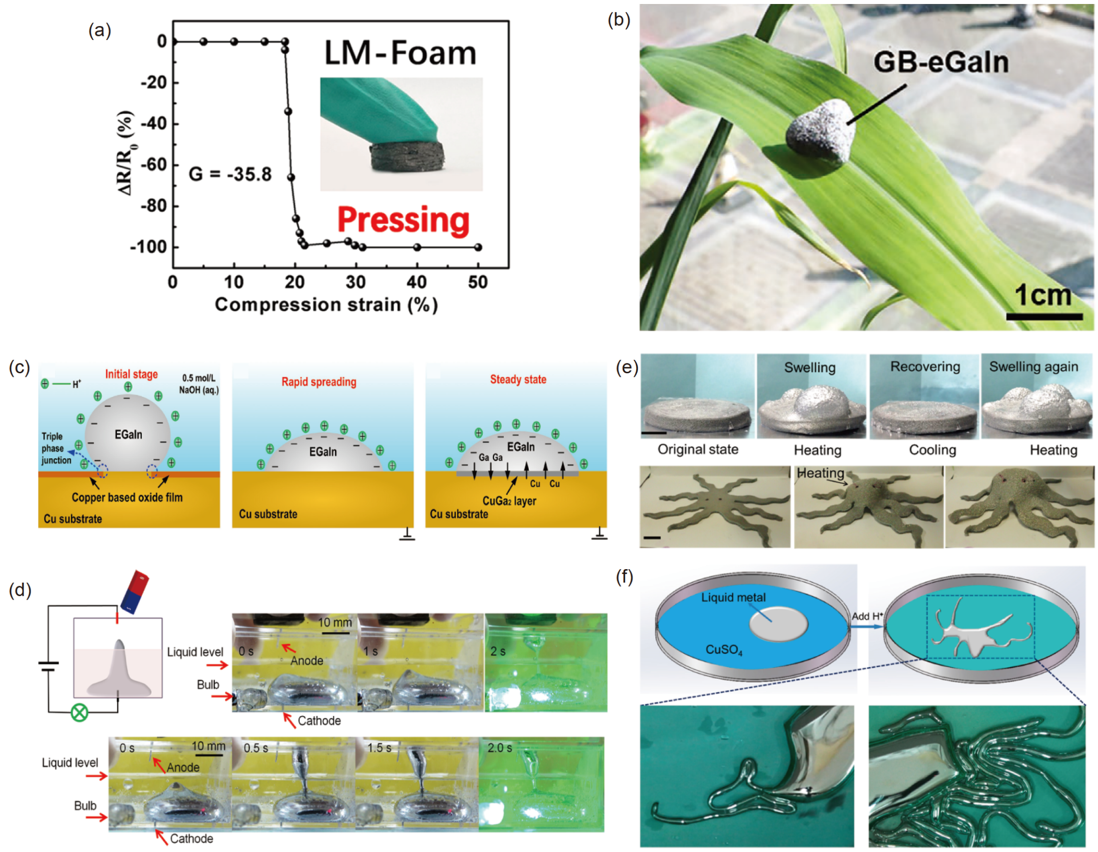

Figure 3 (Color online) (a) Schematic illustration of the *in situ* formation of LM-Foam-*x*. Reproduced with permission from ref. [47]. Copyright 2020, American Chemical Society. (b) A heart-shape GB-eGaIn standing on a crop leaf. The volume of GB-EGaIn is 10 mL. Reproduced with permission from ref. [55]. Copyright 2020, WILEY-VCH. (c) Schematic of the electrically induced wetting and spreading of EGaIn when the Cu surface was connected to cathode. Reproduced with permission from ref. [58]. Copyright 2019, Elsevier. (d) MLMD can stretch and move in the vertical direction. Reproduced with permission from ref. [29]. Copyright 2019, American Chemical Society. (e) A cylindrical shaped LMC is selectively heated and cooled along with swelling and contraction reversibly. LMC-made octopus transforms from a 2D shape to 3D shape. Reproduced with permission from ref. [57]. Copyright 2019, American Chemical Society. (f) Self-growing and serpentine locomotion of liquid metal induced by copper ions. Reproduced with permission from ref. [56]. Copyright 2018, American Chemical Society.

field, LM-based materials often applied in actuation and therapeutic bioengineering [29,59], as illustrated in Figure 3(d). Beyond that, through controlling heat reaction, Guo et al. [60] fabricated a $FeGa_3$ film by *in-situ* hot-reaction successfully between $Ga_{65}In_{22}Sn_{13}$ and T91 steel at 600°C. The film was characterized, with a thickness of 26.8±3.7 μm, the bonding force of 18.9±1.0 N and the micro-hardness of 7.63±0.31 GPa. Even though the reaction temperature is high, the research provides a technical support for some applications, such as protecting the steel, and magnetic robot. Park et al. [28] proved that the reconfigured 3D structures of LM can flow high current density (~10^{10} A/m^2), which is at the same order of magnitude compared to three traditional fragile and unstretchable metals (Au, Cu, and Ag). Combined the excellent conductivity and wettability on substrates, it will offer a promising strategy for highly integrated and flexible devices. The conductivity and density comparison can be summarily seen in Table 1.

