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Recent progress in eutectic gallium indium (EGaIn): surface modification and applications

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In the field of stretchable electronics, eutectic gallium–indium alloys (EGaIn) have become an ideal conductive material due to their exceptional electrical conductivity and natural fluidity. However, high surface tension poses an obstacle to the widespread application of EGaIn. To cope with these challenges, a fundamental and comprehensive understanding of surface tension is required. This paper reviews research on the surface tension of EGaIn, covering (1) the principles of oxide layer formation, (2) factors influencing surface tension, and (3) methods for surface modification of liquid metals. This is followed by an introduction to the applications of EGaIn surface modification in different fields and concludes with a summary of the challenges still faced and an outlook for the future.

1. Introduction

Flexible electronics are becoming increasingly significant in the domains of wearable technology, electronic skin, intelligent robots, and biomedicine as current technology advances.[159,168] As opposed to traditional electronics, flexible electronics can adjust to various working situations and work well under a range of deformations (bending, folding, twisting, compression or stretching).[205] According to different deformations, flexible electronics can be classified into a variety of types and applications, such as bending electronics, foldable electronics, *etc.*,[192,210] where stretchable electronics occupy a significant place. Stretchable electronics are composed of stretchable substrates, stretchable conductive materials, sticky layers, and electronic devices, and researchers place a significant deal of focus on the requirement that stretchable conductive materials maintain strong electrical conductivity throughout the stretching process, since this is a very difficult aspect of the process that defines the overall performance of stretchy electronics. Metals, carbon-based materials, conductive polymers, and their composites are frequently used to create stretchy conductive materials.[1–3] Stretchable conductive materials come in three varieties. Stretching in structural terms is the first. Under normal circumstances, stretchable devices are unable to meet the demands of use because the majority of metals with excellent electrical conductivity, such as silver and copper, are solid at room temperature and lack stretching properties. Their electrical conductivity is also significantly reduced or even lost under vigorous stretching conditions.[4] Conducting materials without stretching capabilities can be treated to take on diverse forms, creating structures with certain stretching properties. For example, copper nanowires themselves do not have tensile properties, but after laser treatment they will form a grid structure that can be stretched and has good electrical conductivity.[213–215] Similarly, silver nanowires can form similar mesh structures that increase stretchability while retaining good electrical conductivity.[216–218] Furthermore, these mesh structures can also be applied to the field of flexible transparent electronics.[219–221] The second is the creation of composites using different polymers and conductive additives.[8–10] However, poor tensile characteristics, irregular filler distribution, and low mechanical strength are typical issues with single filler conductive composites.[183] Additionally, they are inappropriate for use. The third is that the material itself can be utilized in stretchy electronics without any further processing because it is stretchable and electrically conductive (liquid metals, for example). Gallium-based liquid metals as a promising material have a wide range of applications in flexible electronics and wearable electronics.[5] A liquid metal at room temperature presents the shape of a droplet, which makes the liquid metal maintain strong liquidity without affecting its electrical properties. For example, liquid metals can easily fill the microchannel and maintain a stable state.[6,7] However, liquid metals

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typically generate tiny droplets during processing, making fine-tuning shaping challenging, and after molding, they easily come together to create a short circuit. Also, when used as a wire, the resistance of the liquid metal increases as the stretching rate increases. Surface tension and these application barriers are closely related, which makes processing more challenging.[11] So reducing the surface tension of liquid metals becomes the focus of research.

In recent years, researchers have investigated various methods to reduce the surface tension of liquid metals, for example, removing the oxide layer with acidic or alkaline solution to increase surface tension and using an electric field to almost eliminate surface tension,[12] using ultrasonic or shear treatment to destroy the initial state of the oxide layer and generate a smaller new oxide layer to increase adhesion and rheology,[13] and adding additives such as PDMS,[14] sodium alginate,[15,16] TPU,[17] Ecoflex,[164] *etc.*, to reduce the surface tension *via* forming different chemical bonds with liquid metal surfaces. These methods can effectively reduce the surface tension of liquid metals. As shown in Fig. 1, since the first article on EGaIn in 2008,[6] EGaIn's surface tension related fields have been studied, and the number of studies has shown an increasing trend. In terms of research content, the research on surface tension is not only limited to theoretical research, but also includes the control methods of surface tension and the modification of EGaIn. Therefore, it is necessary to summarize the recent research.

This essay examines recent developments in liquid metal surface tension. There have been studies on surface tension and uses of liquid metals in the past,[174,177] but most of them focus on the measurement and regulation of surface tension and the corresponding applications, while ignoring the various factors that affect the surface tension. Surface tension is of great importance for many research fields. Reducing surface tension facilitates high-precision molding of metals, promotes wetting, and has value in flexible electronics. Secondly, regulating

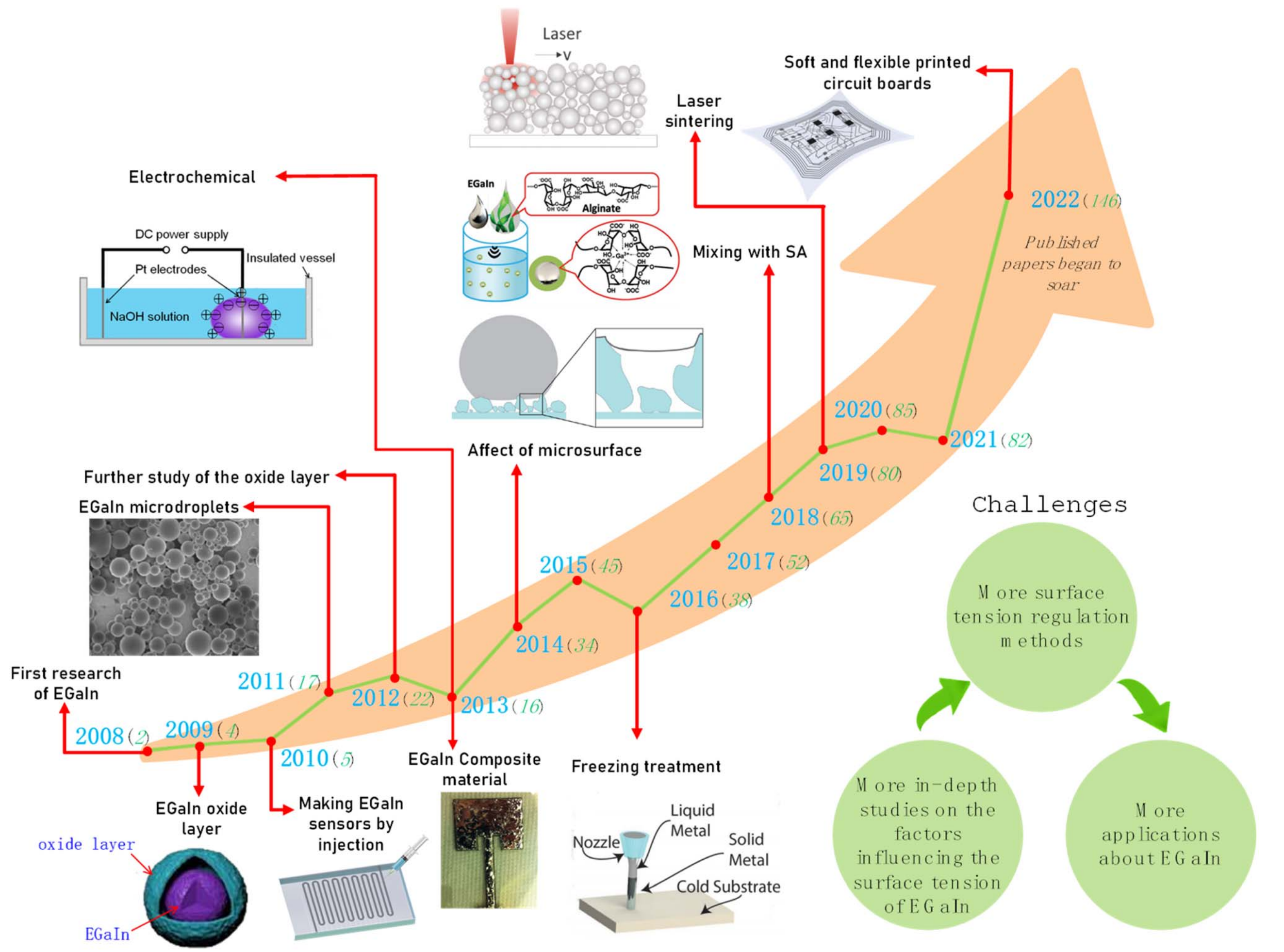

Fig. 1 The number of publications in different years and important studies, including 2008 (reprinted with permission from ref. 6. Copyright 2008, Wiley-VCH), 2009, 2010, and 2011 (reprinted with permission from ref. 190. Copyright 2011, American Chemical Society), 2012 and 2013 (reprinted with permission from ref. 54 and 191. Copyright 2014, Nature. Copyright 2013, AIP), 2014 (reprinted with permission from ref. 36. Copyright 2013, American Chemical Society), 2016 (reprinted with permission from ref. 91. Copyright 2016, Wiley-VCH), 2018 (reprinted with permission from ref. 16. Copyright 2018, Wiley-VCH), 2019 (reprinted with permission from ref. 94. Copyright 2019, Royal Society of Chemistry), and 2022 (reprinted with permission from ref. 85. Copyright 2022, Science).

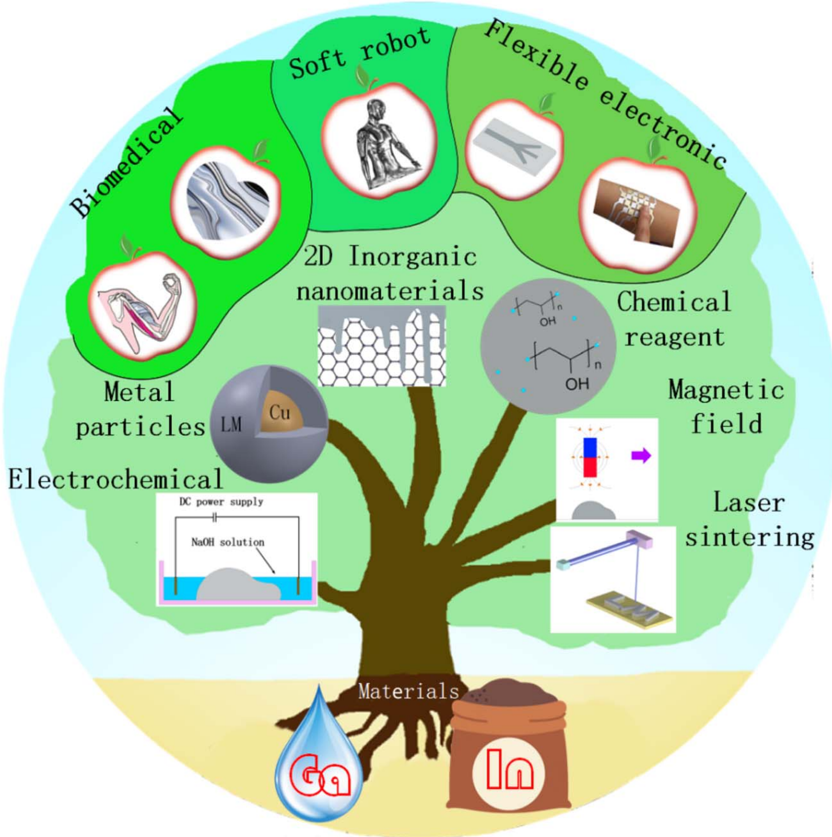

Fig. 2 The surface tension of liquid metals is controlled by electrochemical, additive and physical treatment methods and is used in the biological field, soft robotics and flexible electronics.

surface tension is of great importance in soft machines, actuators, *etc.* Finally, increasing surface tension, for example, can be useful in the release of drugs from the surface of small metal droplets. As such, the summary of the factors affecting the surface tension is very important to provide reference for future research. Fig. 2 illustrates how carefully studying the nature of liquid metals as a base is necessary. As a result, this paper first introduces the causes of the formation of a surface oxide layer and the principle of surface tension generation, and then lists the variables influencing the liquid metal's surface tension. After that, we summarize the research of modification methods based on the study of liquid metal properties, and then we summarize the most recent applications of modified liquid metals in the fields of tumor therapy, medical devices, wearable flexible electronics, and soft robots. Finally, we provide thoughts and prospects for the modification of liquid metals and optimization of processing methods.

2. Surface tension of liquid metals

One of the challenges faced by liquid metals in applications is surface tension, a characteristic of the material surface. Studying the surface tension behavior of liquid metals is particularly essential since surface tension is the energy source needed to change a material's surface area and also dictates the form and other properties of liquid metals at the free surface or interface.[18] Similar to most metals, the liquid metal's surface in air develops an oxide layer that encases the internal liquid phase portion,[19] enabling the liquid metal to cling to an uneven surface. The presence of the oxide layer has a significant impact on the subsequent processing of liquid metals because its structure is generally stable and challenging to break on flat surfaces, releasing the interior liquid phase component.[163]

Surface tension is tension that acts at the surface interface of a liquid due to an imbalance of molecular forces. At the demarcation between the liquid and the gas, an extremely small tensile force is generated due to the attractive forces between the molecules. Suppose a thin film layer exists on the surface of a liquid which is subjected to a tensile force at the surface, this force is surface tension. This film layer stops the flow of the liquid, making it less susceptible to breakage and also regulates the viscosity of the liquid. In the case of liquid metals, gallium combines with oxygen to create an oxide film, and as a result, the oxide layer plays a crucial role in the investigation of the surface tension of liquid metals.

2.1 Causes of oxidation layer formation

The term "liquid metal" describes a metal that exhibits a liquid state at ambient temperature and has a melting point below that. Common liquid metals include mercury, gallium, and others. The eutectic gallium-indium alloy (EGaIn) is a common liquid metal in the field of flexible electronics. At room

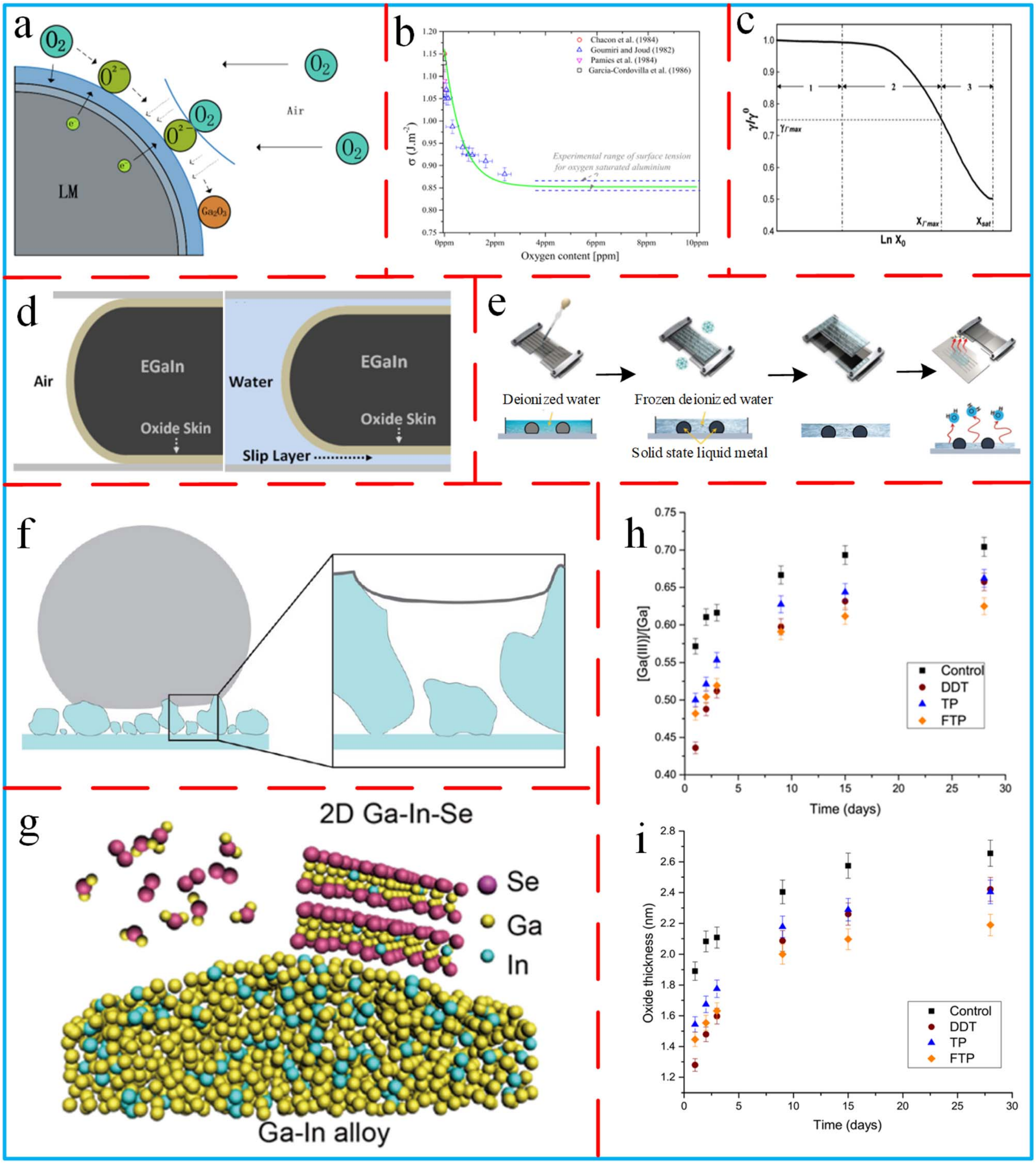

Fig. 3 (a) The principle of oxide film formation. (b) Prediction of oxygen content as a function of surface tension (reprinted with permission from ref. 30. Copyright 2019, Nature Research). (c) The relationship between air pressure and surface tension, where the air pressure increases at point 2 (reprinted with permission from ref. 31. Copyright 2010, Elsevier). (d) The state of the liquid metal in a dry microfluidic channel *versus* in a deionized water-treated microfluidic channel (reprinted with permission from ref. 32. Copyright 2014, American Chemical Society). (e) High-resolution liquid metal wire obtained by freezing and stretching operation (reprinted with permission from ref. 34. Copyright 2018, Wiley-VCH). (f) State of the liquid metal oxide layer on a rough surface (reprinted with permission from ref. 36. Copyright 2013, American Chemical Society). (g) Se atoms are embedded in the liquid metal surface (reprinted with permission from ref. 161. Copyright 2016, American Chemical Society). (h) Variation of gallium ion content after mercaptan treatment (reprinted with permission from ref. 44. Copyright 2017, American Chemical Society). (i) Variation of thickness of the oxide layer after mercaptan treatment (reprinted with permission from ref. 44. Copyright 2017, American Chemical Society).

