Surface Modification of Liquid Metals and Patterning towards Biomedical Applications

Ziyang Huang[#], *Ziting Bao*[#], *Duo Zhang**, *Guozhen Liu**

Integrated Devices and Intelligent Diagnosis (ID^2) Laboratory, CUHKSZ-Boyalife Joint Laboratory for Regenerative Medicine Engineering, School of Medicine, The Chinese University of Hong Kong, Shenzhen, 518172, China

[#]Contribution equally

E-mail: liuguozhen@cuhk.edu.cn (G.L.), duozhang@cuhk.edu.cn (D.Z.)

Abstract

Liquid metals are a category of emerging materials possessing massive potentials in biomedical engineering, including biosensing, drug delivery, patterning and wearable electronic devices. Besides their high electrical conductivity and flexibility, the high surface activity and shape fidelity allows liquid metals to achieve improved printability. However, as liquid metals are prone to oxidation, preliminary surface treatment was critical in various applications with desirable performances. The modification methods generally include sonication in ligands solution, galvanic replacement reaction and electroplating, aiming to reduce the oxidation of liquid metals while introducing functional groups for the subsequential bio-designs and manufacturing. Herein, recent development in strategies for liquid metal surface modification and patterning, is reviewed and discussed. Various patterning techniques and biomedical applications utilizing liquid metal inks are summarized, and perspectives of liquid metal additive manufacturing in future applications are proposed.

Keywords

Liquid metals, Surface modification, Patterning, Wettability, Bioengineering

Article Highlights

- Various modification methods were explored to reduce the oxidation of liquid metals while introducing functional groups for the subsequential bio-designs and manufacturing.
- Liquid metal-based bio-ink can be used for patterning towards various biomedical applications.
- Challenges include scaling up production methods, improving biocompatibility and long-term stability, and addressing potential safety concerns.

1. Introduction

Liquid metals, also known as liquid alloys, are a special type of metallic materials that are liquid rather than solid at room temperature[1-4]. Liquid metals demonstrate excellent biocompatibility[5], flexibility[6-7], as well as electric and thermal conductivity[7-8] for various applications. Liquid metals have been utilized in a variety of bioengineering applications including biosensing[9-11], drug delivery[12-13], microfluidics[14-16], soft electronics[17-18], etc. Mercury, cesium, and rubidium haven't been widely used, due to their inevitable toxicity or high chemical activity[19]. Therefore, more and more research has focused on gallium-based liquid metals, which are non-toxic and remain stable in both air and water; scientists have revealed a series of unique properties of such materials[20-21]. For example, Gallium-based liquid metal, particularly eutectic gallium indium (EGaIn) and Galinstan, is an alloy composed of metallic elements such as gallium and indium in the liquid state at room temperature[22-24]. Galinstan was first reported by Duwez when they discovered ways to rapidly quench gold-silicon alloys to produce non-crystalline alloys[25]. The high surface tension of Galinstan makes it compatible with biological samples, and applicable in biomedical applications including biosensing and drug delivery[26-27].The low melting point and low toxicity characteristics also enabled Galinstan to be directly used in the human body for disease treatments and hydraulic operations in surgery[28-29].

The surface tension of Galinstan with different compositions is between 500-700 mN m^{-1}under room temperature, higher than that of water (~72.8 mN m^{-1})[30-31]. In particular, the surface tension of pure EGaIn droplet is about 435 mN m^{-1}, while the surface tension of EGaln droplets grown in ambient condition is about 624 mN m^{-1}[32]. As generally the increase in surface tension indicates smaller particle size[33], the increase in surface tension implies that EGaIn can form larger droplets. At the same time, gallium oxide film also alters the mechanical properties of EGaIn droplets, making EGaln droplets to have elastic properties. When the surface stress exceeds 500 mN m^{-1}, the droplets show liquid fluidity. Due to high surface tension, liquid metals are difficult to adhere to most substrates and tend to form sphere patterns[34-35]. In the previous study regarding to the adhesion characteristics of EGaIn ink with different substrates[36], it can be seen that compared with pure EGaIn, the oxidized EGaIn ink has better adhesion properties with the substrate. In addition, the adhesion of EGaIn ink to different substrates varies. Liquid metals have different adhesion characteristics on different substrates, which can be used to screen the matching liquid

metal inks and printing substrates. Subsequent research on direct writing flexible electronic circuits and devices also indicates that the oxidation process of liquid metals is an important way to regulate the adhesion of such inks to specific substrate materials[37]. However, the existence of oxidation layers would significantly weaken the performance of EGaIn in electric and thermal conductivity. As a solution, the modification of ligands could inhibit the growth of the oxide layer on liquid metals, while providing functionalization and high stability for biomedical applications[38]. Therefore, the modification of liquid metals are usually required before being utilized for patterning or printing.