In all, as conductive materials, gallium-based liquid metal or composites have many practical application problems that need to be solved. Several aspects should be focused. The first is to develop a simple and convenient manufacturing technology to prepare the composites owning high flexibility and good conductivity. Secondly, the inherent high surface tension of LM and the adhesion between LM and substrate should be further improved in the development of liquid metal-based multi-functional materials. Thirdly, the applications of multifunctional LM-based materials can be further extended in more areas, such as soft robot, reconfigurable antenna, and neural probe. Last but not the end, it is still worth exploring the mechanism of surface modification of LM with different kinds of materials, which is helpful to understand the principle of combination.

3 LM particles-based conductive materials

Metallic and carbon nanomaterial have been widely applied

Table 1 Conductivity and density comparison of different liquid metal composites

Composites	Conductivity	Density	Ref.
EGaIn	3.4×10^{6} S/m	>5 g/cm^3	[34]
EGaIn	5.3×10^{5}–1.1×10^{6} S/m	>5 g/cm^3	[13]
$Ga_{68.5}In_{21.5}Sn_{10}$	1.93×10^{6} S/m		[26]
EGaIn/Ag NW	<3.4×10^{6} S/m		[39]
Ag-LM	2×10^{6} S/m		[61]
O-GaIn	2.9453×10^{-7} Ω/m		[3]
POLMs/NLF	1.14×10^{5} S/m		[27]
EGaIn	10^{10} A/m^2		[28]
Ga-In-SiO_2	13 Ω/m		[46]
Fe-GaIn	1.53×10^{6} S/m		[45]
PVA-LMPs	3.75×10^{-1} S/m		[62]
PEGDA/EGaIn	~1–10^{7} Ω		[63]
PU@PMA@EGaIn	10^{5} S/m		[40]
PUS-PDMS-LM	10^{6} S/m		[36]
PUS-PDA-LM	4.78×10^{4} S/m		[64]
CNT/LM	3.3×10^{10} A/m^2		[52]
EGaIn/Cu/Cr	1.77×10^{-6} Ω/m		[44]
LM/ polyurethane	3.9×10^{4} S/m	<1 g/cm^3	[47]
GB-eGaIn		2.010–0.448 g/cm^3	[55]

in flexible electronics. As microparticles and nanoparticles overcome the rigidity of bulk metal and the surface tension of bulk liquid metals, film formation and patterning can be easier. The particular processes produce some nanostructures with both high conductivity and stretchability, such as carbon nanotubes coated on fabric [65,66], silver nanowires [67,68] and gold/silver nanostructures generated by reaction [69,70]. Nano-carbon is easily coated on the support but it naturally lacks of stretchability. Nano-carbon-based flexible devices rely on combination with other soft materials, but compared to liquid metal-based materials, their electrical conductivity is relatively low and their electrical conductivity drops significantly under applied strain.

Metallic particles as raw materials in fabricating flexible devices do not require complex synthesis and are convenient to manufacture. However, most dispersed metallic particles have poor or no conductivity. To achieve multi-functional electronic applications, metallic particles are sintered to make them coalesce. Moreover, metallic particles facilitate the formation of composite materials with other functional materials due to their micro-nano structures and the presence of oxide layers. In this section, the preparation and corresponding application methods of liquid metal conductive nanomaterials and their composite materials are mainly reviewed.