temperature, the liquid metal is divided into an external oxide layer and an internal metal core. Due to gallium's ease in losing electrons, the liquid metal is oxidized to Ga^{3+} when exposed to air. The most stable form of gallium is the trivalent ion, and this gallium ion reacts with ambient oxygen to form a passivation film on the liquid metal's surface.[20] The formation process of the oxide film on the surface can be well described by the Cabrera–Mott oxidation model

$$1/x = A - B\ln t \tag{1}$$

where x is the oxide layer thickness at time t.[21] As shown in Fig. 3a, the liquid metal forms an initial thin oxide film with oxygen, which provides the basis for subsequent reactions. Further oxidation reaction is driven by ion transfer.[22–24] Due to the tunneling effect, electrons from the metal are transported over the thin oxide layer to the free side of the oxide layer, where they ionize the surface-attached oxygen. This mechanism creates an electrostatic potential between the oxidant-oxide and oxide-metal interfaces, and the cations are driven by the generated electric field to diffuse through the surface oxide layer, promoting growth. The established potential reduces the energy required for electron transfer, resulting in a high oxidation rate. As the oxide layer becomes thicker, the oxidation rate gradually decreases, and at a critical thickness the oxide growth process stops, and the well known passivation film is formed.[25]

Many academics have recently undertaken in-depth research on surface tension and are constantly putting out new theoretical frameworks. Initially, it was generally accepted that liquid metals have higher surface tension than nonmetallic liquids, and this high surface tension is caused by the characteristics of metals, which is also the foundation of electrical theory.[26] In the following development, the surface tension of liquid metals was satisfactorily characterized by R. Evans *et al.* who proposed a straightforward statistical mechanics theory based on the scanning ion pseudopotential model.[27] γ could be expressed in terms of the anisotropy of the stress tensor 0 in the surface. The researchers used the language of classical mechanics to apply the γ derivation process to metals. The mathematical model obtained can provide a useful check on the consistency of our formulation for the macroscopic stress tensor in terms of microscopic quantities. YIN *et al.* established surface reconfiguration theory on the basis of quantum mechanics, which provides a good explanation of surface tension in the category of classical mechanics theory with the surface elastic film model.[28] The molecules on the liquid's surface are subjected to a non-uniform force, unlike the molecules inside the liquid, and the combined force is expressed as a molecular force with the direction pointing inward. Therefore, the surface molecules have a tendency to shrink inward, and the liquid's surface layer acts like an elastic film encasing the interior under the combined action of forces in various directions. This is a specific description of the elastic film model. The surface tension of the liquid metal is about 624mN m^{-1}, the liquid metal produces an oxide layer, the intermolecular attraction drastically reduces since the created oxide molecules are not charged, and the surface tension falls to 350–365 mN m^{-1}.[29]

2.2 Influencing factors of surface tension

The factors that affect the nature of the oxide layer can also affect the surface tension of liquid metals. Numerous variables, including oxygen concentration and pressure, humidity, temperature, structure and type of contact surface, *etc.* all affect the surface tension of liquid metals. Recently, many reviews have summarized the influence of common factors such as temperature and oxygen content on the surface tension, while ignoring the influence of the structure and type of the contact surface, impurity elements and other factors on the surface tension. Therefore, it is necessary to fully study and summarize the influencing factors of liquid metals.

2.2.1 Oxygen concentration. The most significant pollutant of liquid metals is oxygen, and even relatively small concentrations of oxygen can affect surface tension. The surface tension of liquid metals is constant in the absence of oxygen, but it fluctuates constantly in the presence of various oxygen concentrations. Gheribi *et al.* have computationally obtained an equation that predicts the relationship between oxygen concentration and surface tension and have experimentally verified it by using liquid aluminum (Fig. 3b).[30] With the constant increase of oxygen concentration, the surface tension of the liquid metal is lower in the environment of high oxygen concentration for the same time. And as the oxygen concentration gradually increases, the surface tension shows different trends in different concentration ranges (Fig. 3c).

(1) Region 1 is the state when oxygen concentration is low, where oxygen concentration $X_0 \approx 0$ and surface tension is close to the surface tension of the liquid metal itself;

(2) Region 2 is the state when oxygen concentration gradually increases and approaches the maximum adsorption value. At this time $X_0 = X_{\mathrm{rmax}}$ and surface tension reaches γ_{rmax}, where $r_{\max}$ is the maximum adsorption value;

(3) In region 3, the oxygen concentration is greater than the maximum adsorption value and reaches the saturation value. At this time, $X_0 = X_{\mathrm{SAT}}$ and the surface tension reaches γ_{SAT}.

In an environment with low oxygen content, there is a linear relationship between surface tension and oxygen concentration. With the increase of oxygen content, the atoms on the liquid metal surface gradually begin to react with oxygen, because this is related to the segregation capacity of the liquid metal. When the oxygen concentration reaches the maximum adsorption value, the liquid metal surface also reaches the maximum saturation. At this time, the reaction between the liquid metal and oxygen reaches its peak, so the surface tension decreases linearly when the oxygen concentration continues to increase, and only when the surface tension reaches its lowest point and the oxygen concentration reaches its saturation value does the process come to an end.[31] Similarly, there is a positive correlation between the thickness of the oxide layer and the oxygen content. When the oxygen content on the surface of EGaIn is low, the oxidation reaction rate is slow and the thickness of the oxide layer is thin. This is because the reaction rate of oxygen and the metal surface depends on the adsorption rate of oxygen molecules on the metal surface, and when the oxygen content is low, the adsorption rate of oxygen molecules is low, so the thickness of the oxide layer is thinner. In contrast, when the oxygen content on the surface of EGaIn is higher, the oxidation rate is faster and the thickness of the oxide layer is thicker. High oxygen content will increase the adsorption rate of oxygen molecules on the metal surface, thus accelerating the oxidation reaction, resulting in an increase in the thickness of the oxide layer.

2.2.2 Humidity. The formation process of the oxide layer under wet conditions is different from that in pure oxygen.[165] The modulus of the liquid metal in the microchannel falls by an order of magnitude under wet conditions, and the adhesion of the liquid metal also decreases. On the pristine surface, the adhesion of the oxide layer is very high, and moving the liquid metal will lead to the rupture of the oxide film. However, the liquid metal will slide freely on the substrate treated with deionized water and will not adhere to the substrate (Fig. 3d).[32] The composition of the oxide film has changed, which has caused a change in the mechanical properties. Analysis of the oxide layer with XPS revealed that in the presence of water the composition of the oxide becomes a gel complex of gallium oxide mono-hydroxides (GaOOH).[32] The mechanism of water changing the composition of the surface oxide layer is divided into two parts. First, when there is water present, gallium ions go from the liquid metal to deionized water. The second part is gallium ions enter water where they create hexahydrate species.

$$[Ga(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Ga(H_2O)_5OH]^{2+} + H_3O^+ \tag{2}$$

Water and oxygen compete for space on the metal surface when it is exposed to moisture, resulting in the formation of oxides. The reaction of the oxides with water gradually takes control, and the reaction of Ga_2O_3 with oxygen also continues to occur over time.

$$2Ga_2O_3 + 2H_2O \rightarrow 4GaOOH \tag{3}$$

In the presence of 1Torr water vapor, the peak-area ratio of Ga_2O_3 is 60%, which is lower than that of Ga_2O_3 pure oxygen, proving that the reaction between water and the oxide layer changes the original proportion. However, when the content of water reaches a certain degree, the composition of the oxide layer will not change. The initial reaction conditions of the liquid metal and water vapor are much higher than those of pure oxygen. When the lowest pressure is 10^{-6}Torr, oxygen reacts significantly with the liquid metal, while water vapor still does not react at 10^{-4}Torr. This difference in the pressure threshold reflects the different reaction mechanisms of water vapor and oxygen. Under the conditions of low pressure, water exists in the form of an adsorbed monomer on the surface of the liquid metal and does not react with Ga. With the increase of pressure, the monomer gradually turns into a dimer or larger aggregates, leading to the start of an interface reaction and the formation of an oxide film.[33] After the liquid metal was immersed in water for a period of time, the thickness of the oxide layer visually increased, and the subsequent elliptic measurements also confirmed this idea. This phenomenon also proves that the chemical change of the liquid metal oxide layer in water is the cause of the weakening of the oxide layer.

Humidity affects the surface tension by changing the composition of the surface oxide layer. The change of composition also significantly changes the thickness of the oxide layer. When the humidity is higher, the formation of the oxide layer is faster, and the GaOOH content on the surface is larger, so the thickness is larger than that in the environment with lower humidity. Although the influence is relatively small compared with other factors, the humidity factor is particularly important in the control of liquid metal microfluidics. Controlling the humidity in microfluidics can make the liquid metal move more easily, so the humidity factor is a very important influencing factor.

2.2.3 Temperature. When the temperature increases, the molecular thermal motion intensifies, the average kinetic energy increases, the intermolecular attraction decreases, and the surface molecular density decreases. The increase in thermal motion and the decrease in intermolecular force are macroscopically manifested by the decrease in surface tension due to the increase in temperature. At the same time, the thickness of the oxide layer increases. The empirical formula is often used to calculate surface tension:

$$\gamma = \gamma_0(1 - bT) \tag{4}$$

where T is the absolute temperature, γ_0 can be regarded as the surface tension at absolute zero, and b is a constant that varies with the system and its value is related to the critical temperature of the material. The mobility of the liquid metal steadily decreases when the temperature is dropped, and processing the frozen liquid metal eases shaping. This also gives an idea for the production of high resolution patterns in liquid metals. Kim *et al.* froze a liquid metal and then stretched it, and after stretching, the mobility of the liquid metal was restored by heating, and they succeeded in forming a refined pattern on the substrate, reducing the line width to 10 μm.[34] This method does not require complex operations, and only freezing, stretching and heating are needed to obtain the target line width pattern, and the resulting line width is reduced by 60 times compared to the initial size (Fig. 3e). Compared with the traditional technology, the frozen processing has the advantages of simple operation, less residue and so on, effectively reduce the processing difficulty caused by the surface tension, make full use of the advantages of fluidity, through the mold to make any pattern,[35] and it is possible to obtain high resolution patterns without modifying the liquid metal.

The temperature has a great influence on the surface tension of liquid metals, which is also the most common influencing factor. However, in the processing of liquid metals, the influence of temperature is often ignored, because it is difficult to precisely control the surface tension by temperature, and there are few relevant research studies. Next, the research on temperature factors can be deepened to establish an accurate theoretical model, which can explain and predict the state and surface tension of liquid metals at different temperatures. Additionally, research can go on to find new ways to accurately manage liquid metals by altering temperature, offering a new answer for the use of liquid metals on a wide scale.

2.2.4 Roughness and type of contact surface. The surface interface behavior of liquid metals is different from that of ordinary liquids. The surface oxide covers the inner metal, and its shape is determined by the oxide layer on the surface. The state of the oxide layer determines the surface properties of liquid metals. Different contact surfaces have varying effects on the surface oxidation layer when a liquid metal comes in contact with other substances. Among the various properties of the contact surface, the roughness of the contact surface and the type of the contact surface have a great influence on the surface tension, which all affect the wettability of the liquid metal on the contact surface.

In the case of the same material, the contact angle of the liquid metal becomes smaller on the substrate with a smooth surface, and the wettability is better, while the wettability is worse on the substrate with a rough surface, and even repulsion occurs, and this phenomenon is caused by the oxide layer (Fig. 3f).[36] The surface oxide layer is capable of contacting the protrusions and wrapping around the interior to form a stable structure when in contact with a rough surface. This oxide layer can resist the surface tension up to 0.5 N m^{-1}, so it is difficult for the rough surface to destroy the oxide layer, and also proves that the magnitude of surface tension is also related to the roughness of the contact surface.

The state exhibited by the liquid metal varies with the type of contact surface, the wettability of the liquid metal on different planes is represented by the contact angle, and the larger the contact angle is, the worse the wettability of liquid metal is. The difference between the surface energy of the liquid metal and the contact surface leads to different wettability. When the surface energy of the liquid metal is higher than the surface energy of the contact surface material, it is not wettable (showing a droplet shape); however, when the surface energy of the liquid metal is lower than the surface energy of the contact surface, the wettability is very strong, and the contact angle of the liquid metal on these materials decreases, and the contact area with the material increases. The wettability of the liquid metal on metals with higher surface energy (E) such as copper ($E = 1.44$ J m^{-2}), nickel ($E = 2.22$ J m^{-2}), and iron ($E = 2.50$ J m^{-2}) is better than that of other materials.[37] At the same time, the better the wettability, the better the adhesion to the substrate, the wettability can be measured from the wetting tension F

$$F = \gamma_{LV} \cos \theta \tag{5}$$

where θ is the contact angle, and it can be seen that the better the wettability, the better the adhesion to the substrate. Johnston *et al.* made use of the strong wettability of a liquid metal on gold to reduce its fluidity, so that the liquid metal formed a fixed shape, realized accurate printing, and reduced the cost.[38]

The influence of the contact surface on the liquid metal is mainly reflected in the influence on the oxide layer and the wettability on different surfaces, and it has a great impact on the mixing of liquid metals and other materials as well as the high resolution printing of liquid metals on different substrates. Moreover, the specific value of the surface energy of EGaIn has not been measured or calculated, which makes it difficult to judge the wettability.

2.2.5 Impurity elements. From the microscopic point of view, the interatomic attraction on the surface is the cause of surface tension, while adding other elements can weaken the interatomic attraction, reduce the surface tension and reduce the surface energy. Elements with very small atomic volume, such as O, N, S, *etc.*, easily enter the atomic gap in liquid metals and be pushed out to the metal surface and aggregate on the surface, becoming active substances enriched on the surface. Due to the few free electrons of these elements, the surface tension is small, which can effectively reduce the surface tension of liquid metals. There are many ways to dope elements in liquid metals, such as chemical vapor deposition,[39,40] electrodeposition,[41] and self-deposition.[42] As shown in Fig. 3g, selenium atoms are embedded between liquid metal atomic layers by vapor deposition, weakening the connection between different atomic layers. Usually, 2D materials such as graphene have very low solubility in liquid metals; however, the thermal motion of liquid metal atoms allows carbon atoms to embed. During the cooling process, the atoms are arranged in a periodic structure, and the escape of carbon atoms is blocked.[43,161] Therefore, after embedding graphene, the molecular forces between liquid metal molecules are weakened and the surface tension is reduced.

In addition to the embedding of impurity atoms, the introduction of impurity functional groups on the surface of liquid metals is also a method. As shown in Fig. 3h and i after adding mercaptan to the surface of liquid metals through solution treatment, the content of gallium on the surface of liquid metals decreases, proving that mercaptan treated liquid metals can effectively reduce the growth rate and thickness of the oxide layer. After the treatment, mercaptan and metal compete for the position of the surface, which changes the chemical composition of the surface and changes the process of oxygen adsorption. The mercaptan on the surface can remove or transfer electrons to the metal surface according to the dipole direction, which increases the distance between oxygen and the liquid metal surface, making the formation of an oxide film more difficult. At the same time, the thickness of the oxide film is controlled by changing the metal work function, thus changing the surface tension.[44]

The influence of impurity elements on the surface tension of the liquid metal is realized by introducing other elements on the surface of the liquid metal. These impurity atoms are embedded between the liquid metal atoms by different methods, weakening the attraction between the atoms. Therefore, embedding impurity atoms in liquid metals can greatly reduce the surface tension, which is one of the future research directions.

2.2.6 Pressure. Compared with the influence of oxygen concentration in the environment on the surface tension, pressure also has a great influence on the surface tension. However, the principle of changing pressure and oxygen concentration is to increase the partial pressure of oxygen on the liquid metal surface, which has a similar effect on the surface tension. And changes in pressure also bring about changes in the temperature coefficient, so this knock-on effect makes the measurements inaccurate. At present, due to different reasons, the factor of pressure has not been studied separately. In many studies, it exists in the form of partial pressure of oxygen.

3. Methods to reduce surface tension

Surface tension has been one of the obstacles in the application of liquid metals. Excessive surface tension makes EGaIn wires less stable, and the intersection of wires is prone to aggregation when stimulated by the outside world, and EGaIn will gather together to form a large droplet, resulting in the destruction of the original structure. Secondly, the existence of surface tension makes many processing methods such as screen printing inapplicable to EGaIn, which poses a greater challenge to the application of EGaIn.

The reduction of surface tension expands the application scenarios of liquid metals (Fig. 4), such as soft robots, artificial organs, the preparation of composite conductive materials, *etc.* At present, the methods to reduce liquid metals mainly include electrochemical methods, additive methods and physical methods. The surface tension can be easily adjusted by changing the voltage in the electric field, but this method is more demanding for environmental conditions and requires the liquid metal to be immersed in an acid or alkali. The additive method is the easiest way to change the surface tension, and the properties of composite materials vary with the mixed materials. In the process of mixing, different chemical bonds are formed between materials and liquid metals, and the effect of an external force is achieved to reduce the surface tension; however, it is not an easy thing to choose the right material among many materials. Physical methods include many modifications, such as changes in temperature affecting the attraction between atoms; the magnetic field breaks the original force balance between atoms and also changes the surface tension. Current methods to change surface tension have certain advantages and disadvantages, so it is necessary to review and summarize these methods in order to find more effective modification methods.[45]

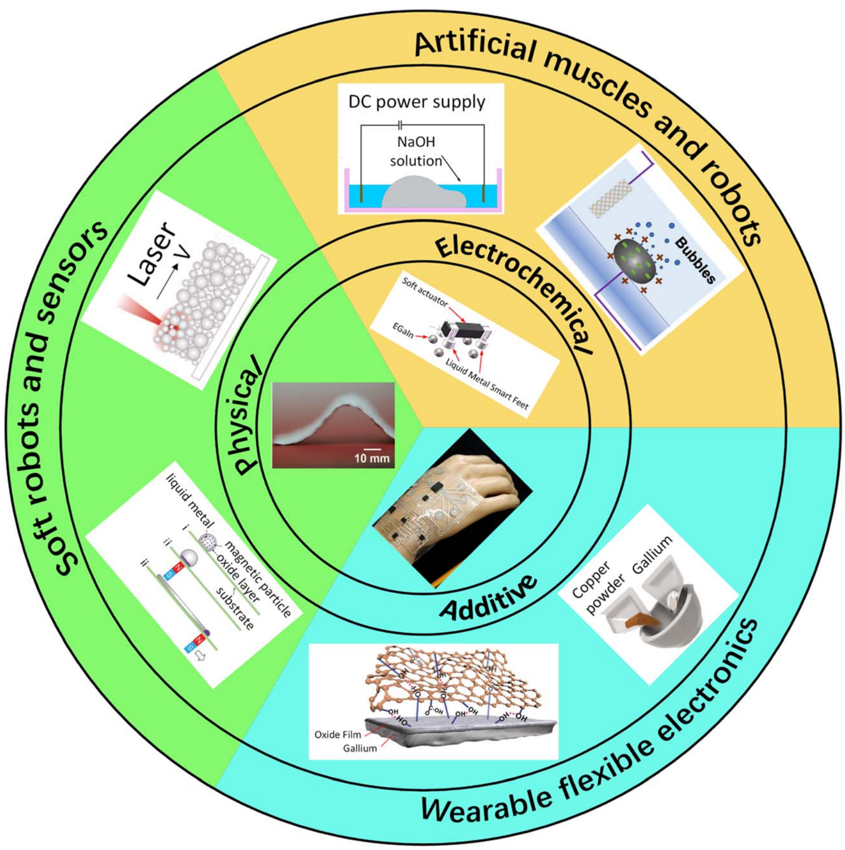

Fig. 4 The modification of liquid metals requires electrochemical (reprinted with permission from ref. 48. Copyright 2021, Wiley-VCH), additive (reprinted with permission from ref. 66 and 76. Copyright 2020, American Chemical Society. Copyright 2021, Wiley-VCH.), and physical methods (reprinted with permission from ref. 94 and 96. Copyright 2019, Royal Society of Chemistry. Copyright 2019, Wiley-VCH.), which have different modification effects and applications, including soft robots and sensors (reprinted with permission from ref. 139. Copyright 2020, Wiley-VCH), artificial muscles and robots (reprinted with permission from ref. 136. Copyright 2021, American Chemical Society), and wearable flexible electronics.