Soft electronics patterning is an emerging manufacturing technology in recent years. It uses traditional printing methods such as silk-screen printing and inkjet printing to transfer conductive, dielectric or semiconductor materials onto the substrate, so as to fabricate electronic devices and systems[39-40]. Comparing to traditional methods of electronic manufacturing, printed electronics offers significant advantages including large-scale production, cost-effectiveness, personalization, flexibility, low energy consumption, and environmental-friendly processes. Due to their high surface tension and native oxides, liquid metals are difficult to spread uniformly over large areas on solid surfaces, and they provide stable conductivity over long periods of time on a variety of substrates[41]. Therefore, surface modification and sonication of liquid metals are popular strategies in manufacturing inks towards liquid metal patterning. The conductive ink used in flexible electronic additive manufacturing is mainly composed of conductive fillers, binders, additives, and solvents[42]. The substrates used in printing electronic technology can be plastic, metal, glass, textiles, ceramics or paper[43-45]. Printing electronics is closely related to organic electronics, plastic electronics, flexible electronics, paper electronics, etc. For instance, Dickey highlighted techniques to pattern the shape of liquid metals (such as EGaIn) focusing on their applications in stretchable electronics, reconfigurable antennas, soft robots, wearable sensors, and e-skins[46].

In this review, a detailed summary of the liquid metal surface functionalization and biomedical applications is provided (Figure 1). The chemical modification processes of liquid metals and its applications in physical patterning is introduced, highlighting the advantages of liquid metals in biomedical engineering applications and emphasizing their enormous potentials in the field of precise medicine. In terms of chemical modification, different modification methods were summarized, including small molecules, polymers, carbon nanomaterials, etc.. As for the

patterning, a detailed introduction was given to the printing methods of liquid metal and elastomer composite materials, including direct writing[47], silk-screen printing[48], inkjet printing[49], sound penetration printing[50], sealing transfer[51], laser etching[52], and other patterning technologies[53]. In addition, in depth applications based on liquid metal materials in biomedicine were summarized. Finally, the prospective view and challenges of liquid metals as new functional materials in biomedical engineering are discussed, providing insights on liquid metals for future precision medicine development[46].

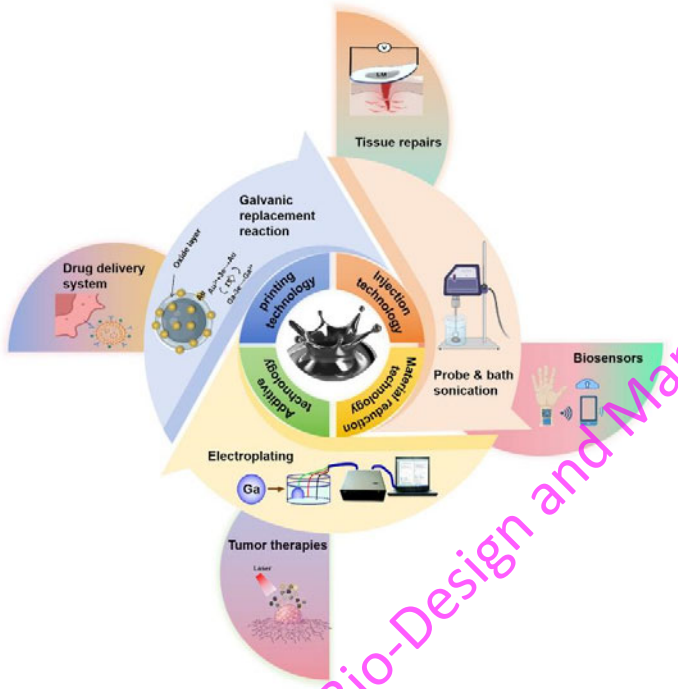

Figure 1. Schematic illustration showing the content of this review.

2. Modification of Liquid Metals

The fabrication and modification of liquid metal nanoparticles (LMNPs) usually involves probe sonication and energy to break down the EGaIn droplets into nanoparticles[54-56], together with other methods including nebulization[57], microfluidic[58-59] and filtration[55]. During the fabrication process, as the liquid metals are also prone to oxidation, the oxides on liquid metal bulks are fractured and a new layer of oxide is formed, preventing recombination of the liquid metal. Nevertheless, during sonication, the oxide film formed on liquid metals is not as conductive and stretchable as the liquid metal itself. The oxide layer of Ga_2O_3 is also prone to react with water to

form rod-like crystals (GaOOH), further degrading the performance of the material. Therefore, inhibiting the growth of oxide is crucial for enhancing the performance of liquid metals. It is reported that chemical modification has been utilized for oxide inhibition as well as functionalizing for liquid metal droplets[38]; the oxide thickness is decreased to 30% by modifying the thiolate molecules. Surface modification is also necessary for applications that do not require high conductivity (such as drug delivery), in order to stabilize and functionalize the LMNPs with desired properties[60].