3.1 Preparations and applications of LM particles

Gallium-based liquid metals are emerging as conductive, flexible, and fluidic inorganic materials in various research fields. Compared with conventional micro-nano materials, micro- and nanoparticles of liquid metals have recently received particular attention because of their low toxicity in most cases [71–73] and accessibility in ambient conditions [74,75]. For biomedical purposes, liquid metals have shown applications in tumor therapy [73,76,77], neural connections [78], and imaging contrast agents [79]. The shape conversion and photothermal properties of liquid metal particles (LMPs) can be used as nanomachines for medical applications [71]. Simultaneously, the applications of LMP in thermal management [80], energy conversion [81,82] and catalysis [83] have developed rapidly in recent years, and LMP also has important value as a conductive material. Micro/nano-sized liquid metal particles can be produced in a controllable size by a bottom-up process such as physical deposition and thermal decomposition [84–87]. These methods usually require high temperature and vacuum. The more commonly used methods of making liquid metal nanodrops are top-down processes, such as sonication and shearing [88–93]. In top-down processes, surfactants such as thiols are usually used to overcome the high surface tension of liquid metal which drives adjacent droplets to combine [94]. This method is usually used to prepare sub-micron-level nanoparticles, and it is currently difficult to prepare smaller size LMNPs with uniform size and high yield. Figure 4 shows top-down and bottom-up synthetic approaches of micro/nano particles of liquid metal. In addition, LMs with different micro-nano structures can also be prepared, such as nanowires [71] prepared by template method and nanorods [95] prepared by ultrasonic-chemical method. This type of micro-nano structure liquid metal is expected to be applied to conductive and sensing composite materials based on the reported biomedical application potential due to its specific structure and shape.

3.2 Manufacturing circuits based on liquid metal particles

Liquid metal nanoparticles are semi-conductive due to the presence of the gallium oxide film on the surface. Sintering is an effective method to solve the problem that liquid metals are difficult to be patterned using conventional inkjet printing methods due to oxides and large surface tension. Various conventional metal sintering methods include thermal sintering [96], photonic sintering [97–99], plasmatic sintering [100], chemically sintering [101–103], and laser sintering [104]. For liquid metal particles, low pressures can be applied to LMNPs to rupture the Ga_2O_3 layers covering the surfaces and coalesce the particles at and below room temperature, which are termed as mechanical sintering. LMNPs can be mechanically sintered on large areas of entire deposits or locally to create traces of electrical connections within

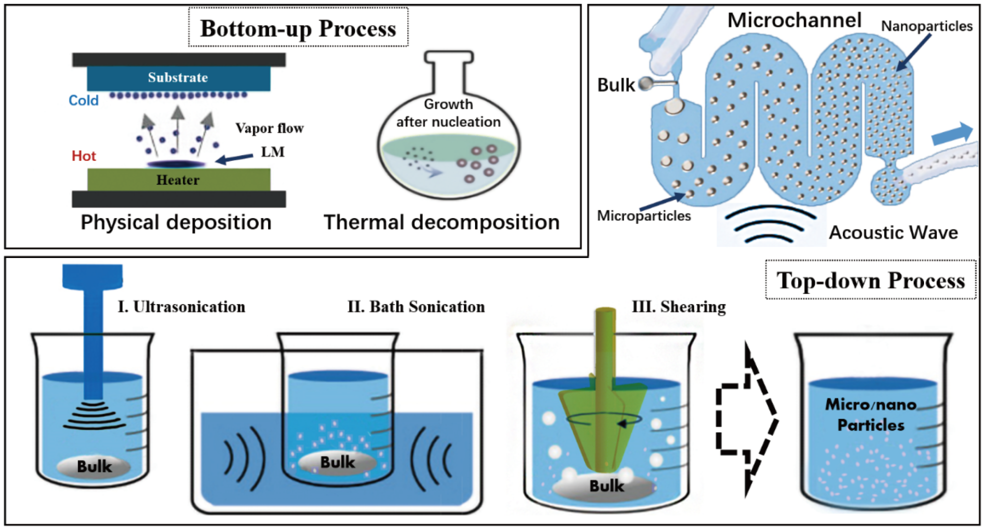

Figure 4 (Color online) Schematic of synthetic methods of liquid metal micro/nanoparticles.

deposits. Compared with other sintering methods, mechanical sintering does not require heating to facilitate the integration of liquid metals with other materials to produce functional devices as shown in Figure 5(a) [105].

As one of the most common examples for mechanical sintering process, LMNPs are embedded between two pieces of elastomer for the fabrication of flexible device. In the initial state, the electrically insulating composite material can be sintered into conductive traces by applying local mechanical pressure. The conductivity increased by a factor of ~4×10^8 after sintering (Figure 5(b)) [106]. In another example, Ren et al. [93] proposed a method to achieve the mechanical sintering of eutectic Gallium-Indium-Tin (EGaInSn) nanodroplets via direct printing and proved the superconductivity of the printed matter. Changing the compositions of Ga, In, and Sn in EGaInSn alloy can increase its superconducting critical temperature (T_c) to above the liquid helium critical point (4.2 K).