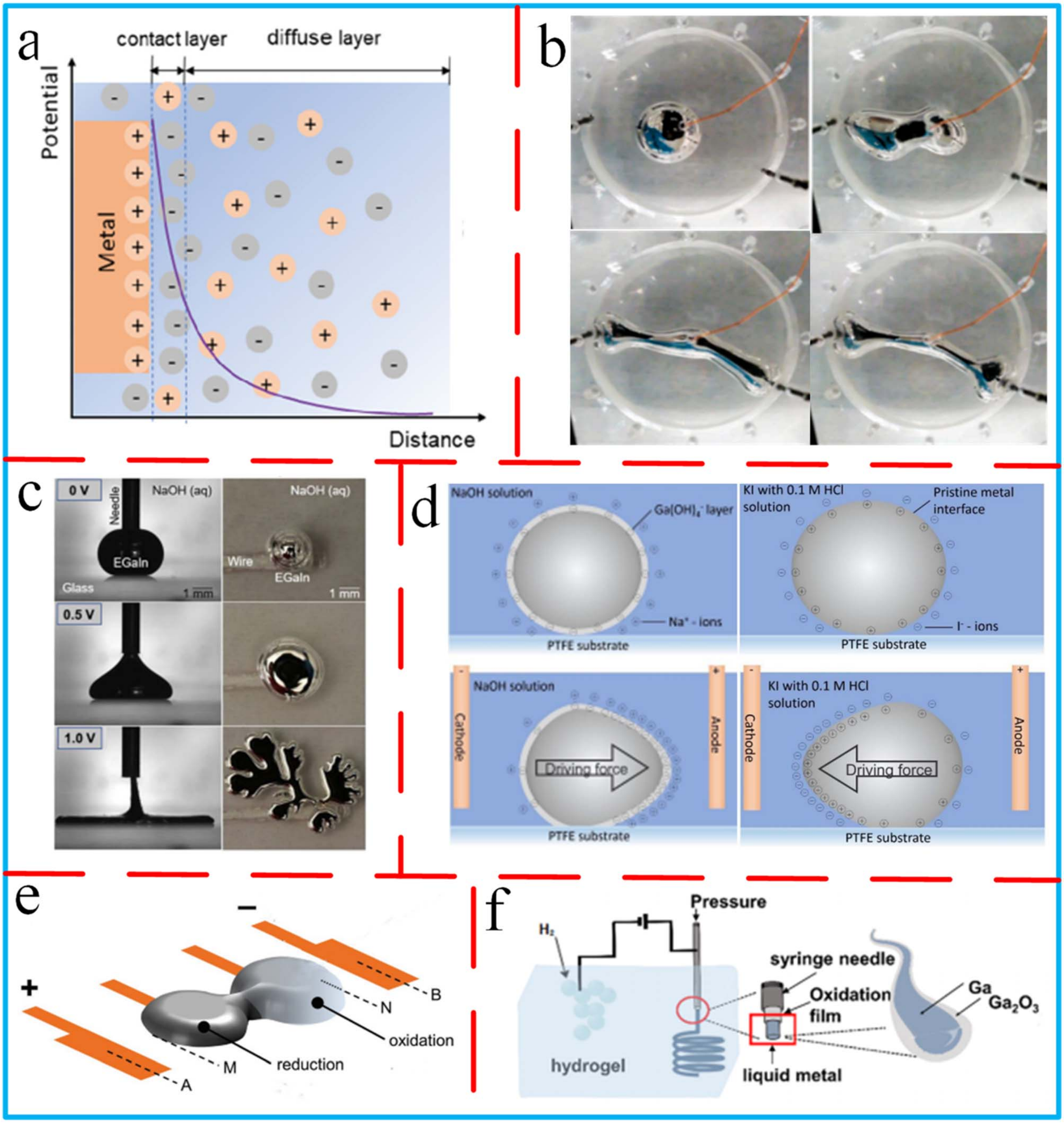

Fig. 5 (a) A bilayer model explaining the interfacial behavior (reprinted with permission from ref. 47. Copyright 2021, Wiley-VCH). (b) Liquid metal changing flow direction with the movement of electrodes (reprinted with permission from ref. 58. Copyright 2019, MDPI). (c) Liquid metal changing state with the change of voltage (reprinted with permission from ref. 189. Copyright 2014, PNAS). (d) Principle of electric actuation of the liquid metal under acidic as well as alkaline conditions (reprinted with permission from ref. 52. Copyright 2018, American Chemical Society). (e) Switching function using electrochemical control of the liquid metal (reprinted with permission from ref. 56. Copyright 2017, Wiley-VCH). (f) Electrochemical squeezing using the capillary effect with its own gravity (reprinted with permission from ref. 60. Copyright 2020, American Chemical Society).

3.1 Electrochemistry

It is a common method to change the surface tension of liquid metals by an electrochemical method.[196] Liquid metals will produce an "electrochemical capillarity effect" in the electric field. Compared with other methods, the electrochemical method only needs little energy to realize the rapid control of the surface tension and has no requirement on the performance of the substrate, which can be widely used in soft robots and other fields. When the liquid metal is in the electrolyte, different types of charges in the electrolyte accumulate in the interfacial layer between the droplet and the electrolyte. At present, the classical model used to explain the electric phenomenon of the interface behavior is the electric double layer model (Fig. 5a). When the power is switched on, the electrode exerts an electric potential to attract the counter ions from the surrounding electrolyte solution to the interface surface of the electrolyte side. The attracted counter ions strengthen the electric double layer of the electrolyte and metal interface and play the role of a capacitor, the atoms on the liquid metal surface are subjected to an outward force,[46,47] while the interatomic force is inward, and the two forces oppose each other, thus reducing surface tension.[48] But in order to prevent the Faraday reaction, only the lowest potential can be applied to the metal, which limits the ability to reduce surface tension.[49]

After being connected to a power supply, the electrowettability of the liquid metal can be enhanced. The liquid metal shows a droplet shape on the plane, but when it is in an electric field, its shape will change with the change of the direction of the electric field and the voltage (Fig. 5b and c).[50,51] There are various options for electrolyte selection during electrochemical control. Both acidic and alkaline electrolytes can remove the surface oxide film. As shown in Fig. 5d, electricity in both acids and bases can cause liquid metals to move; however, compared with alkaline conditions, the voltage required for electrochemical control in an acidic medium is lower, and the acid concentration required is also lower.[52,53] When sufficient voltage and electrolyte concentration are reached, the liquid metal can undergo a reverse shape change, that is, from a spreading state to a droplet.[54] The use of electrochemical control of surface tension to increase the wettability for the application of liquid metals provides a good choice, by controlling the contraction and stretching of liquid metals to make the air vibrate to produce sound, to achieve the role of sound.[55]

Furthermore, the surface tension can be altered by two electrodes that are not directly in contact with the liquid metal, known as two-electrode chemistry. Different from the traditional single electrode, under the action of two electrodes, the anode and cathode of the liquid metal droplet undergo oxidation and reduction, respectively, which changes the balance of surface tension and forms a surface tension gradient, making the droplet tend to separate. When the droplets are reoxidized, the surface tension returns to equilibrium and the droplets gather together again (Fig. 5e).[56] This two-electrode driven method of controlling the separation of liquid metals combined with single electrode manipulation of liquid metals enables programmable circuits and is a catalyst for the future of liquid metal microfluidics.

When printing a liquid metal, the liquid metal is squeezed out of the nozzle by pressure. However, in the microflow channel, the surface oxidation layer of the liquid metal will adhere to the inner wall, making it very difficult for the liquid metal to move in the microflow channel. Changing the roughness of the inner wall of the microchannel to reduce the adhesion of the oxide layer is an effective method, but this method is very difficult to process and has limitations on the material, so it is not easy to achieve. Another method is to remove the oxide film by acidic or alkaline treatment to eliminate the adhesion of the oxide layer to the inner wall of the micropassage, but this method lacks control, and it is difficult to control the extrusion speed of the liquid metal during printing and may damage the nozzle material.[57] The electric drive method can effectively avoid the above disadvantages and realize the movement of the liquid metal in the microchannel. In the electrochemical control of the flow of the liquid metal, if the relative position of the electrode is changed, the flow direction of the liquid metal will also change and always move towards the direction of the electrode. Therefore, the movement of the liquid metal can be accurately controlled through the regulation of the voltage and electrode position.[58,59] The chemical potential applied to the liquid metal in the microchannel can eliminate the surface oxide layer, and the liquid metal will be subjected to capillary action in the absence of the oxide layer. Under the action of voltage, the surface tension of the liquid metal decreases, and it can move along the microchannel. The application of the drive mode in the microchannel to the electrochemical extrusion of the liquid metal provides a possibility for 3D printing of the liquid metal by changing the surface tension of the liquid metal in the electrolyte and extruding it using the capillary effect and its own gravity (Fig. 5f).[60]

Electrochemistry is a widely used method to control surface tension. It can drive liquid metals by electric fields that change the charge distribution between the surface of the liquid metal and the solution. And this modification does not affect the electrical conductivity of the liquid metal, and the liquid metal can play its advantages of high electrical conductivity in the process of application. However, this method requires an external power supply and solution environment, which makes it more complicated than other modification methods, and these drawbacks have limited the application of electrochemical methods in areas such as wearable electronics.

3.2 Additive

The addition of additives provides a convenient and effective method for the modification of liquid metals. By mixing with additives, the leakage problem of liquid metal devices is solved and the influence of base materials on liquid metal printing is reduced.[61,62] When mixing liquid metals with other materials, the good compatibility of liquid metals is used to compound two or more materials with liquid metals to obtain a composite material with good properties.[63,225] Liquid metals modified with additives are well suited for flexible electronics because they retain high electrical conductivity and low square resistance while treating the surface oxide layer for easier processing as well as patterning. The selection of right additives to compensate for defects in the liquid metal or to enhance advantageous properties is the key to this method. The additives added can be metals, such as copper or iron; various inorganic nanomaterials; or some chemical reagents, each of which has a certain impact on the properties of the liquid metal. The simplicity of operation and the high performance of the composites make the additive strategy a major development in the modification of liquid metals.

3.2.1 Metallic particles. The low viscosity and high surface tension of liquid metals have proved unsuitable for direct printing. Changing the physical structure of liquid metals by filling them with conductive nano- or micro-particles can make liquid metals suitable for printing. In recent years, researchers have conducted a lot of research on liquid metal doped metal particles. Adding other metal materials to a liquid metal can change its electrical properties, mechanical properties and magnetic properties, and change its physical properties according to needs. For example, adding magnesium can increase its photo-thermal properties and adding iron can engender its magnetic properties. The addition of metal particles by stirring or ultrasonic treatment increases the viscosity of the liquid metal, significantly reducing surface tension and increasing wettability, while retaining its high electrical conductivity and ductility. At the same time, the surface tension and fluidity of the liquid metal are also reduced, which provides a new method for liquid metal printing.

When metal particles and liquid metals are combined, particle engulfment occurs. This engulfment behavior is related to the wettability of liquid metals to different metals. The wettability of liquid metals on the substrate of different materials is proportional to the wetting time after engulfment. In the process of engulfment, different metal particles need to overcome different energy barriers, and under acidic conditions, metal particles can enter liquid metals independently, while under alkaline or neutral conditions, they need to be assisted by electricity. The energy barrier equation is used to determine whether metal particles need to be assisted when being swallowed.[64] The equation is shown below:

$$\Delta E = 4\pi R_0^{\,2}\gamma_{12}F_1(X)\Big|_{\mathrm{eq}}^{0} = \pi R_0^{\,2}\gamma_{12}\left(1-\cos\theta_{\mathrm{W,eq}}\right)^2 \tag{6}$$

for the selection of mixed metal particles, metal particles with a contact angle less than 50°, such as copper and nickel, are usually chosen (Fig. 6a).[175] The copper particles are well integrated into the liquid metal, but there is a non-uniform distribution, which can be improved by grinding and ultrasonic treatment to obtain a paste with better properties, allowing it to be printed directly using a 3D printer (Fig. 6b);[65,66] however, high-precision printing has high requirements for the diameter of the metal particles, and the smaller the particle diameter the higher the printing accuracy. It has been shown that changing the shape of the metal during the addition of metal particles can also have an effect on the properties of the liquid metal. Different shapes of copper have different effects on the mixture, and the common shapes are copper particles, copper sheets and copper wires. Various copper forms were combined with liquid metals to create various combination states; tests revealed that the smaller the particular surface area, the better the performance of the resulting mixture. Ga_2O_3 will adhere to the surface of copper to form a combination, which has poor thermal conductivity and electrical conductivity. However, the channel created by the combination can improve the thermal conductivity and electrical conductivity, as demonstrated in Fig. 6c. The mixture's conductivity and thermal conductivity will rise as the amount of copper added rises. The surface area of spherical copper is smaller than that of copper sheets and copper wires, and the adhesion of Ga_2O_3 on the surface is less, so the performance is better.[67] As shown in Fig. 6d and e, when directly mixing copper particles with a liquid metal, in order to remove

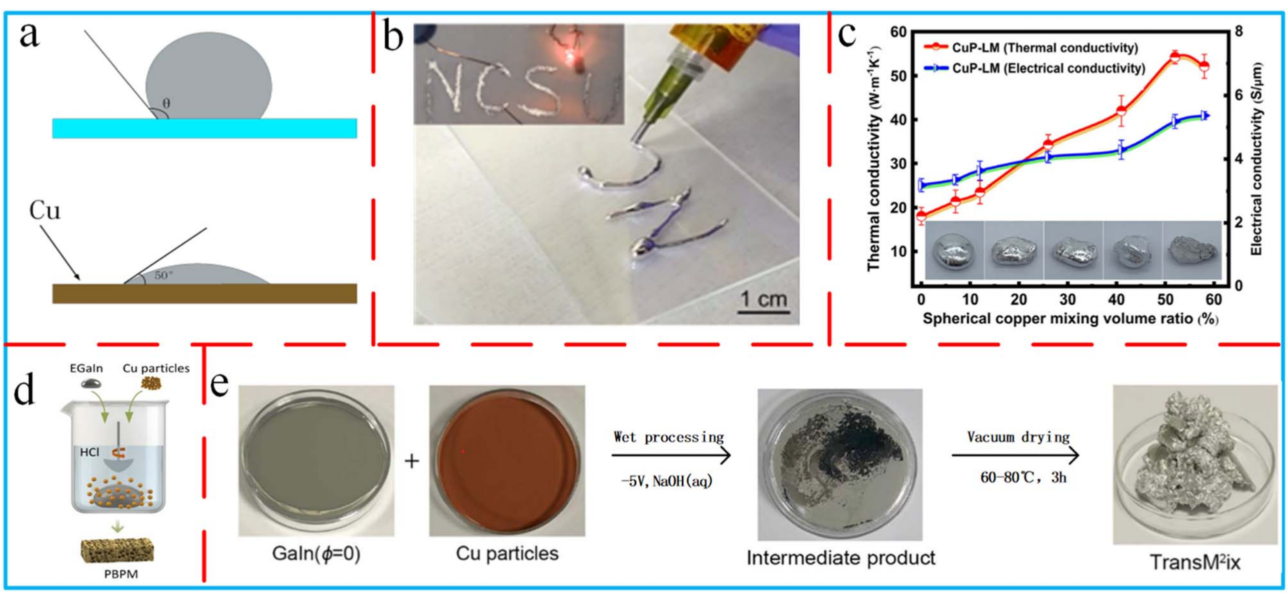

Fig. 6 (a) Comparison of the contact angle of a liquid metal on a normal substrate and copper substrate. (b) Direct printing of paste formed by mixing the liquid metal with copper powder (reprinted with permission from ref. 66. Copyright 2020, American Chemical Society). (c) As the percentage of copper powder in the liquid metal paste increases, the conductivity and thermal conductivity of the paste are gradually enhanced (reprinted with permission from ref. 67. Copyright 2022, Wiley-VCH). (d) Liquid metal and copper particles mixed under acidic conditions (reprinted with permission from ref. 69. Copyright 2020, American Chemical Society). (e) Liquid metal and copper powder mixed under alkaline conditions (reprinted with permission from ref. 68. Copyright 2017, American Chemical Society).

the surface oxide layer of the liquid metal as well as the oxides on the copper surface, hydrochloric acid or sodium hydroxide is usually added to the mixture, which can obtain a mixed material with enhanced electrical conductivity.[68,69] The material after mixing copper particles shows significant improvements in electrical, thermal and mechanical properties: when doped with 20% of the particles, the electrical conductivity is enhanced by about 80% and the thermal conductivity by about 100% relative to the pure liquid metal. At the same time, after the addition of copper particles, the liquid metal has better adhesion to various surfaces and it possesses plasticity, which makes the liquid metal more widely used in electronic printing and heat conduction and other fields.