Flexible electronic devices based on mechanical sintering of LMNPs do not need to be constrained by surface tension like bulk liquid metals, which facilitates the production of circuits on more diverse substrates and demonstrates extremely high feasibility. For example, manufacturing paper-based liquid metal electronic devices is a viable solution for environmentally friendly electronic equipment. Liquid metal particles can be mechanically sintered into lines on paper. The narrowest line width of the liquid metal circuit on paper reaches 10 μm by controlling the sintering force. The used LM-paper circuit can be further recycled by sonication which can transform LM back into LMP suspension. The LMP suspension can be used to fabricate another circuit again (Figure 5(c)) [107]. Based on the mechanical sintering method, the LMNPs can be used for fabrication of various functional flexible and stretchable devices to meet the demands of different application scenario. A recent study reports a flexible skin with energy harvesting properties made of LMNPs conductive materials. The stretchable energy-harvesting tactile interface is based on triboelectric nanogenerator and is composed of a Galinstan nanoparticle film as a stretchable electrode and patterned PDMS as a friction and encapsulation layer. The device can provide excellent output performance and pressure sensitivity [108]. Apart from energy harvesting devices, the biomedical field also presents huge demands for flexible electronic devices based on liquid metals. Therefore, in order to produce a biocompatible conductive ink of liquid metal, Li et al. [109] encapsulated EGaIn nanodroplets into microgels of alginate, through aqueous ultrasonication. The microgel not only prompted the nanometerization and stability of EGaIn colloids but also improved their biocompatibility and wettability for multifunctional composite materials. Owing to its adhesion, the microgel-LM droplets could pattern on various substrates as coating layers and achieve a conductivity of 4.8×10^5 S/m through mechanically sintering, as shown in Figure 5(d). It is believed that in the future, there will be more research and applications of liquid metal with biological shell structure.

To improve the conductivity of LMP-based conductive materials, Zheng et al. [1] fabricated LMPs with a silver shell which exhibit better initial conductivity than LMPs covered with an oxide layer. The Ag-LMP structure is prepared by coating nano-Ag on the surface of LMP through *in situ* chemical reduction. The critical stress at which rigid Ag shells rupture can be controlled by adjusting the Ag shell thickness during the synthesis process, so that LM cores with low moduli can flow out, achieving self-repairing within 200 ms under external destruction. Due to the functional core-shell structure, the flexible circuits utilizing the LMPs

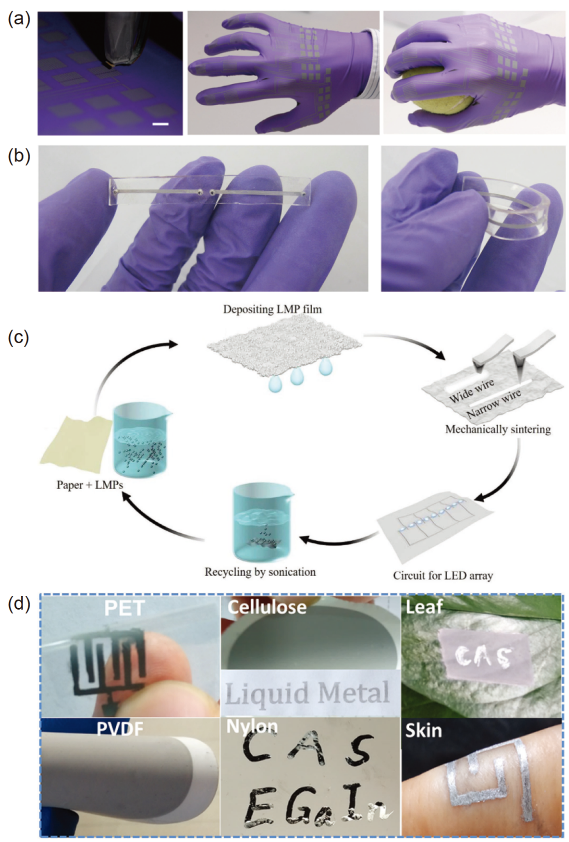

Figure 5 (Color online) (a) Photograph of inkjet system printing liquid metal nanoparticles dispersion and human hand wearing inkjet functionalized nitrile glove. Reproduced with permission from ref. [105]. Copyright 2015, WILEY-VCH. (b) Flexible antenna printed by EGaIn suspension (conductive lengths 15–25 mm). Reproduced with permission from ref. [106]. Copyright 2015, WILE-VCH. (c) Liquid metal circuits based on the reversible conversion from particles to wires are fabricated on paper using mechanical sintering and sonication. Reproduced with permission from ref. [107]. Copyright 2018, WILEY-VCH. (d) Pattern or coating EGaIn layer with alginate shells on different substrates. Reproduced with permission from ref. [109]. Copyright 2018, WILEY-VCH.

wrapped in a silver shell exhibit outstanding stability and durability (R/R_0<1.65 after 10000 bending cycles, and conductivity is maintained at 2.0×10^5 S/m) [1]. The sinterable electrically conductive functional shell structure is an effective way to achieve the stability and functionalization of LMP. In addition to the above-mentioned silver shell and polysaccharide microgel shell [109], the gold shell generated by the replacement reaction [110] and the shell formed by the coating of nano copper powder [111] is also functional application potential of flexible electronic devices.

The studies reported above that promote the electronic conduction of LMPs all use mechanical stimulation to destroy the outer shell of LM. Thermal sintering, laser sintering and evaporation-induced sintering are different methods to destroy the outer shell in order to achieve electrical connection. Heating can generate thermal stress to partially rupture the liquid metal oxide film to form a conductive path, and the oxide film crystallizes and conducts electricity as the temperature increases. In order to prevent the flexible substrate from being damaged by high temperature, the laser can replace heat as an energy source to generate local heat to achieve rapid sintering [112]. Laser sintering uses a pulsed laser source to rupture and ablate the oxide layer and coalesce LMNPs into a conductive film [35]. Using pulsed laser to convert liquid metal to solid-liquid composite phase is another method for making stretchable and stable circuit devices. When the solid-liquid LM patterns are under large tensions, the liquid phase conductive part could fill in the gap where the solid matrix opens, rendering the entire pattern conductive [113]. In addition, the colloidal suspension of EGaIn droplets containing bio-nanofibers can be sintered by evaporation at room temperature. Li et al. [114] showed that during evaporation-induced sintering process, the cellulose nanofibers generated a local pressure that was sufficient to destroy the encapsulating shell of LMNPs.

3.3 Synergy with other micro/nano structures

Liquid metal has the property of interacting with other metallic micro/nano structures to achieve better electrical conductivity. For example, due to its liquid nature, liquid metal particles act as anchor conductive fillers in nanosilver filled superelastic conductors [115]. Ag nanoparticles are directly mixed with LMNPs (without polymer) to make electrodes that can be self-healing repeatedly, and exhibit sufficiently high conductivity of 2×10^6 S/m [61]. A variety of flexible sensors can be made by combining a stretchable device with LMP bridged Ag flakes as a conductive circuit and different sensing active materials (graphite, Ag/AgCl, CNT, Ag_2O) [116]. Nickel nanoparticle-based flexible electronic equipment is similar to that of silver-based, and it also enhances the stable conductive performance in the stretched state due to the bridging of liquid metal in the liquid phase [117]. The platinum-coated LMP is used as a micro-nano motor, which can react with acid vapor at room temperature to micro-weld silver nanowires to construct electrical paths [118]. EGaIn can also assist the sintering of silver nanoparticles at room temperature that drastically improves the conductivity and mechanical deformability of Ag-based conductive ink circuits printed on temporary tattoo paper. Its conductivity is as high as 4.8×10^6 S/m. Compared with traditional sintering, this method forms a heterogeneous structure, the AgNPs interact with the LM to form AgNP-In-Ga clusters, and the periphery of which is surrounded by a Ga film [119].

3.4 Composite conductive material of liquid metal particles

For fabrication of flexible devices, soft or flexible materials such as elastomers, rubbers, polymers, gels and even fluids are necessary substrates either as substrates or as carrier to construct particle-based conductive materials. For liquid metal particles, several soft materials have been applied to prepare composite conductive materials.