After the liquid metal engulfs the metal particles there is no chemical bond with the surface of the metal particles, so the existence of metal particles in the liquid metal is not stable, and it is easy to separate from the liquid metal under a strong external force (such as high air pressure and large stretch), leading to the destruction of the structure. The metal particles will also eventually settle under the influence of gravity over an extended length of time, causing an uneven mixing of the liquid metal and reducing effectiveness. However, this method has no significant effect on the electrical conductivity of the liquid metal, and the measured conductivity of EGaIn was 3.28×10^6 S m^{-1}, and the conductivity of EGaIn mixed with nickel powder is $3.93 \times 10^6 \pm 9.50 \times 10^5$ S m^{-1}. Compared with pure EGaIn, the electrical conductivity is enhanced and even the electrical conductivity of the mixed material increases when the liquid metal is mixed with silver or copper powder.

3.2.2 Inorganic oxide nanomaterials. Inorganic oxide nanomaterials are not inherently conductive, so they are mixed with a liquid metal to reduce the surface tension mainly by forming metallic conductive pastes,[70] and metallic conductive pastes are widely used in the medical field. Chang *et al.* mixed

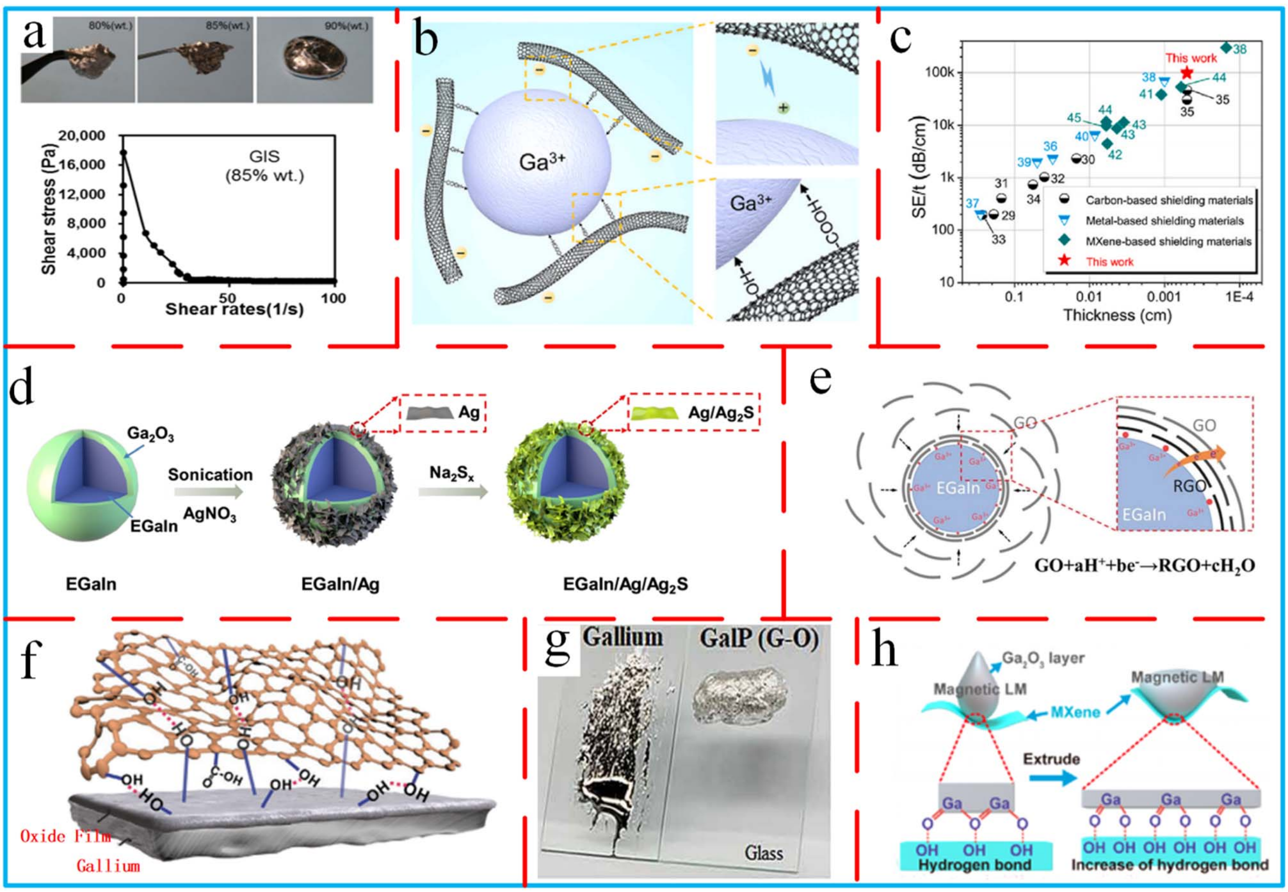

Fig. 7 (a) Relationship between the shear rate and shear stress for different liquid metal concentrations in GIS (reprinted with permission from ref. 71. Copyright 2020, American Chemical Society). (b) Carbon tubes wrapped around the liquid metal surface by chemical bonding and electrostatic interaction (reprinted with permission from ref. 74. Copyright 2022, Elsevier). (c) Comparison of SE/t of the composite formed from a liquid metal and carbon tubes with previously reported shielding materials (reprinted with permission from ref. 74. Copyright 2022, Elsevier). (d) Preparation process of EGAaIn/Ag/Ag_2S core–shell composite particles (reprinted with permission from ref. 75. Copyright 2022, Wiley-VCH). (e) Liquid metal and graphene under acidic conditions after mixing graphene react to form graphene oxide and adsorb on the surface of the liquid metal to form a core–shell structure (reprinted with permission from ref. 178. Copyright 2020, Wiley-VCH). (f) A tight connection is formed between the hydroxyl groups on the surface of graphene and the hydroxyl groups on the surface of the liquid metal (reprinted with permission from ref. 76. Copyright 2021, Wiley-VCH). (g) The viscosity of the liquid metal increases when a large amount of graphene is added to the liquid metal (reprinted with permission from ref. 80. Copyright 2021, American Association for the Advancement of Science). (h) MXene is connected to the surface of the liquid metal by hydrogen bonding (reprinted with permission from ref. 81. Copyright 2022, American Chemical Society).

a liquid metal with SiO_2 nanoparticles to produce a printable metal paste (GIS).[71] GIS has strong electrical conductivity and can effectively lower the surface tension of the liquid metal, and the mass fraction of SiO_2 in GIS progressively grew, reaching 15% when the shear stress is close to zero (Fig. 7a). In addition to having outstanding malleability, printability, and electrical conductivity, GIS also offers significant financial benefits due to its capacity to recover the liquid metal in either an acidic or an alkaline environment. Overcoming surface tension to generate stable nanoparticles is one issue with applications of liquid metals in medicine. Encapsulating the liquid metal with ZrO_2 and treating it with PEG to make them biocompatible is an effective approach.[72] When enclosed in ZrO_2, they are more easily absorbed and incorporated by cells than liquid metal droplets. When combined with liquid metals, inorganic oxide nanoparticles are less toxic to people and are employed in medical applications to carry out numerous bodily processes. They are, however, infrequently employed in liquid metal-based conductive composites since they are not naturally conductive.

Although there are many different types of inorganic oxide nanoparticles, only a few are commonly employed. As more novel materials are discovered, more applications will be made possible.

3.2.3 Inorganic semiconductor nanomaterials. Due to their unique electrical, optical, acoustic, and magnetic capabilities, inorganic semiconductor nanoparticles are employed in a wide variety of applications.[194,195] Semiconductors have conductivities that fall between those of conductors and insulators. Comparing semiconductor nanomaterials to precious metal nanoparticles, semiconductor nanostructures stand out because of their high earth abundance, low cost, straightforward fabrication process, and ease of surface modification.[73] Compared to other materials, composites of liquid metals with inorganic semiconductor nanomaterials are relatively less studied. The use of inorganic semiconductor nanomaterials unquestionably greatly expands the applicability of liquid metals.

Carbon nanotubes are one of the inorganic semiconductor nanomaterials that are most commonly researched due to their unique structure and excellent physical properties.[172] Single-walled carbon nanotubes are highly chemically inert, while multi-walled carbon nanotubes are much more active and have many functional groups on their surface, providing a basis for mixing liquid metals. Yi *et al.* treated a liquid metal in ethanol using ultrasonication for 10 min. After that, they added aqueous carbon nanotube solution and stirred for another 10 min.[74] Ga^{3+} in solution undergoes a complexation reaction with the carboxyl groups on the carbon tube's surface, which when combined with electrostatic interactions causes the carbon tube to firmly encircle the liquid metal droplet's surface (Fig. 7b). The presence of carbon tubes on the surface of liquid metals allows for the stable presence of liquid metal microdroplets in solution and improves the material's electromagnetic shielding capability, which is superior to that of carbon-based and metal-based materials (Fig. 7c).

In addition to carbon tubes, Liu *et al.* used an electrical substitution reaction to create silver shells on the liquid metal surface, which they then sulfurized to create core–shell composite particles made of EGaIn/Ag/Ag_2S (Fig. 7d).[75] Because of the superior qualities of the semiconductor material Ag_2S, the EGaIn/Ag/Ag_2S-based humidity sensor performs exceptionally well. Ag_2S has the capacity to take in airborne water molecules and receive electrons from them. Additionally, the metal sulfide experiences stronger adsorption of water molecules, resulting in a continuous water layer and ion-conducting channels.

Semiconductor materials are more suited for functional components like sensors than liquid metals since they not only have electrical conductivity but also many other special capabilities. As a result, the combination of liquid metals and semiconductor materials not only addresses how surface tension affects applications, but also broadens the uses of liquid metals. However, as there have not been a lot of studies done on composites of liquid metals and semiconductor materials, future research into this area is therefore needed to achieve more functionality using liquid metals.

3.2.4 2D nanometer materials. The addition of graphene to a liquid metal is the method most frequently utilized in 2D materials.[76,77] When a liquid metal and graphene are combined, a new structure will be created chemically. As seen in Fig. 7e, when a liquid metal and graphene are combined in an acidic environment, the liquid metal reacts with hydrogen ions to form Ga^{3+}, and then gallium ions accumulate on its surface to give it a positive charge, and graphene exhibits a negative charge under acidic conditions and is adsorbed onto the liquid metal's surface. Graphene can also be reacted to form graphene oxide

$$\mathrm{GO} + a\mathrm{H}^{+} + b\mathrm{e}^{-} \rightarrow \mathrm{RGO} + c\mathrm{H_2O} \tag{7}$$

On the graphene shell's side closest to the liquid metal, graphene oxide is produced. The graphene oxide shell's poor oxygen permeability and hydrophobicity prevent the liquid metal inside from oxidizing.[79,178] In the process of mixing a liquid metal with graphene, the oxide layer is crucial. The hydroxyl groups on the surface of graphene will join with the oxide layer to form a structure with superior qualities (Fig. 7f).[80] As can be shown in Fig. 7g, the mixture's wettability and viscosity are proportional to the mass of graphene. When the filling ratio reaches 42vot%, the surface tension is reduced by 73% compared to pure gallium, and it also exhibits greater wettability. As the filling ratio increases, the mixture's viscosity steadily increases.[80] In contrast to previous additives, the two-dimensional graphene material improves the conductive paste's electrical and thermal conductivity by not forming compounds with the liquid metal, consuming the liquid metal, and having a flat surface after mixing. The introduction of graphene along with a variety of functional groups provides a variety of options for paste modification and is a promising modification method.

Another 2D material, MXene, has also been used to combine with liquid metals in addition to graphene.[193] Magnetic liquid metals were altered by Yi *et al.* using MXene, who also created composite fibers.[81] As in Fig. 7h in the composite fiber, MXene wraps around the liquid metal, which not only enhances the adhesion of the liquid metal to the substrate, but also connects the two connected liquid metal droplets to form a conductive pathway, enhancing the electrical conductivity of the fiber as well as the tensile properties. Compared with graphene and other materials, the research of MXene started late, although it is commonly used in energy storage, catalysis, electromagnetic shielding and lubrication, but its surface has more hydroxyl groups, can have a good combination with the liquid metal, and its electrical conductivity is also very good, so in the next research the study of the reaction between MXene and liquid metals and its application in conductive materials can be increased.

3.2.5 **Other chemical reagents.** In addition to the studies mentioned above, the use of chemical reagents offers a fresh concept for the modification of liquid metals, and by combining various chemical reagents to create conductive composites allows the liquid metals to be printed with high resolution by printers. Table 1 lists the tensile and electrical conductivity of the composites made from liquid metals and various chemical reagents. It is clear that some liquid metal composites have tensile qualities that are superior to those of the liquid metal itself and that they can reduce surface tension. However, the high tensile rates come at the sacrifice of other factors, such as fluidity and electrical conductivity.[222,223] For instance, the maximum stretching rate of the composite conductive material made of a liquid metal and Ecoflex is 450%; however the resistance change while stretching is very significant, with a resistance change of 10^7 at a stretching rate of 350%.[146] Lopes *et al.* combined a liquid metal with the binders styrene–isoprene–styrene (SIS) block copolymer and silver to create a conductive ink that could be printed directly in order to address the issue of decreased conductivity after stretching (Fig. 8a).[82] This ink is highly ductile and conductive, and it sticks to the substrate nicely (Fig. 8b). A conductive route is created by joining a liquid metal and silver particles with the adhesive SIS. In-depth research has been done on SIS to link materials like nickel, iron, and other metals in addition to silver.[83] In this way, the surface tension can be effectively reduced and the problem of leakage when the liquid metal is used as a wire can be solved.

Table 1 Summary of the tensile properties and electrical conductivity of liquid metal-based conductive composites

Material	Strain [%]	Sensitivity	Ref.
LM/SIS/Ag	500	$R/R_0 = 1.5$@100%	82
LM/TPU	200	$\Delta I/I_0 = 40\%$@200%	143
LM/PVA	20	$\Delta R/R_0 = 5\%$@20%	144
LM/PDMS	100	$\Delta R/R_0 = 3.8\%$@100%	145
LM/PDMS/MWCNTs	120	$R/R_0 = 2.1$@120%	84
LM/Ecoflex	450	$R/R_0 = 107$@350%	146
LM/PVA/CNC	NA	$\Delta R/R_0 = 0$@twisting 180°	147
LM/PEVA	NA	$R/R_0 = 1.25$@500%	148
LM/TPU/ethyl cellulose	1000	$R/R_0 = 1.083$@30–80%	149
LM/PDMS/Fe	30	$R/R_0 = 0.025$@10%	150
PAA-LM/rGO	3000	$R/R_0 = 11\,000$@1000%	151
LM/PVP/IPA	100	$R/R_0 = 1.3$@75%	152
LM/TA	70	$\Delta R/R_0 = 1.17\%$@50%	153
LM/PCL/TPU	480	NA	154
LM/PVA/TA	340	$\Delta I/I_0 = 135\%$@50%	155
LM/SA	100	$\Delta R/R_0 = 300\%$@100%	16
LM/SA/PAm	800	$\Delta R/R_0 = 600\%$@300%	156
LM/PEDOT:PSS	20	NA	157
LM/PDMS/CNF	900	NA	158
LM/PDMS/CNTs	200	$\Delta R/R_0 = 3\%$@200%	169
LM/SA/AM/MBAA	4000	$\Delta R/R_0 = 6000\%$@1800%	160
LM/PU	500	$R/R_0 = 1.75$@100%	227

The most commonly used material in liquid metal composites today is undoubtedly polydimethylsiloxane (PDMS).[167,173] Numerous investigations on PDMS systems have led to various strategies for integrating liquid metals with PDMS, despite the fact that PDMS is typically utilized as a substrate material for other applications.[141] Mixing a liquid metal with PDMS through mechanical stirring to form a slurry is the original mixing method; adding multi-walled carbon nanotubes (MWCNTs) on top of this can result in materials with higher performance.[84] This material, which has been successfully employed to create sensors, has the advantages of high electrical conductivity, low elastic modulus, high tensile strength, and strong adherence to PDMS substrates. Beyond mixing it with a liquid metal to create conductive pastes, research on PDMS has led to many more applications. Lee *et al.* created continuous wires out of liquid metals in PDMS by ultrasonically processing the liquid metals in PDMS (Fig. 8c).[85] Due to the structure of PDMS, liquid metals cannot interact with one another and create conductive pathways. However, after the mixture is ultrasonically processed, the liquid metal will separate into small droplets, which will create conductive pathways between the droplets and give the material good conductivity.