Both liquid metals and hydrogels are conventional materials for use in flexible electronics. Due to their flexibility and compliance, LMs is mechanically compatible with hydrogels, and their excellent electrical mutual connection, thence hydrogels and LMs can be easily used in the on-demand manufacturing of patterned electrodes. Intrinsic self-healing of LM-hydrogel (LMH) can be easily achieved by its liquid properties via simply reconnecting the separated pieces. Furthermore, the hydrogel-LM composite electrodes have high sensitivity sensing performance [61,62,120,121]. For instance, a polyvinyl alcohol (PVA) hydrogel was reported to stabilize the liquid metal. The composite exhibited mechanically self-healing ability and excellent electrically (3.75×10^{-1} S/m) [62]. Shay et al. [122] demonstrated that the combination of hydrogel and EGaIn can produce completely flexible electrodes. The impedance of this LMH system can be tuned by chemically altering the hydrogel. These types of electrodes provide a conductive path that can be detected more safely without direct contact with the human skin, as shown in Figure 6(a). Park et al. [63] presented liquid metal hydrogels suitable for printable electrical conductors. This type of LMH is synthesized from EGaIn particles and polyethylene glycol diacrylate (PEGDA) hydrogel (Figure 6(b)). Controlled friction on the surface removes the PEGDA covered on the surface, thereby rupturing the oxide layer of the particles in the scratch area to achieve electrical connection. The surface is reconstructed as a droplet and the written circuit is eliminated when the LMH is hydrates and swells. LMH shows great potential in 2D and 3D printed circuit applications due to its unique internal structure and its multi-style application of electrodes. Choi et al. [123] demonstrated the composite materials made by filling 3D patterned hydrogel with liquid metal. The moisture protectant layer on the surface and the oxide layer of liquid metal can improve the lifetime and self-healing properties of the hydrogel. The hydrogel-liquid metal self-healing electrode composed of a photoresistor, a thermistor and a tilt switch has been successfully applied (Figure 6(c)). The electrodes made of a combination of liquid metal and hydrogel for bioelectrical signal (ECG, EMG, and electrodermal activity) detection perform as well as current commercial electrodes.

In addition, the liquid metal-gel system can also achieve both electrical conductivity and magnetic actuation by adding magnetic metal particles [124]. Furthermore, liquid metal hydrogel also has the capability to serve as transient epidermal sensors [62], strain-sensing materials [125] and asymmetric force-sensing materials [126]. The liquid metal hydrogel system presented heretofore has shown more sensory performance in the fields of tissue engineering, wearable devices, etc., rather than simply as a conductive material.

Other non-rigid materials similar to gels, such as elastomers [80,127,128] and polymers [129,130], can be combined with liquid metal particles to form advantageous materials for wearable electronic devices. Although a wearable device made of an elastomer material is flexible, it still needs to face such damage situations as being easily torn and punctured. Markvicka et al. [121] introduced a composite material composed of liquid metal particles suspended in a soft elastomer. When it is punctured, the internal particles rupture to establish new connections with the neighbors and the electrical signal is not interrupted (Figure 6(d)). This self-healing is caused by a phenomenon similar to mechanical sintering described previously in the case of shear damage. It is completely spontaneous and does not require other operations. Wang et al. [115,131] introduced a liquid metal polymer composite conductor with a unique electrical conduction mechanism that can be switched between an insulated state and a conductive state. The state switching process is controlled by temperature. As the temperature is reduced to 212 K, the resistance of the material drops by 10^9. After the temperature increases, the insulation is restored. The mechanism is that liquid metal droplets undergo phase change and expansion when cold, and when heated, they return to liquid state, shrink in volume, and are wrapped as an insulator. Furthermore, this conductor exhibits excellent tensile capacity up to 680% strain.

A recent liquid metal elastomer composite can also respond more accurately to external mechanical stimuli. Yun et al. [132] reported a magnetic EGaIn microdroplets-filled magnetorheological elastomer. This composite material can achieve a positive piezoconductivity similar to mechanical sintering. It reaches the maximum resistance in its original state, and its resistivity drops under mechanical deformation. The resistivity is also sensitive to magnetic field as the liquid metal droplets contain magnetic Fe and Ni nanoparticles. For Fe-containing elastomers, the resistance did not change significantly when the magnetic flux density was less than 40 mT. As the magnetic flux density continued to increase, the resistance change R/R_0 dropped sharply and reached 48.7% of its original value at 200 mT. Because the magnetic permeability of Ni is much lower than that of Fe, the Ni-containing elastomers are less magnetic influence. This type of composite has prospective applications in sensors, stretchable conductors, and responsive thermal interfaces, as shown in Figure 6(e).

Gallium-based liquid metals have been regarded as potential materials for forming heterojunctions due to their oxides to manufacture junction-based functional devices. Recently, it has been reported that due to the rich oxide of LMP, the gas sensor of LMP-based monoclinic Ga_2O_3 crystal has been manufactured [133]. Therefore, the vision of manufacturing junction-based functional devices may be