Some metals have high wettability rates for liquid metals, and this characteristic has been used to pattern liquid metals.[86–88] This can further improve the wettability of liquid metals when copper ions are added (Fig. 8d).

$$\mathrm{Ga} + 3\mathrm{CuCl} \rightarrow \mathrm{GaCl_3} + 3\mathrm{Cu} \tag{8}$$

As a result, the liquid metal in the copper ion solution loses its liquid drop structure and its surface tension rapidly decreases. Fig. 8e and f demonstrate how the copper particles and the surface of the liquid metal create a primary cell in the acidic solution. This primary cell creates a potential difference through the transfer of electrons, which causes a gradient of surface tension to appear and causes the liquid metal to experience a serpentine extension.[89] Similar to this, after the liquid metal is exposed to a copper chloride solution on a copper metal plate, gallium displaces the copper ions in the copper chloride solution to form the copper element, and the copper is absorbed by the liquid metal, causing the contact angle to fall below 5°.[90]

Viscose additives are chemically bound to the surface of liquid metal droplets when chemical reagents are used, creating a shell–core structure. Most liquid metal conductive pastes are prepared this way, either by stirring or ultrasonically, which

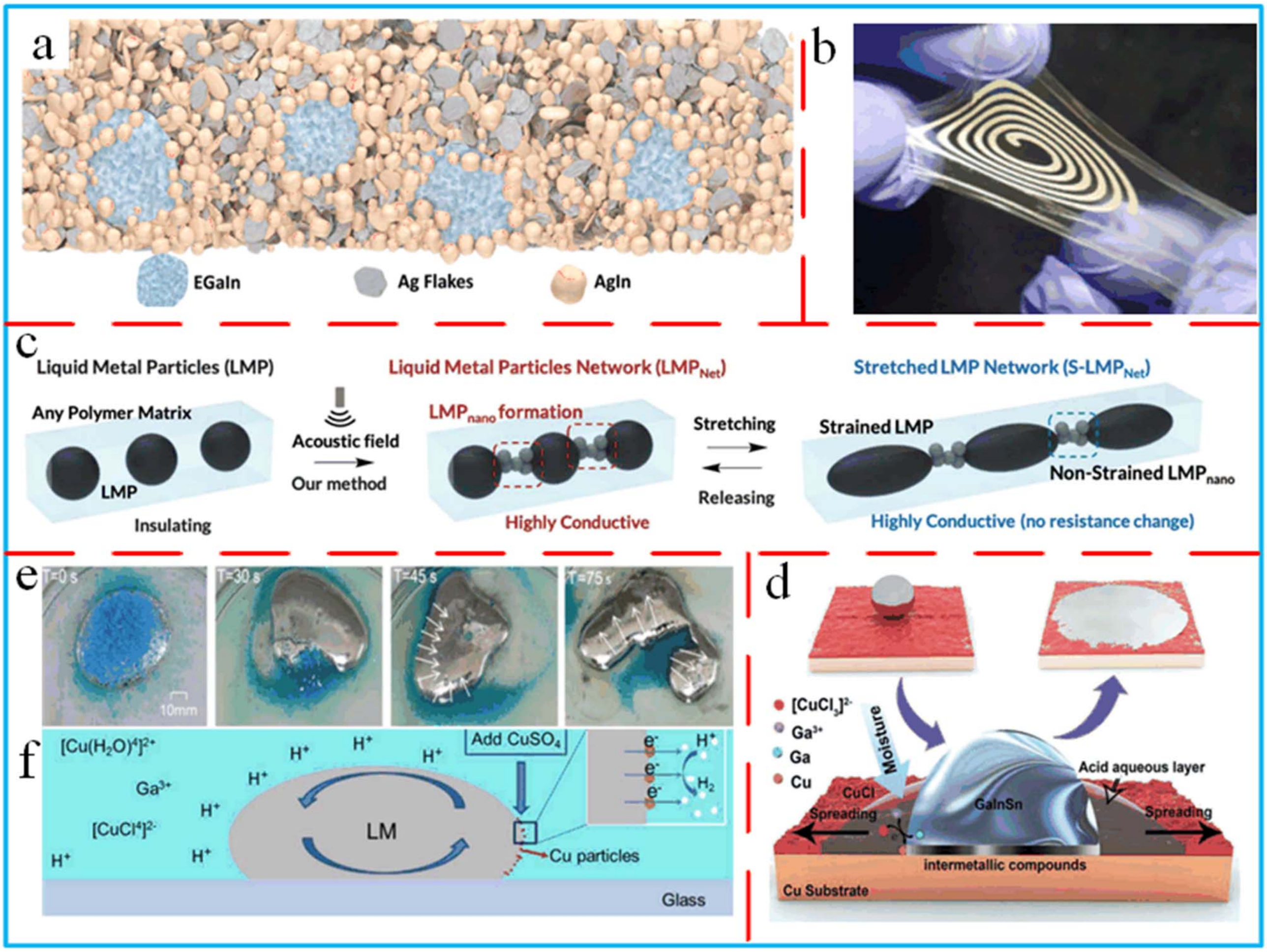

Fig. 8 (a) Liquid metal and silver powder forming conductive paste from SIS (reprinted with permission from ref. 82. Copyright 2021, American Chemical Society). (b) Liquid metal conductive paste formed from SIS with excellent stretchability and good adhesion to the substrate (reprinted with permission from ref. 82. Copyright 2021, American Chemical Society). (c) Conductive pathway formation process of a liquid metal in PDMS (reprinted with permission from ref. 85. Copyright 2022, American Association for the Advancement of Science). (d) Enhanced wettability of the liquid metal on copper by adding copper ions (reprinted with permission from ref. 90. Copyright 2021, Wiley-VCH). (e) Chemical reaction principle carried out by the liquid metal in copper ion solution (reprinted with permission from ref. 89. Copyright 2018, American Chemical Society). (f) Reduction of surface tension of the liquid metal in copper ion solution (reprinted with permission from ref. 89. Copyright 2018, American Chemical Society).

reduces the surface tension during application. Due to the encapsulation of non-conductive chemicals in the surface layer, this approach necessitates the destruction of non-conductive compounds in order to obtain a conductive pathway during application. This undoubtedly has a great impact on the electrical conductivity of liquid metal composites.

3.3 Physical methods

By only altering the external environment, the surface tension of the liquid metal can be lowered. These techniques manage the surface tension without the need for additives by utilizing the physical characteristics of the liquid metal itself. Since liquid metals have a melting point between 8 and 24 °C and behave like liquids at normal temperature, and they combine some liquid characteristics with the characteristics of metals. When the temperature falls below the melting point, stiffness rises, and surface tension falls, making it perfect for shaping. Cryoprinting was used by Gannarapu and colleagues to print vertical wires made of a liquid metal without the requirement for a support.[91] Surface tension is less of an issue for liquid metals after freezing; however this technique needs to be done under certain circumstances and remain stable at low temperatures. Additionally, a liquid metal can be processed using the sintering technique.[92,93] Laser sintering and heat sintering are the two most often used sintering techniques. The liquid metal is more flexible and electrically conductible after being laser sintered, and the laser sintering process can be carefully regulated to produce high-resolution processing (Fig. 9a).[94,212] Cho *et al.* used a laser to treat EGaIn and AgNWs. The treated EGaIn not only reduced the surface tension, but also combined with the AgNWs and wrapped on the surface of the silver nanowires to form a new structure.[219] Sintering converts the liquid metal's interior from discrete droplets to a continuous network, improving electrical conductivity, and it is easy to prepare high-resolution patterns.[199]

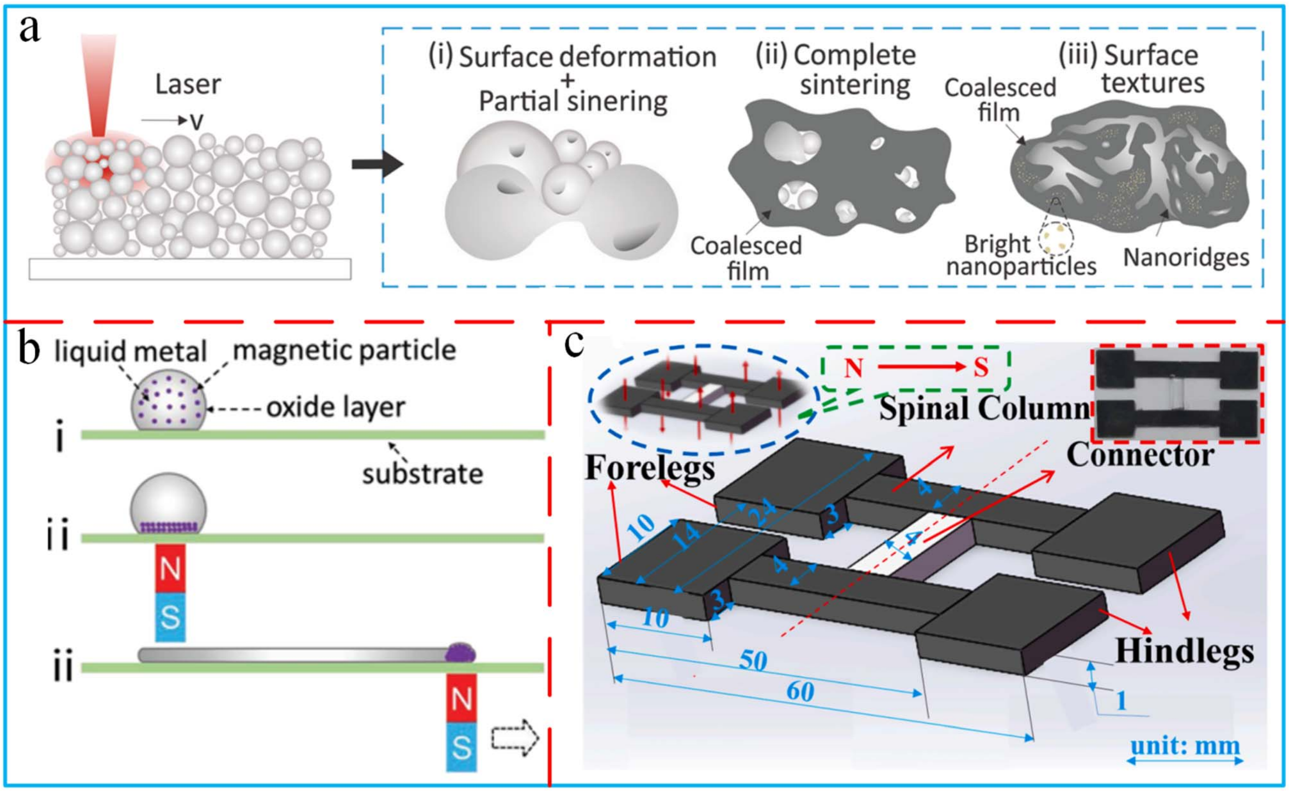

Fig. 9 (a) Destruction of the oxide layer on the surface of the liquid metal by laser sintering, releasing the internal liquid phase portion to form a coherent whole (reprinted with permission from ref. 94. Copyright 2019, Royal Society of Chemistry). (b) Control of the liquid metal by adding magnetic particles inside the liquid metal allowing it to pass through a magnetic field (reprinted with permission from ref. 96. Copyright 2019, Wiley-VCH). (c) Magnetic-driven flexible robot based on the liquid metal and PDMS (reprinted with permission from ref. 98. Copyright 2023, Elsevier).

A very important physical method is magnetic, which is able to pattern liquid metals by applying a magnetic field to magnetically drive the liquid metal.[95] The size of the magnetic field and the characteristics of the liquid metal itself determine the magnetic field's ability to drive, as seen in Fig. 9b, and adding magnetic particles to the liquid metal is necessary to increase the magnetic field's ability to exert control.[96] The presence of magnetic particles makes it easier to pattern the liquid metal. There are numerous varieties of magnetic particles, including iron nanoparticles in addition to the more common iron oxide and NdFeB.[97] Through the interaction of electric and magnetic fields, this technique can precisely regulate the direction of motion of liquid metals, offering a mechanism for the creation of precise devices like soft robots. Similar to this, Guan *et al.* added PDMS to NdFeB with a liquid metal to obtain a flexible magnetically driven robot that can move in a magnetic field (Fig. 9c).[98]

Physical methods do not have a great impact on the electrical conductivity of liquid metals, whether it is laser treatment or ultrasonic treatment or magnetic field control to maintain good electrical conductivity, and the need to mix with magnetic materials during magnetic field control may reduce the electrical conductivity.

There are several different approaches to modifying liquid metals.[224] One is to change the liquid metal directly through chemical deposition. The flaw of the high surface tension of liquid metals is essentially fixed by this method, but its use is constrained by the difficulty of processing. The second approach, which is also the most popular and straightforward, involves combining the liquid metal with various components to create a hybrid polymer, in which the properties of various substances are used to specifically change the liquid metal. However, the focus and challenge of this method are choosing an appropriate material to mix with the liquid metal to accomplish the desired result. This calls for researchers to have a profound grasp of the nature and structure of liquid metals and other materials. Finally, external factors like magnetic and electric fields are used to control liquid metals. Since the liquid metal cannot be permanently altered, this concept is currently only used in real-time control applications like soft robotics. The benefits and drawbacks of numerous frequently used modification techniques are compiled in Fig. 10. We rate five factors: the conductivity after modification, the complexity of modification, the effect of modification, the persistence of effect of modification, and the applications of modification methods. Higher scores indicate better performance. It is vital to choose an appropriate modification method in accordance with the application because each modification method has a different score but a distinct application scenario.

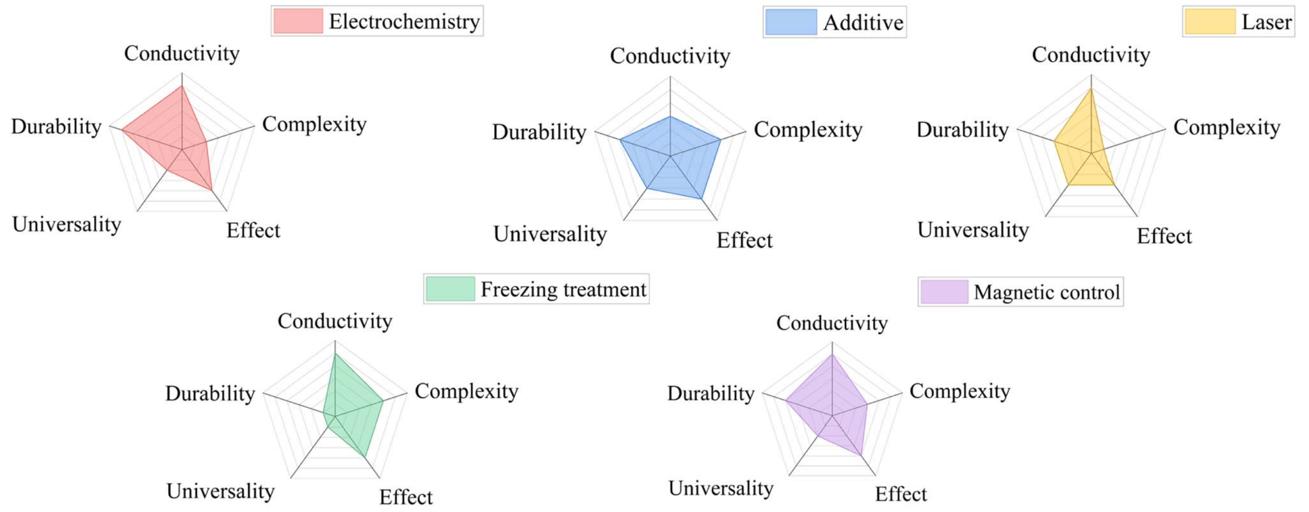

Fig. 10 Comparison of several different modification methods and their advantages and disadvantages.

4. Applications

Liquid metals and their composites function well under mechanical deformation conditions including tensile, bending, and torsion. And due to their great fluidity and electrical conductivity, they are also suitable for usage in a wide range of applications. Applications where surface tension control is necessary are the main topic of this section. Table 2 lists the modification techniques applied for each application and their results.

4.1 Tumor therapy

One of the difficulties in the medical field has always been the treatment of tumors. The medicine used in treatment destroys tumor cells while harming healthy cells in the process. Due to its superior photothermal conversion efficiency and biosafety, liquid metals, a new form of biomaterial, provide more options for treating tumors.[166,184] The first consideration in the application of liquid metals in therapy is cytotoxicity, and liquid metals and their composites are non-toxic to the body, so they can be applied in tumor therapy.[226] In order to enter and function better in the human body, liquid metals need to be processed into droplets of a small diameter and be stable in the body and able to carry drugs, which requires surface modification of liquid metals. Fan *et al.* modified a liquid metal by mixing it with methotrexate (MTX) and chitosan (CS).[99] Because of the excellent photothermal capabilities, it is possible to rapidly warm the tumor area when exposed to NIR laser light and release MTX there to harm cancer cells and tumor cells (Fig. 11a). In experimental mice, CS/LM/MTX microspheres are highly toxic to tumor cells while being relatively non-toxic to other organs, showing excellent potential for the synergistic treatment of tumors.

Using a drug-modified liquid metal as a carrier to transport drugs to the lesion in the body and release it precisely allows the drug to reach the designated location and deliver the treatment. This strategy not only lessens the harm done to the body's other organs but also improves the effectiveness of the therapy. Kim *et al.* made a liquid metal convey the cancer therapy medicine Adriamycin using a straightforward ultrasound procedure, and when the liquid metal arrived at the cancer location, the drug was released by light treatment or heat treatment for the goal of drug transport.[103] But a crucial problem in the process of getting

Table 2 Modification methods, modification effects and number of studies of different applications

Application		Modification method	Modification effect	Number of studies
Tumor therapy	Drug transportation	Additive	General	43
	Cryoablation	Physical methods	Poor	
Medical equipment	Artificial muscle	Electrochemistry	Good	61
	Intracerebral sensors	Additive	Good	
Wearable flexible electronics		Additive	Good	442
Soft robotics	Magnetic drive	Additive	Good	198
	Electrochemical drive	Electrochemistry	Good	
	Optical drive	Additive	General	
Catalyst		Additive	Good	111
TENG		Additive	Good	30

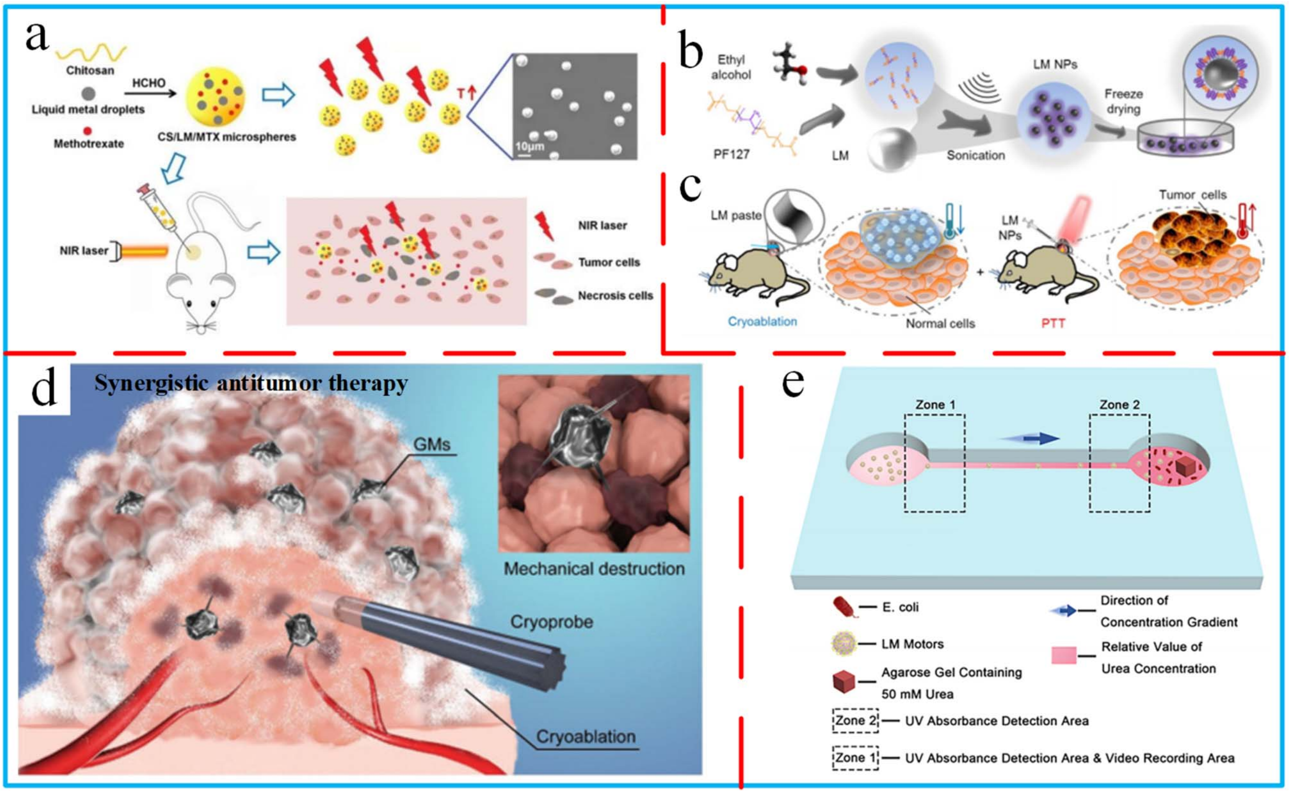

Fig. 11 (a) Schematic diagram of CS/LM/MTX microsphere preparation and chemophotothermal treatment processes under NIR laser irradiation (reprinted with permission from ref. 99. Copyright 2020, American Chemical Society). (b) Preparation of LM NPs (reprinted with permission from ref. 100. Copyright 2020, American Chemical Society). (c) Illustration of LM hybrid platform enhanced cryoablation and PTT (reprinted with permission from ref. 100. Copyright 2020, American Chemical Society). (d) Schematic diagram of dual-modality synergistic antitumor therapy based on cryoablation and gallium particle-induced mechanical destruction of tumor (reprinted with permission from ref. 101. Copyright 2020, Wiley-VCH). (e) Schematic diagram of the macroscopic positive convergent behavior of nanorobots inside agarose gel containing 50 mM urea (reprinted with permission from ref. 102. Copyright 2021, American Chemical Society).

the liquid metal into the body and working is accurately driving the movement of the metal and releasing the medication. A liquid metal nanorobot that is propelled by urease was demonstrated by Xu *et al.*[102] The liquid metal can transport pharmaceuticals thanks to the poly(dopamine) (PAD) that was wrapped around it. This nanorobot can also be collectively steered in urea solution for selective transport along the urea concentration gradient, and it has good tropism (Fig. 11e). This kind of drive efficiently utilizes bio-available fuel and streamlines the transportation of drugs.