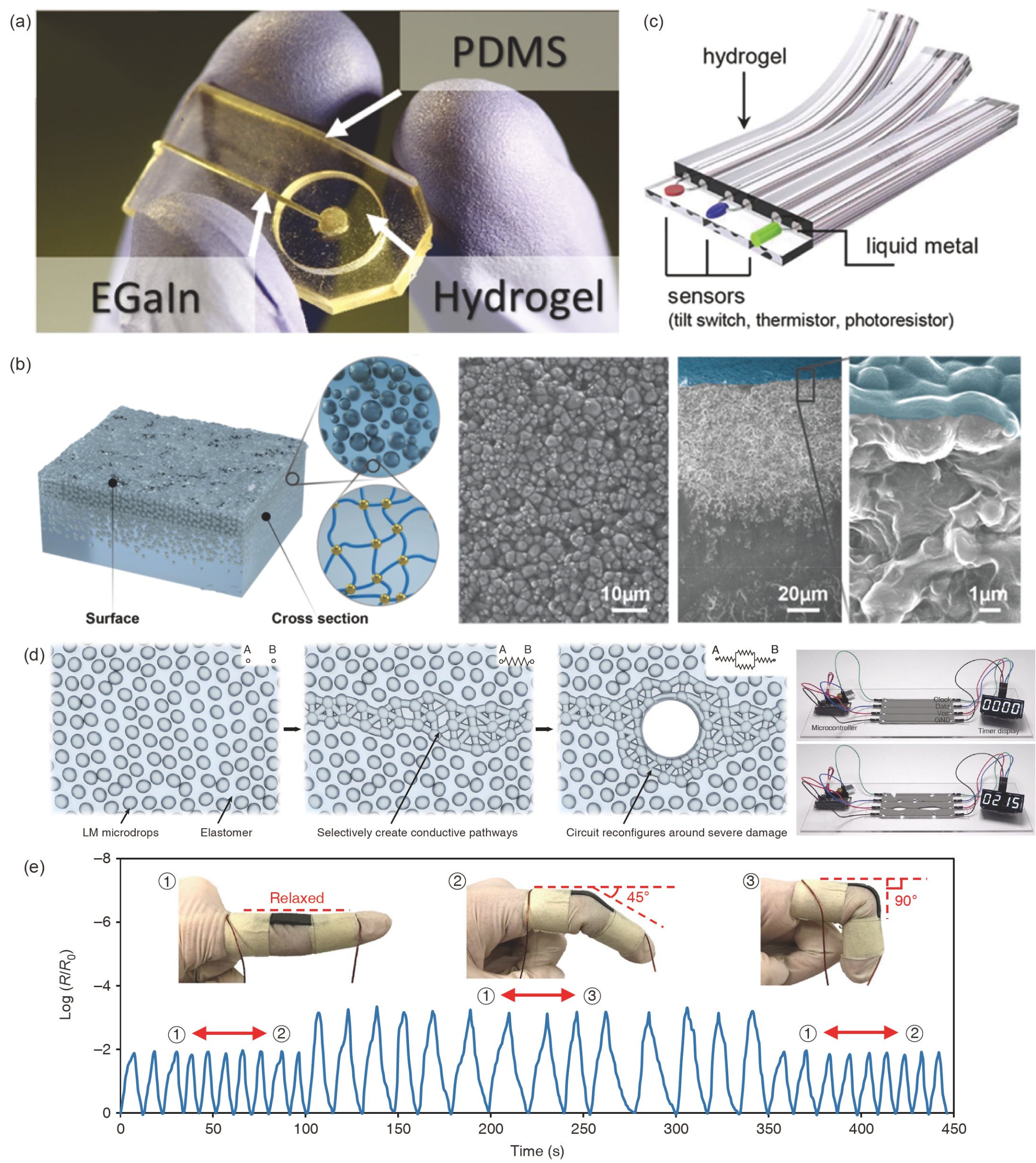

Figure 6 (Color online) (a) ECG electrode made of a combination of liquid metal and hydrogel. Reproduced with permission from ref. [122]. Copyright 2018, The Royal Society of Chemistry. (b) Schematic illustration and scanning electron microscopy (SEM) images of the liquid metal hydrogel. Reproduced with permission from ref. [63]. Copyright 2019, American Chemical Society. (c) Illustration of a customizable and self-healable hydrogel-liquid metal multimodular sensor system. Reproduced with permission from ref. [123]. Copyright 2020, American Chemical Society. (d) Schematic diagram of the self-healing mechanism of the LM-elastomer composites and a display diagram of the self-healing ability. Reproduced with permission from ref. [121]. Copyright 2018, Springer Nature. (e) Resistance changes of LMMRE under cyclic bending. The strip sample was attached to the index finger. Reproduced with permission from ref. [132]. Copyright 2019, The authors.

more realized in LMP-based research field.