In addition to transporting medicines, liquid metals have the ability to destroy tumor cells through cryoablation and photothermal therapy thanks to their unique characteristics and state changes. The temperature in close proximity to the tumor cells can be made extremely high or extremely low through external energy intervention, producing a therapeutic effect. The liquid metal's surface tension changes in response to the temperature change, making manipulation easier. The accuracy of single cryoablation or photothermal therapy is however constrained, and the treatment range is small with low targeting, which greatly restricts the clinical application. In contrast, the multi-level treatment mode combining multiple modalities can bring the benefits of each modality into play and have better results in actual applications. For example, Hou *et al.* used a liquid metal for a multimodal treatment with cryoablation combined with photothermal therapy (Fig. 11b and c).[100] With this technique, tumor cells can be damaged by a sudden change in temperature from extremely low to very high. During the process, the liquid metal acts as a very effective conductor, and the paste created by combining the liquid metal with copper powder offers great heat transfer. The liquid metal has the potential to treat more damaged cells than only tumor cells in the future, resulting in painless and symptom-free cancer treatment. In addition to the commonly used methods, researchers have discovered other physical properties of liquid metals and used them in therapies. According to Sun *et al.*, a liquid metal expands during freezing, puts pressure on the nearby chitosan ice crystals, and even creates spikes. These spikes are capable of destroying the nearby tumor cells. By combining this mechanical destruction phenomenon with traditional cryoablation, better therapeutic results can be obtained (Fig. 11d).[101] During the procedure, the ice balls can reach a minimum temperature of −150 °C and completely cover the tumor cells in 90 seconds. Insulation is required because heat is absorbed from the body while receiving therapy. And the direction of the spikes produced by the liquid metal particles while working should be controlled to avoid harming other cells.

Liquid metals are a new alternative for drug delivery and tumor treatment because of their low body toxicity and ability to be manipulated by a number of techniques, including magnetic fields, light, and heat. The aforementioned techniques may be more effective for treating skin cancers, because PTT is less effective for treating internal tumors and techniques like temperature control may have an adverse effect on other organs. Additionally, more research must be done on removing liquid metals from the body after use and expanding the range of medications that can be transported.

4.2 Medical equipment

Medical devices are crucial for identifying physiological signals, monitoring the body's health, and creating artificial organs. However, the majority of biological devices on the market today are made of inflexible parts, which can be quite uncomfortable for patients. The deformability and high electrical conductivity of liquid metals are in line with the future demand for materials in the biomedical field.[104,105] Future medical device development will now focus on artificial organs made from liquid metals and various medical sensors.

Different human movements are controlled by muscle diastole and contraction; when a muscle contracts, its volume drops; when it relaxes, its volume increases. This volume and form change is comparable to the control of liquid metals, which an electrochemically controlled liquid metal does a good job at simulating. When exposed to an electric field, liquid metals will progressively overcome surface tension and spread out across the substrate, resulting in a decrease in height; however, when the electric field is withdrawn, the liquid metal will condense back into droplets. This technique for adjusting surface tension is ideal for simulating muscular movement. Shu and colleagues created an artificial muscle by sandwiching a liquid metal and an electrolyte containing sodium hydroxide between two substrates joined by copper plates. They were able to mimic muscle contraction and diastole by using the liquid metal's change in shape in response to electricity, and they were also able to lift heavy objects (Fig. 12a).[106] A mechanical bionic fish built with liquid metal artificial muscles is depicted in Fig. 12b. Using a battery at the fish's head and a circuit board to alter the fish's shape, the tail's shape is controlled by the liquid metal. This causes the tail to swing from side to side. Fig. 12c displays a graph of displacement *versus* time for fish with and without tail fins. It is clear from this graph that the bionic fish can move quickly thanks to its liquid metal-driven tail fin. Fig. 12d shows the tilt of the substrate formed by the contraction of liquid metal droplets at a fixed position by modulating the electric field, forming a transport line. Although liquid metal artificial muscles are currently only able to move relatively small items, with further research, it is anticipated that they will

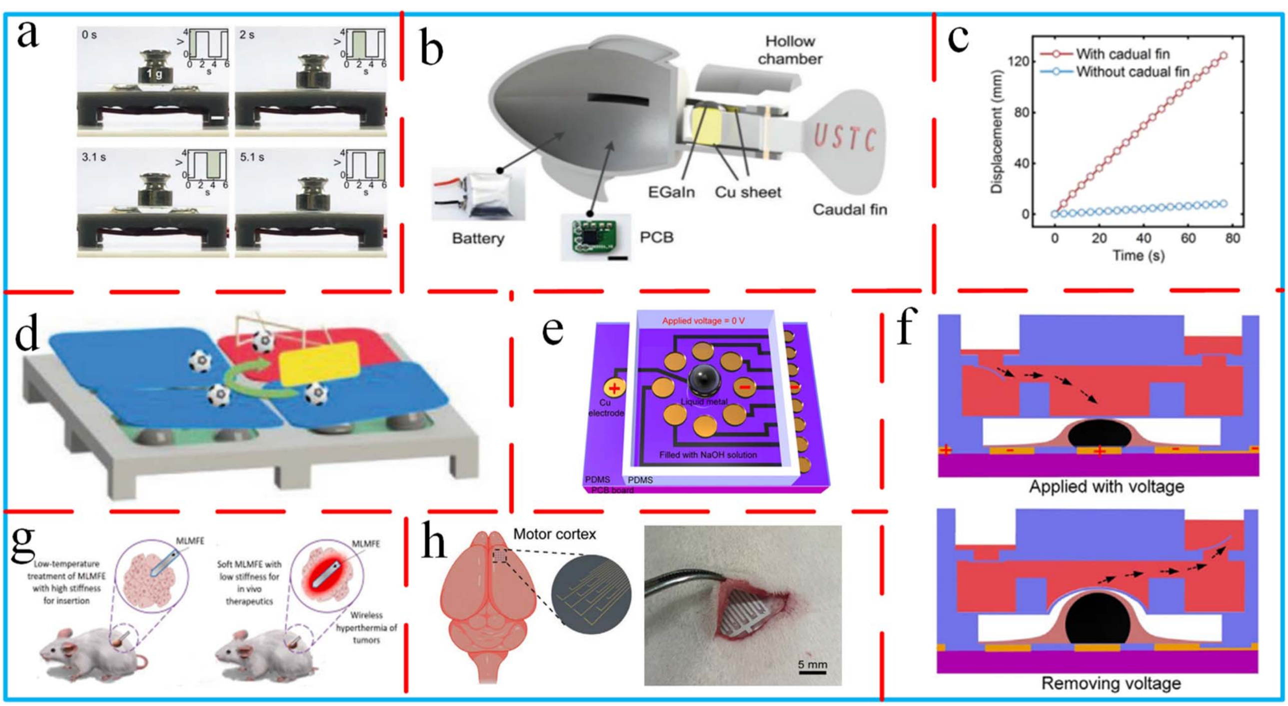

Fig. 12 (a) Artificial muscles made by contraction and diastole of a liquid metal to lift heavy objects. (b) Mechanical bionic fish made from liquid metal artificial muscles. (c) Mechanical bionic fish with and without tail fin moving speed in water. (d) Liquid metal contraction to tilt the lifting plate to form a transport pathway (reprinted with permission from ref. 106. Copyright 2021, Wiley-VCH). (e) Liquid metal artificial heart controlled by multiple electrodes (reprinted with permission from ref. 107. Copyright 2019, Wiley-VCH). (f) Liquid metal contraction and diastole controlled by voltage conversion to achieve blood pumping function. (g) Implantable electrodes with variable stiffness (reprinted with permission from ref. 111. Copyright 2022, Elsevier). (h) Bioelectrodes made of a liquid metal can be installed in the organism to achieve monitoring (reprinted with permission from ref. 162. Copyright 2021, Wiley-VCH).

eventually be able to lift bigger objects and be utilized in more applications. Electrochemical treatment of liquid metals can also be used to make artificial hearts.[107,108] The device of Fig. 12e can control the different states of the liquid metal through multiple sets of electrodes to reach the heart by precisely controlling the electric field. The blood supply function of the heart is shown in Fig. 12f, which is accomplished *via* voltage control of the liquid metal's expansion and contraction. Fake blood will temporarily be stored in the chamber above the liquid metal while it is contracted, and when it is expanded, the liquid metal will squeeze the artificial blood out of the chamber. Although there is a significant difference when compared to the blood supply capacity of the human heart, the liquid metal artificial heart's blood supply capacity reaches its optimum at an electric field frequency of 2 Hz, which is around 70 L min^{-1}.

Due to their excellent biocompatibility, liquid metals are frequently used as conductive materials in implantable sensors. Liquid metal sensors produce changes in resistance or capacitance through changes in external circumstances.[109,110] Similar to *in vitro* sensors, implantable sensors require the modification of liquid metals for their preparation, and the most suitable modification method for the sensor field is the use of liquid metals mixed with other materials to form composites. The preparation of composite materials is a good solution to the problems of liquid metals in the preparation of sensors, such as easy leakage and difficult processing. A magnetic liquid metal was used by Sun *et al.* to create implantable electrodes. The magnetic material gained changeable stiffness qualities after being mixed with ferric tetroxide (Fig. 12g). The implanted electrode's operational stability and comfort are improved due to the change in stiffness, which enables the electrode to adapt to the surrounding biological tissue.[111] A new fabrication method for stretchable neural electrodes was presented by Dong *et al.*, who screen printed a liquid metal onto PDMS to create neural electrodes. With the ability to detect the epileptic activity of the brain in various seizure states and maintain stable conductivity when stretched, the manufactured liquid metal electrode arrays open up a new path for neurodiagnosis and monitoring with additional potential use in diagnosing brain-machine interfaces (Fig. 12h).[162] The electric drive and its superior biocompatibility are the major reasons liquid metals are used in the field of medical devices. At present, the functions that can be achieved by liquid metal artificial organs are still very few, and the performance is not up to the demand of use. Therefore, the future is to simulate other organs through a liquid metal and replace them with artificial organs for patients.

4.3 Wearable flexible electronics

The demand for very flexible materials is rising as wearable and implantable electronics become more common,[208] and the introduction of a liquid metal has greatly improved these devices. Due to the gradual maturation of liquid metal modification technology, many wearable electronics based on a liquid metal with high transparency and stable electromechanical properties are widely used.[112]

When bent, flexible electronics continue to work as intended and are more durable than conventional electronics.[113,176] The formulation of composite materials solves the problems of leakage and the difficulties caused by surface tension during processing when a liquid metal is used in wearable electronics. However, throughout the bending process, flexible electronic devices may experience long-term stress that will cause cracks and other damage.[180] For this reason, many flexible electronic devices use a liquid metal, which has stable electrical conductivity and self-healing capabilities.[114,115] In order to achieve self-healing, Zheng *et al.* wrapped nano-silver around the exterior layer of a liquid metal to achieve self-healing and modification. When the circuit was damaged, the outside shell of nano-silver could be shattered by applying an external force to liberate the liquid metal inside (Fig. 13a). The service life and stability of flexible circuits are significantly increased by this technique.[116] Sensors for flexible wearable technology are preferably highly transparent, ductile, and conductive,[117] and for the purpose of detecting the heart rate or other vital signs, embedded liquid metal sensors make use of the change in electrical resistance that occurs when something is pressed or pulled (Fig. 13b and c).[118–120] Additionally, the forked-finger capacitive sensor developed by Zhang *et al.* using a liquid metal and PDMS resolved the issue that conventional sensors cannot differentiate between in-plane strain and normal stress, and its use in wearable devices can precisely identify the extension of the elbow or wrist (Fig. 13d).[171] Wu *et al.* improved the compatibility between a liquid metal and PDMS by a selective wetting and transfer process, reduced the response time of the sensor, broadened the response range, and successfully applied it to the field of mechanical control (Fig. 13e).[122]

Electronic skin represents a significant use of liquid metals. In contrast to sensors, electronic skins have very high requirements in terms of thickness and size, which places high demands on the wire width and stability of the wires within the e-skin. A pure liquid metal has many drawbacks that need to be addressed and modification to liquid metals is a good way to do this. Traditional electronic skin is processed primarily by patterning conductive materials on a flexible substrate, and is similar in function to sensors in that they transmit electrical signals by means of tension or compression. The addition of a liquid metal improves the functionality of electronic skin even more.[123] Based on this, Xiang *et al.* added the capability of frictional power generation, where the electrical charge produced by friction between the skin and substrate flows through the wire and is used to power the circuit components.[124] Making electronic skin more comfortable is another evolutionary path, in addition to the self-powered realization. By spinning a thin layer of PDMS atop a patterned liquid metal, Mou *et al.* have successfully decreased the thickness of electronic skin and boosted the breathability, which also offers a method and direction for the creation of other flexible electronics.[125] The capacity to stay in close contact with the skin while engaging in vigorous exercise is still a significant challenge. By combining polyethylene glycol and PDMS-based adhesives, Cheng *et al.* created metal polymer conductors (MPCs), which they then utilized to encapsulate liquid metals in

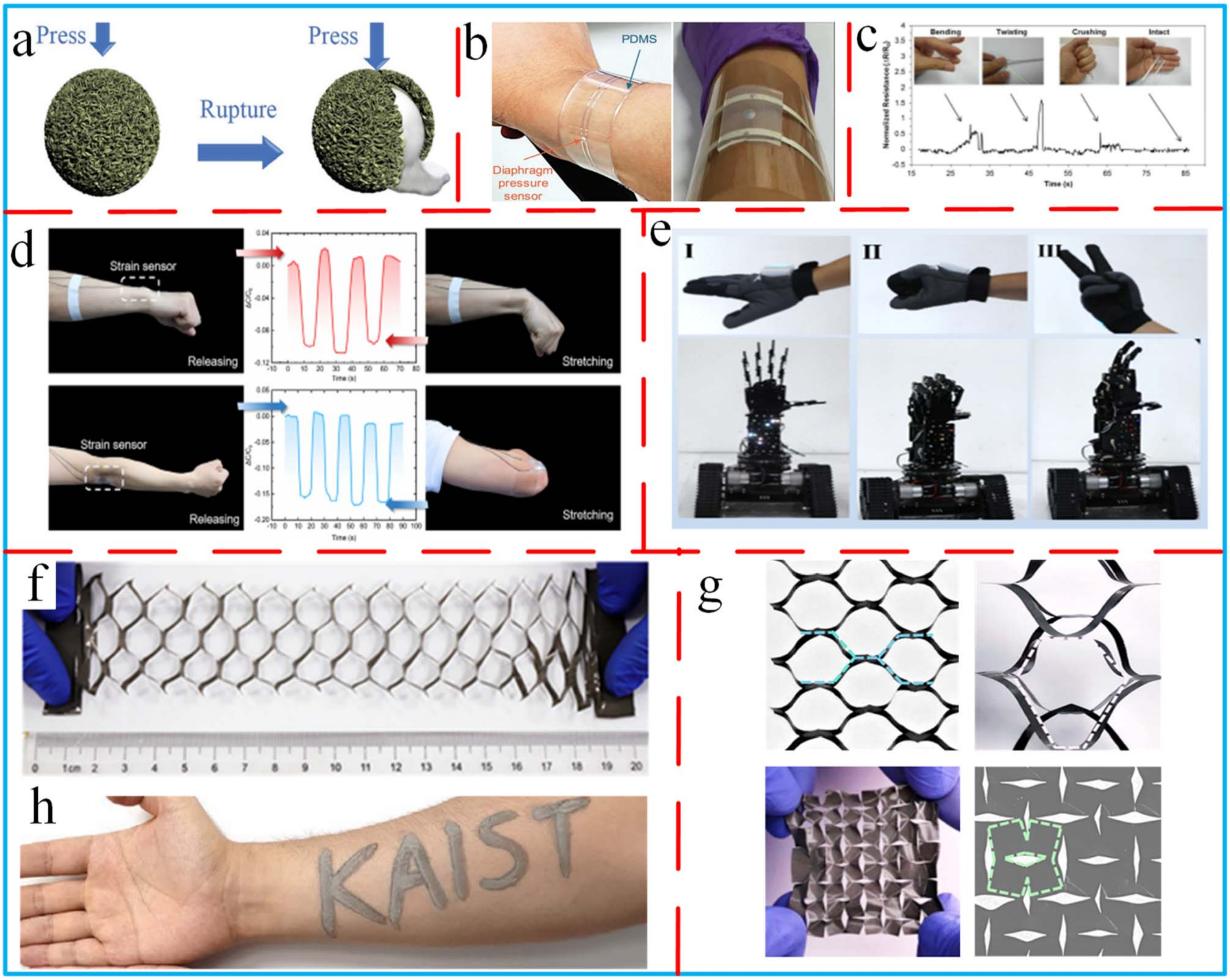

Fig. 13 (a) Nanosilver shell wrapped around a liquid metal, which ruptures under force and releases the liquid metal inside (reprinted with permission from ref. 116. Copyright 2020, Wiley-VCH). (b) Liquid metal embedded sensor (reprinted with permission from ref. 118. Copyright 2017, Wiley-VCH). (c) Embedded sensor measurement converts mechanical signals into electrical signals (reprinted with permission from ref. 119. Copyright 2013, Royal Society of Chemistry). (d) Finger fork capacitive sensor accurately recognizes wrist rotation (reprinted with permission from ref. 171. Copyright 2021, Wiley-VCH). (e) Improved process with a low response time sensor used in mechanical control (reprinted with permission from ref. 122. Copyright 2021, Wiley-VCH). (f) Paper-based electronic skin with high stretchability (reprinted with permission from ref. 127. Copyright 2022, American Chemical Society). (g) Paper cutouts enable a variety of shapes with high stretchability. (h) New electronic skin material obtained by mixing platinum modified carbon tubes with a liquid metal (reprinted with permission from ref. 128. Copyright 2022, Wiley-VCH).

electrical devices.[126] The device is permeable, and the mixed polydimethylsiloxane (PDMS)-based adhesive (PPA) maintains conformal contact with the skin throughout the exercise. Additionally, because to its excellent skin adhesion, it keeps good contact with the skin even when sweating or stretching vigorously. Li *et al.* described a paper-based liquid metal e-skin that could be reused numerous times and that could be stretched by cutting paper (Fig. 13f).[127] Unlike traditional electronic skins, paper-based electronic skins can sustain themselves and be cut into a variety of highly stretchy, ultra-thin shapes (Fig. 13g). This electronic skin has inherent permeability and adhesion problems because paper is used as the substrate. To create a novel electronic skin, Lee *et al.* combined a liquid metal with platinum-modified carbon tubes (Fig. 13h).[128] This electronic skin contributes significantly to the widespread usage of electronic skin since it doesn't need a substrate, has great skin compatibility, and is simple to customize to create a unique electronic skin.