Liquid metal particles are another type of micro/nano materials with potential for application in the manufacture of wearable electronic devices, flexible devices, and physiological signal sensors, other than nano-silver and nano-carbon. This part reveals that the flexible conductor produced using LMPs, like the modified liquid metal, avoids the surface tension of the liquid metal bulk which makes it difficult to pattern, and has good adhesion to the substrate. Flexible circuits based on LMPs that are coalesced using external stimuli are easy to produce on various substrates. Compared to liquid metal bulk materials, it is more stable, less leaky and easier to prepare. The conductive composite materials based on LMPs are made due to the better adhesion of the LMPs to the flexible substrate. Not only does it have good stretchability, but it also has excellent self-healing ability and biocompatibility compared to other nano-conductive materials, and it exhibits good sensing performance.

4 Summary and outlook

To sum up, the preparation and application of LM-based conductive materials in bulk and particulate-based materials were introduced. With excellent conductivity, flexibility, biosafety, fluidity and even small size effect, gallium-based liquid metal, as a rising star, is getting more and more attention. To realize the multi-functionalization, LMs are combined with polymers, other metals, and inorganics generally. On the one hand, in terms of bulk gallium-based materials, numerous researches have been focused on improving the electrical conductivity, adhesion and viscosity of liquid metals through doping, so as to facilitate subsequent application in printing, 3D printing and other new processing methods. It is of great significance for the development of flexible electronics, wearable sensors and soft robotics based on liquid metals. On the other hand, through bottom-up or top-down process, gallium-based particles can be combined to develop multifunctional response materials, which have important application value in manufacturing circuits, tumor therapy and micro/nano structures.

Although liquid metals have been sought after by more and more researchers in the past five years, the gap still exists between research and practical applications. There are still many unknown areas in the liquid metal research fields mentioned in this review, such as manufacturing technology, phase change application (considering the supercooling), surface and interface properties, and synthesis processes. New discoveries in these unknown areas in the future may expand the research of liquid metals, and will impact the field of flexible electronics research and even daily life. The outlook for future research is summarized as follows.

(1) Flexible circuit manufacturing. Among many conductive soft materials, liquid metal is a material with high conductivity and flexibility after molding. In addition, the most attractive element may be that liquid metal is a versatile supporter because of its wettability, adhesion and bonding. Therefore, with the rapid development of functional materials in the field of materials science, liquid metal-based conductive materials are bound to develop towards multifunctionality while improving manufacturing processes and exploring more characteristics of materials.

(2) Application and protection of oxidation. A large number of gallium oxide layers are naturally formed on the surface of LM. Gallium oxides not only cause small surface tension and good adhesion, but also are widely studied semiconductor materials and sensing materials. Based on the conductor-semiconductor structure and the good combination with more nano-silver and nano-carbon materials that are now commercially used, highly flexible sensor devices and functional devices based on LMNPs can be expected to be more widely studied and are expected to appear in electronic and medical devices in the next few years.

For bulk liquid metals and LMP, an oxide layer of appropriate thickness will allow LM-based materials to better perform various functions. However, as an easily oxidized metal, long-term tensile and compression deformation will inevitably cause excessive oxidation of LM. The conductivity of LM-based flexible devices containing more oxides is reduced, and this characteristic currently limits the practical application of liquid metals. Therefore, the use of non-oxidizable metals (Au, Ag, Pt, Ni, etc.) as shell-encapsulated LMPs and encapsulation with flexible materials may provide a feasible method for solving the long-term stability of flexible devices. The combination of bulk liquid metal and other metals is not easy to completely seal off the oxygen, which may not slow down or even increase the oxidation rate of liquid metal. Manufacturing reliable flexible devices for bulk liquid metal relies more on the characteristics of soft materials such as polymers and elastomers and the manufacturing processes and technologies.

(3) Biomedical applications. One of the main functions of flexible and wearable electronic equipment is to serve human physiology and health. At present, a large number of flexible devices with liquid metal combined with hydrogel, polymer, elastomer and other materials have been manufactured. These *in vitro* flexible devices and wearable devices implement many detection functions, such as detecting physiological electrical signals, motion status, body fluids, blood flow, and pulses. They show similar or even exceed the functional level of non-flexible electronic devices currently on the market. In the future, humans hope that devices based on the excellent performance of liquid metals can play a role in the body. This expectation requires better flexibility and biocompatibility of conductive materials, which may be achieved by making composite materials of liquid metal and organic materials or more precisely making light-weight and small-sized devices. The development in this direction will make liquid metal be applied more in implanted medical devices and provide help for the prevention and treatment of clinical diseases. With the development of research, gallium-based composites will show more and more possibilities and bring vitality to the applied fields.

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