Flexible electronics are being studied extensively as an important application area for liquid metals. The benefits of liquid metals over other materials include their high fluidity and electrical conductivity. However, single liquid metals have issues with leakage and high surface tension. In order to maintain high electrical conductivity and a low resistance change rate during stretching, it is now necessary to figure out how to fully utilize the properties of liquid metals. This is because liquid metal composites, when used in flexible electronics, have poor electrical conductivity and need to be sintered and further processed.

4.4 Soft robotics

Soft robots could be used for rescue, detection, and surveillance in limited and complicated environments.[130,179] Soft robots can carry out intricate medical procedures like cell manipulation, medical picture acquisition, and drug distribution in the realm of medicine.[131] Fluid-based soft robots include water droplet robots, ferromagnetic fluid robots, liquid metal robots, *etc.* Due to their tremendous flexibility and electrical conductivity, liquid–metal robots have drawn the most interest.[129,132] Based on different modification methods, at present, the main driving modes of the liquid metal soft robots include electrochemical drive,[133,197,211] magnetic field drive,[134] optical drive,[135] *etc.* Different modes are applied in different fields and environments.

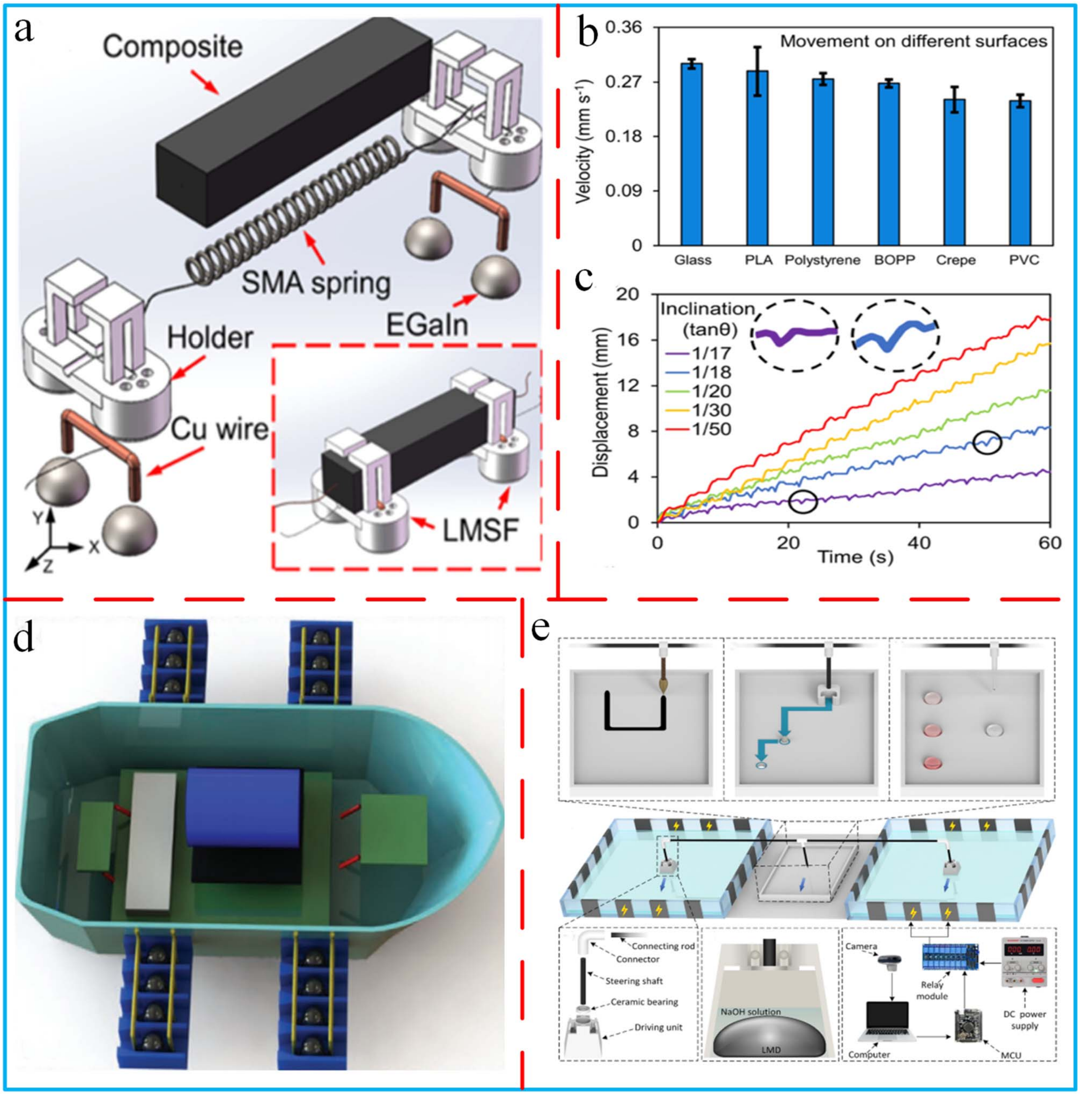

Fig. 14 (a) Soft robot with a liquid metal as a foot. (b) Liquid metal footed soft robot capable of moving on contact surfaces of different materials. (c) Liquid metal footed soft robot moving on contact surfaces of different slopes (reprinted with permission from ref. 136. Copyright 2021, American Chemical Society). (d) Liquid metal driven boat (reprinted with permission from ref. 137. Copyright 2021, Wiley-VCH). (e) Electrochemically driven power transfer system for the liquid metal (reprinted with permission from ref. 138. Copyright 2022, Royal Society of Chemistry).

Fig. 14a shows a soft robot based on electrochemical drive.[136] The electrochemical mechanism of a liquid metal in NaOH solution regulates the formation of a surface oxide coating. In contrast, when the electrolyte is not submerged, a thicker oxide layer will form on the surface of the liquid metal, increasing the friction with the contact surface and stopping the motion. When the solution submerges the liquid metal, the surface oxide layer will be removed, the liquid metal's surface becomes smooth, and the motion of the robot changes to sliding. This technique can move the liquid metal robot on multiple planes as well as up slopes (Fig. 14b and c), giving it the ability to serve as a load transporter. In the future, more liquid metal feet will be used, and each foot's condition will be controlled by a chip, allowing for more precise movement, such as steering. In addition to moving on land, a ship that uses the movement of a liquid metal as forward momentum is also designed (Fig. 14d).[137] Through electrochemical control, the boat is propelled on the water's surface by the driving force produced by the movement of numerous liquid metal droplets on both sides of the hull. The precise control of the control circuit can alter the movement of various liquid metals to achieve various boat movement directions. The liquid metal that is electrochemically controlled must be moved in solution, which restricts its use in other settings. The range of action of the liquid metal can be substantially expanded by adding a robotic arm and syncing the arm's motion with the flow of the liquid metal. This also enables new functionalities with modifications to the actuation unit (Fig. 14e).[138]

Magnetic fields can be used as another means of moving the liquid metal. The liquid metal can travel in a fixed direction under the influence of a magnetic field by adding metals with magnetic properties, such as iron powder. This is due to the magnetic orientation arrangement of the internal magnetic particles under the influence of a magnetic field (Fig. 15a). In

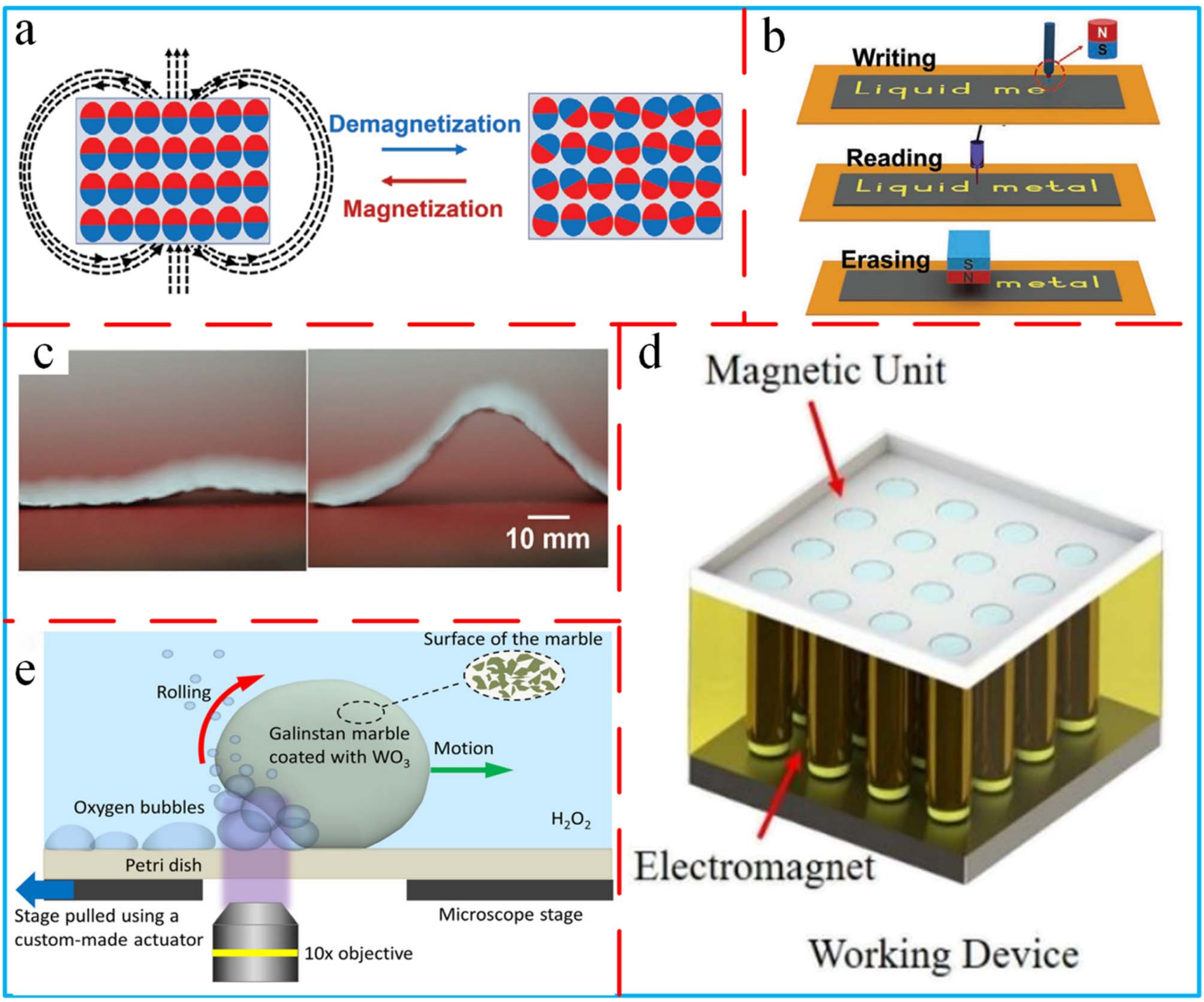

Fig. 15 (a) Distribution of magnetic particles in a magnetic field. (b) Writable and erasable composite materials. (c) Flexible robots that can move in magnetic fields (reprinted with permission from ref. 139. Copyright 2020, Wiley-VCH). (d) Schematic diagram of the PDLM platform (reprinted with permission from ref. 140. Copyright 2020, American Chemical Society). (e) Schematic diagram of the light-controlled liquid metal soft robot (reprinted with permission from ref. 181. Copyright 2013, AIP).

addition to giving the liquid metal the ability to manipulate magnetism, the inclusion of magnetic metal particles also significantly lowers the surface tension of the liquid metal. Cao *et al.* mixed a liquid metal with NdFeB, and the resulting hybrid material was able to write on a flat surface and be erasable (Fig. 15b).[139] And flexible robots made of this material can also move in magnetic fields (Fig. 15c). Utilizing the idea of magnetic field control of liquid metals, Li *et al.* created a programmable digital liquid metal (PDLM) control platform (Fig. 15d).[140] The motion of magnetic liquid metals can be controlled using this control platform to achieve a number of motion modes, such as controlling the separation and aggregation of liquid metal droplets. The precision of this magnetic field control is not very good, and hence more research into magnetic control techniques at the micro- and nano-scales is required.

Light-induced drive is a chemical reaction-dependent drive technique that uses the force created by the reaction to move liquid metal droplets (Fig. 15e).[181] The liquid metal droplet has a coating of WO_3 nanoparticles applied to its surface. The droplet is then submerged in a hydrogen peroxide solution, where the reaction between WO_3 and hydrogen peroxide is catalyzed by UV light to release oxygen, which causes bubbles to form in the solution and move the liquid metal droplet. There are certain requirements for the chemical reaction's intensity in order to propel liquid metal droplets; a reaction that is too sluggish will not provide enough propulsion, while one that is too intense will cause the light beam to move more slowly than the droplets do. Another disadvantage of this strategy is that it cannot be employed in interior or other dark situations because it fails in areas where light cannot penetrate.

4.5 Thermal management

The use of a liquid metal as a thermal conductivity medium is crucial. Liquid metal-based thermal pastes are commonly utilized in computer CPU cooling and are readily available on the market. It is a potential candidate for the next generation of thermal interface materials due to its excellent thermal conductivity and fluidity.[202] Studies that summarize the heat

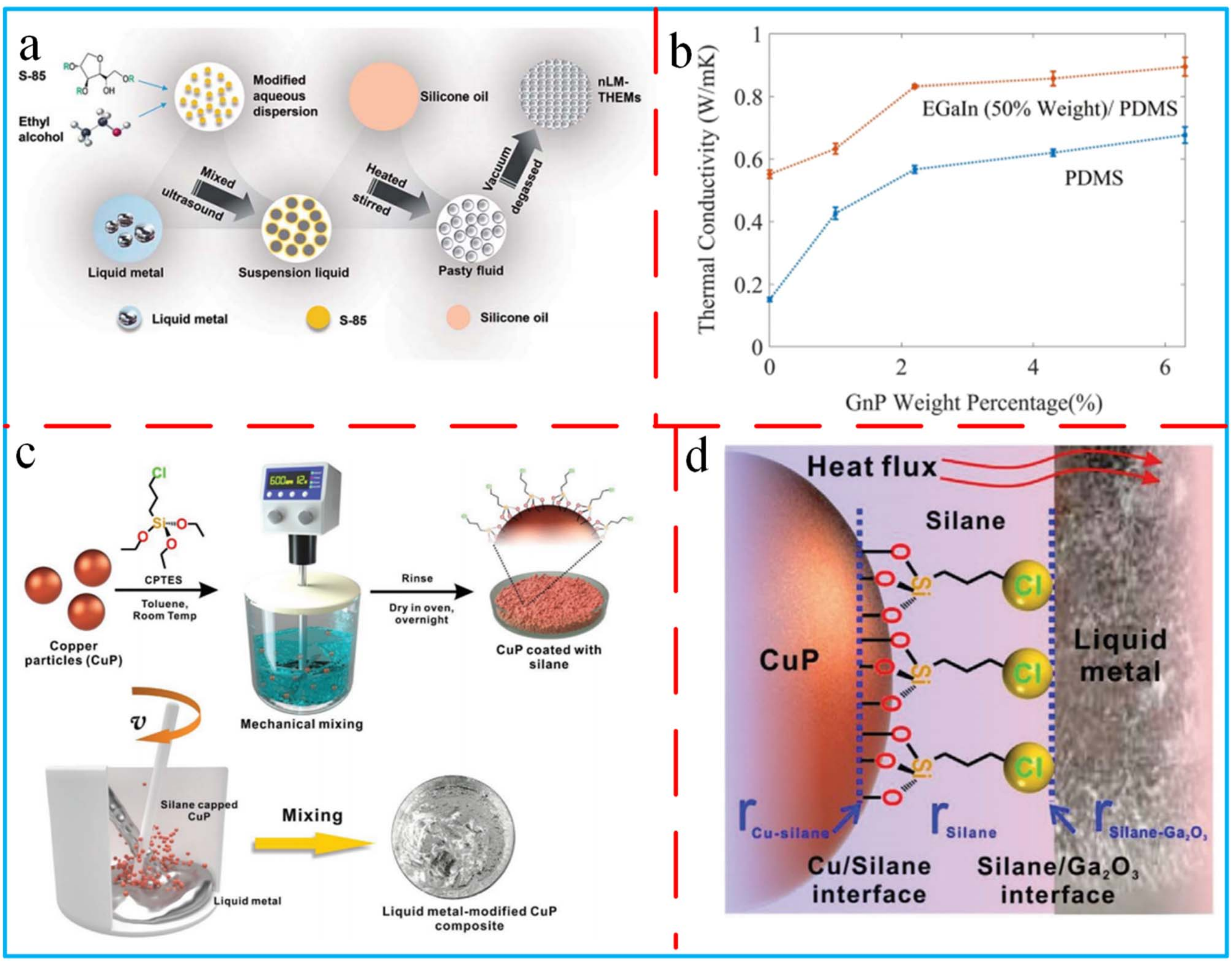

Fig. 16 (a) Preparation process of nLM-THEM (reprinted with permission from ref. 205. Copyright 2018, Royal Society of Chemistry). (b) Graph of GnP weight *versus* material thermal conductivity (reprinted with permission from ref. 207. Copyright 2019, ECS). (c) Flow chart of CPTES for surface treatment of copper powder and mixing with a liquid metal to formulate a thermally conductive material. (d) Schematic diagram of CPTES to increase heat transfer performance (reprinted with permission from ref. 206. Copyright 2021, Wiley-VCH).

transmission characteristics of liquid metals have been conducted, and significant progress has been made.[203] This chapter concentrates on the application of liquid metal modification techniques in the realm of heat transfer, even though many devices, such as thermoelectric generators, can be created utilizing the thermal conductivity of EGaIn itself.[204]

The additive method is the one that works best for the field of heat transfer out of all the different modification techniques. Although the liquid metal itself has good heat transmission capabilities, mixing it with other materials can increase thermal conductivity and decrease fluidity, preventing the difficulty brought about by its excessive fluidity. Fan *et al.* obtained

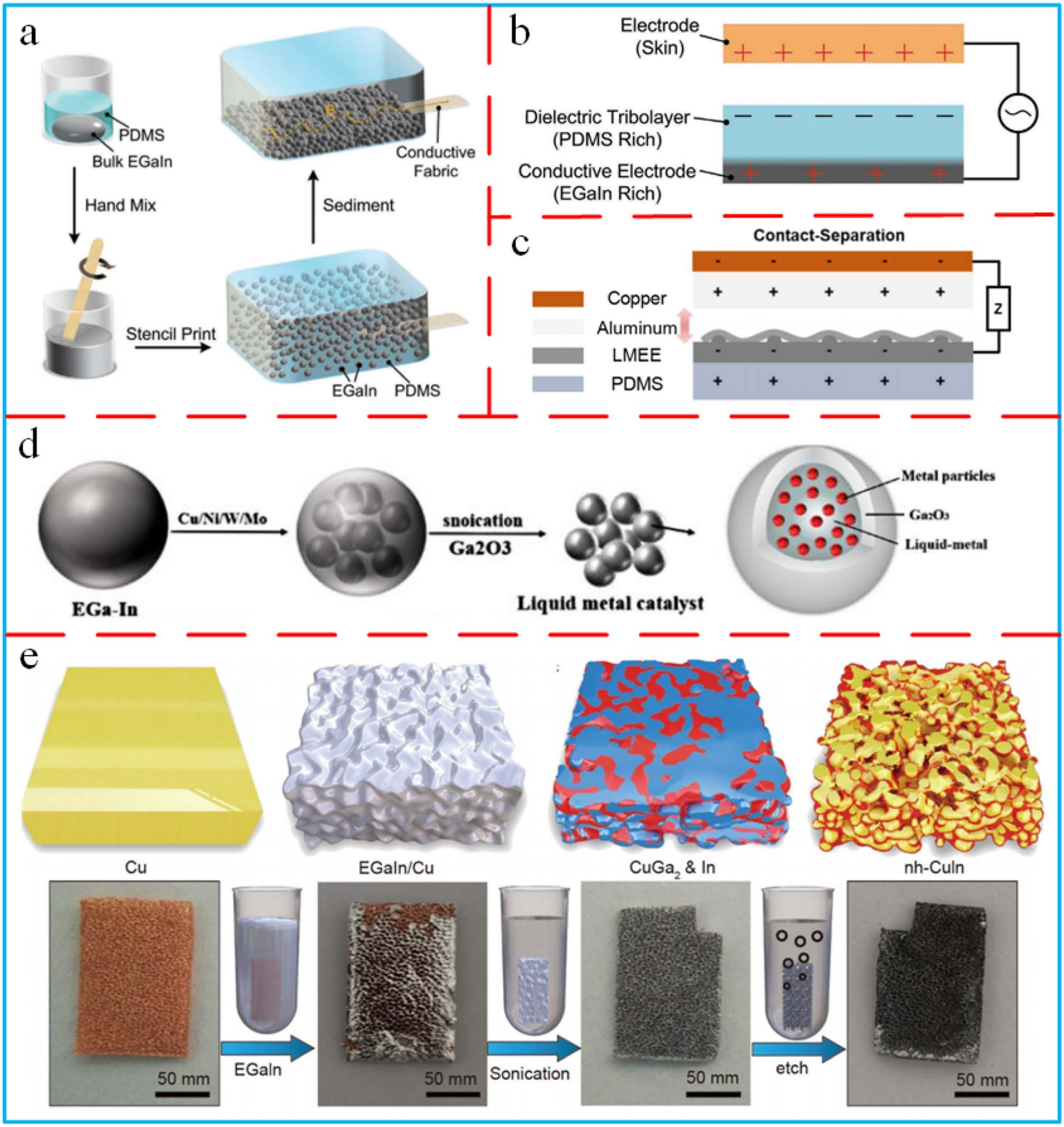

Fig. 17 (a) Preparation process of liquid metal-PDMS hybrid materials and the mechanism of electrical conductivity. (b) Working principle of a TENG prepared from a liquid metal and PDMS hybrid material (reprinted with permission from ref. 185. Copyright 2020, Wiley-VCH). (c) Schematic diagram of LMEE to increase the surface roughness of the TENG (reprinted with permission from ref. 186. Copyright 2022, American Chemical Society). (d) Flow of EGaIn mixed with different metals to form a core–shell structure (reprinted with permission from ref. 187. Copyright 2021, MDPI). (e) EGaIn and copper foam form porous structures (reprinted with permission from ref. 188. Copyright 2022, Springer Nature).

materials with high thermal conductivity and electrical insulation by combining modified polymers and well-dispersed nanoparticles (nLM-THEM) (Fig. 16a).[209] Liquid metal microdroplets can link with one another to create more thermal conductivity pathways and improve thermal conductivity. Additionally, the surface modification ensures a superior electrical insulation effect, allowing for sustained electrical insulation performance even under heavy stress as well as the prevention of leaks and corrosion. The maximum thermal conductivity of LM-THEMs reached 6.73 ± 0.04 W m^{-1} K^{-1} with a filling ratio of 85.7% (v/v), while the volume resistivity at 220 V was 2.09×10^9 Ω m. Similarly, Sargolzaeiaval *et al.* measured the effect of EGaIn and graphene nanosheets (GnPs) on the thermal conductivity of PDMS.[207] According to Fig. 16b, the material's overall heat transfer performance improves when the GnP weight increases and the addition of EGaIn increases the heat transfer level of the material by nearly 1.3 times while maintaining its outstanding electrical insulation.

Despite the fact that many of today's liquid metal thermal conductivity composites are made of liquid metals and metal fillers, and *in situ* metallization between gallium and many metals causes the material to be unstable. Wang *et al.* used 3-chloropropyltriethoxysilane (CPTES) to prepare copper particles and combined them with a liquid metal to create composites that had high thermal conductivity and stability (Fig. 16c).[206] According to Fig. 16d, the silane with the chlorine group at the end acts as a thermal linker between copper and Ga_2O_3, resulting in an overall thermal conductivity of 65.9 W m^{-1} K^{-1}. The silane wrapped around the copper surface also created a barrier between Cu and EGaIn, which significantly slowed the alloy's rate of formation and increased stability.

4.6 Others

The aforementioned applications, which are often utilized, have modified liquid metals to varied degrees. This chapter will provide a comprehensive summary of those applications that use modified liquid metals but have less relevant research and are not extensively used.

The most crucial qualities of frictional electrodynamic nanogenerators (TENGs), which have great stretchability and electrical conductivity, are their application as an energy collecting device in a variety of wearable devices.[198] A liquid metal and PDMS phase were combined to create a liquid metal-based TENG by Pan *et al.*[185] The liquid metal in the PDMS sinks to the bottom due to its own gravity and collects there to form a conductive channel, as seen in Fig. 17a and b. After undergoing friction, the liquid metal at the bottom has the same charge as the skin while the PDMS in the dielectric layer has the opposite charge, creating a circuit. This SLM-TENG has a maximum stretch rate of over 500% and is simultaneously extremely flexible, stretchy, and robust. Further applications are made possible by its incorporation into clothing. A TENG is often generated by frictional charges, and adding surface texture to promote friction with the skin can enhance the transfer of frictional charges (Fig. 17c).[186] The performance of the TENG was greatly improved when the microtextured LMEE electrode was in contact with and separated from the aluminum counter electrode because open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) increased by 18.2% and 16.4%, respectively.

Additionally, there are numerous uses for liquid metals in the realm of catalysts.[200] The capacity of liquid metals to remain liquid at room temperature, enabling the use of liquid-phase catalysis, is their greatest advantage over conventional solid-phase catalysts.[201] To increase the number of reactions that a single material can catalyze and the range of applications it can be used for, liquid metals must be combined with other substances. Liang *et al.* combined liquid metals with nickel, copper, tungsten, and molybdenum, respectively, to construct core–shell structures and used them to catalyze the breakdown of organic contaminants using photocatalysis, as illustrated in Fig. 17d. The electrical structure of liquid metal catalysts can be altered by the addition of precious metals, greatly enhancing the catalytic effect. The mixture of nickel and a liquid metal produced the best catalytic action, with degradation rates for methylene blue and Congo red of 92% and 79%. In addition, Ma *et al.* carried out additional research on the hybrid to produce nanoporous copper-indium heterostructures with effective CO_2 reduction.[188] When the copper foam is covered with EGaIn at room temperature, $CuGa_2$ and In are produced, and an alkali solution treatment yields a porous copper-indium catalyst (Fig. 17e). The porous structure offers more reaction sites than other catalysts that can only react on the surface, considerably increasing the effectiveness of the process. After adjusting the working potential, the H_2/CO ratio increased from 0.47 to 2.0, and after 70 hours of continuous operation, the current density remained at 96%.

5. Challenges

Recently, the modification methods of liquid metals have been researched extensively and have proven their feasibility in many fields such as medical fields and flexible electronics. However, there are still a large number of difficulties in the process of commercial application. Here, we outline the challenges that liquid metals face in practical applications.

(1) The existence of an oxide layer is a double-edged sword in developing liquid metal-based electronics. The presence of an oxide film helps to reduce surface tension and shaping, preventing the formation of liquid droplets; however, the oxide layer on the surface of the liquid metal increases the difficulty of processing, and it is difficult to bring out the excellent electrical conductivity of the liquid metal in the application process. In addition, the surface oxide layer adheres to the contact surface, which creates an obstacle to the driving of liquid metals. Although the oxide layer can be removed using an acid or alkali, this method is too complicated and requires additional equipment.

(2) In the field of transparent electronics, extremely fine line widths are often required to ensure high light transmission.[78] In the case of direct printing on liquid metals, the high surface tension makes it difficult to control the line width during printing, and the presence of an oxide layer makes it easy to

stick to the inner wall of the nozzle during printing and causes clogging. Current research on liquid metal printing usually involves modification to form composites to reduce surface tension; for example, Young-Geun Park *et al.* mixed a liquid metal with carbon nanotubes to enable high-resolution printing with the finest line width of 5 μm.[142] Compared with other materials,[182] this seems to be the limit of what can be achieved with this method at the moment, and no composite material can achieve finer line widths in this way. And there are very few composites that can be printed with line widths of less than 10 microns, which is also a problem at the moment. In the trend of increasingly miniaturized electronic devices, it is urgent to form a variety of material systems to reduce the width of the printed line.

(3) When modifying liquid metals and performing high-resolution printing, turning liquid metals into tiny droplets by ultrasonic treatment as well as stirring is a common method; however, the tiny droplets can easily fuse with each other after removing the oxide layer of liquid metals. At present, many researchers have used various methods to wrap a shell around liquid metal microdroplets to form a shell–core structure and separate liquid metal droplets through chemicals. But this method has a great impact on electrical conductivity and requires external stimulation such as heating and sintering and pressing to make them conductive, which greatly affects the application of liquid metals. Therefore, further research is needed on how to uniformly disperse liquid metal microdroplets without affecting the overall electrical conductivity.

(4) Currently, in flexible electronic devices, electrodes, capacitors, and chips are single-layer structures.[121,170] With the increase of computing power and in the pursuit of transparency, miniaturization, and integration, the single-layer

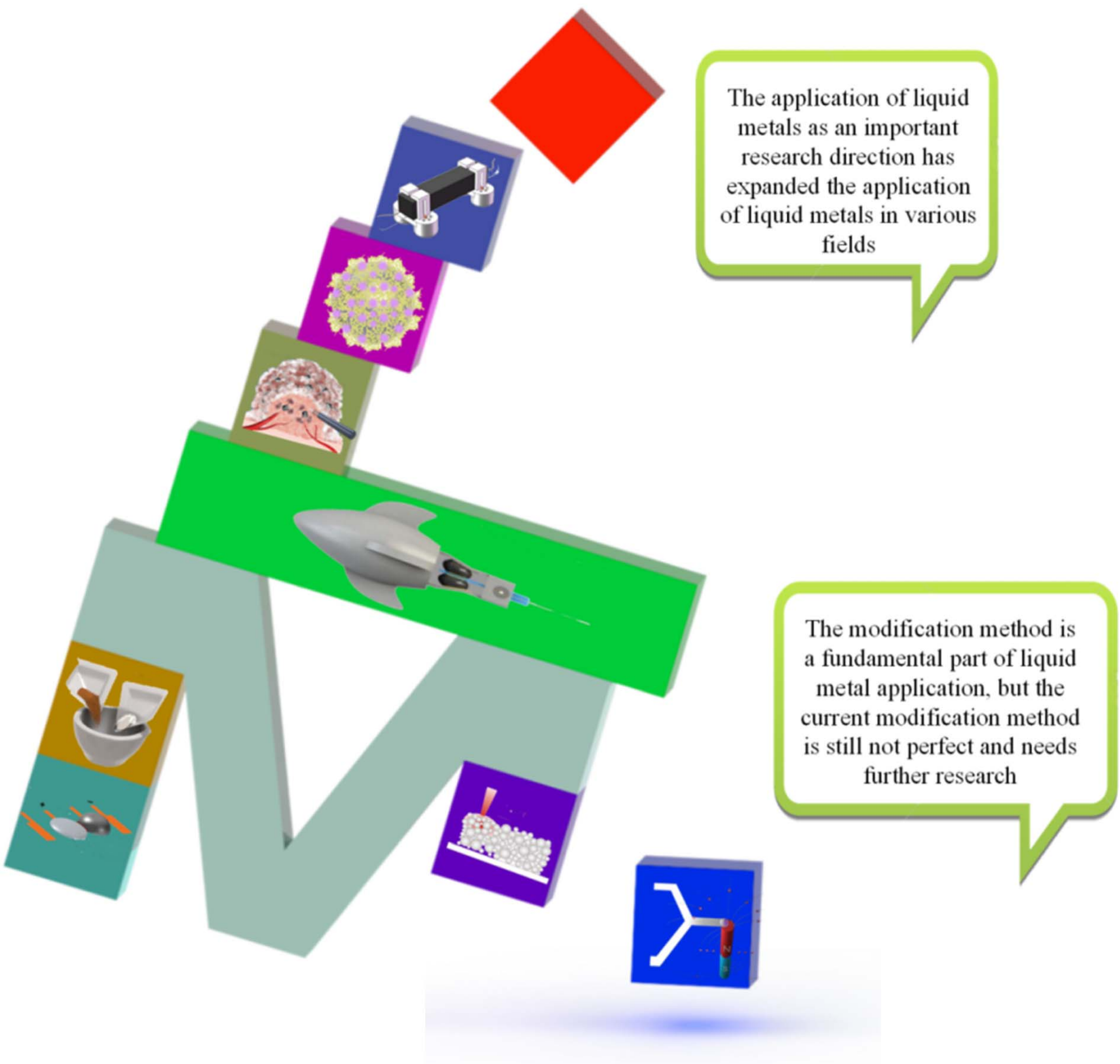

Fig. 18 The development of liquid metal modification is still imperfect, and new methods need to be found to continue to drive wider application.

structure is increasingly unable to meet the demand. Therefore, the multi-layer structure has become the development trend of future electronic devices.[65] Under this development trend, the good liquidity of liquid metals has become an obstacle to the wide application in the field of multilayer electronics, and it is difficult to overcome the fluidity for multilayer printing or even vertical printing. The printing of vertically interconnected wires requires overcoming the fluidity of the liquid metal and ensuring its excellent electrical conductivity, so it is necessary to find suitable materials and methods to modify the liquid metal removing the oxide layer.

(5) The problem of poor wettability and adhesion of liquid metals on some substrates also remains unsolved. The contact angle of the liquid metal on copper or nickel plate can reach about 50°, while the wettability of the liquid metal on other substrates is very poor. At the same time, the adhesion of the liquid metal on the PDMS substrate commonly used in flexible electronics is difficult. The high-resolution direct printing of liquid metals has a great relationship with the adhesion of the substrate, and the printing of smaller line widths can be more easily achieved on a substrate with good adhesion, so enhancing the adhesion of liquid metals to flexible substrates also needs further research.

(6) Recently, the modification methods regarding liquid metals have been widely explored and have been developed with different materials. However, the exploration of the surface interface of liquid metals is still far from enough, and the current research only stays at the application level, and does not study the principle in depth. Therefore, the study of the surface interface of liquid metals is one of the future research directions. Increasing the study of the surface interface can be a deep understanding of the connection between the surface of liquid metals and other materials, which can find new phenomena, and can get more and better modification methods.

6. Conclusions

This paper reviews the causes of surface tension of liquid metals and the influencing factors, including humidity, microscopic surface factors and the influence of chemical substances. It also introduces methods to change the surface tension of liquid metals and their applications in the medical field and wearable devices (Fig. 18). The research on the factors affecting the surface tension of liquid metals is still insufficient, and although many different hypotheses and theoretical systems have been formed for some factors, there are still some factors that are rarely studied. The theoretical system of surface tension of liquid metals should be studied more completely and deeply in the future. At present, the methods to reduce the surface tension of liquid metals are limited and the effect is not ideal. Electrochemical methods need to solve the problems of complex equipment and harsh environmental requirements in the future, so the application range is more extensive. The research of liquid metal polymers still has a great development space. The development of composite materials having excellent performance and processed on a large scale can become an important development direction. In the field of medical devices, flexible electronics has a broad and bright future. Electronic skin can be used in the medical field instead of sensors in the future, with body indicators for real-time and accurate monitoring. However, the comfort and functionality of electronic skin are still difficult to meet the requirements. In the future, it is possible to develop a flexible skin that can sense sweat, stress and blood and other human substances, and in terms of comfort, it can increase breathability, reduce weight and be closer to the skin.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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