Compared with other methods, probe ultrasonic preparation of EGaIn nanoparticles has the advantages of high efficiency, high homogeneity, energy saving, and controllability[61-63], as the ultrasonic preparation method stimulates production speed and tunable nanoparticle size distribution[52]. In addition, the ultrasonic preparation method is resource-saving, more accessible and environmental friendly[64-66]. Therefore, this review presented a comprehensive introduction to the fabrication and modification of liquid metals using sonication. In addition, this article systematically summarized the patterning of modified liquid metals, the integration of their chemical modification, and the patterning processes. By galvanic replacement reaction, metal nanoparticles could be modified on liquid metals, and form coated liquid metal droplets spontaneously, which alter the wettability of liquid metal effectively[67]. In addition, electroplating could accelerate the process and form a stable metallic layer on the liquid metals. Table 1 lists different surface modification methods of liquid metals comparing their advantages and disadvantages. The advances in these modification pathways were discussed in this section.

Table 1. Modification methods of liquid metals with advantages and disadvantages.

Methods	**Mechanism of Fabrication**	**Advantages**	**Disadvantages**	**Characteristics**		**Applications**	**Ref**
Probe & bath sonication	Rely on the affinity between ligands and the liquid	Simple fabrication process, variable ligands,	Inhomogenuous size distribution, extra ligands remain,	Ligand molecules	Higher conductivity, tunable wettability, uniform size	Biosensing, soft robotics, drug delivery,	[68-70]

	metals, ultrasound needed.	particle size down to nanometer	equipment needed		distribution	bioimaging, printing ink, electronics	
				Polymer	Improved biocompatibility, higher stability		[12, 71]
				Carbon	Higher electrical conductivity, higher stability, increased stiffness		[3, 72]
				Silk	Conductivity recovery, high flexibility		[73]
Galvanic replacement reaction	Displacement reaction between ions of Au, Ag, Cu, etc. and Ga to form a metal layer on the surface	No equipment needed, simple process, forming variable metallic composite	High cost of the materials, time consuming	Uniformed decorated morphology of nanoparticles, enhanced thermal conductivity and wettability		Photothermal therapy, micro-patterning, battery material, photocatalysis	[74-76]
Electroplating	Application of a current causing metal ions on the metal anode to oxidize to anode ions	Robust modification, timesaving	Equipment needed, small-scale modification	Tunable wettability of the material, solid modification of bulk liquid metals		Electrode modification, self-propelled motor, modification of liquid metals	[67, 77-78]

2.1 Probe & Bath Sonication

2.1.1 Small molecules

There are several pathways to fabricate LMNPs, and one of the simplest and most common ways is to perform probe ultrasonication in a solution with ligands. Thiolate molecules are commonly utilized in the modification of liquid metals, since they can assemble on the surface of both Ga oxides and EGaIn[12, 79]. The modification process usually involves probe sonicating the liquid metal bulk in the presence of thiol ligands, during which the bulk was dispersed in the solution and a self-assembled monolayer (SAM) of ligands was formed on the particle. SAM reduces the ultimate size of the particles and inhibit the formation of the oxide layer. Some strongly interactive molecules induce surface strain and prompt the particles to split into nanoscale ones. In addition, the structure of the ligand also influences the yield and properties of the nanoparticles. Early in 2011, Hohman fabricated LMNPs with the help of thiolate SAMs as ligands and the size of liquid metal particles was reduced significantly[69]. Liquid alloy was dispersed by ultrasound in ethanolic thiol that self-assembled at the interface of EGaIn, which protected the material from oxidation. 3-Mercapto-N-propionamide (1ATC9), and 1-dodecanethiol (C12) were utilized and nanoparticles capped by both molecules have similar morphologies. However, 1ATC9 capped nanoparticles are formed in higher yields, as the number of nanoparticles is increased and the size is decreased. This is due to the amine group on 1ATC9 forming hydrogen bonding that pulls the nanoparticles toward each other and strains the interfaces which continues the cleavage of particles. Farrell and Tabor utilized thiols to form SAM on EGaIn nanoparticles and found their inhibition effect on the oxide growth [38]. Three different thiols were used to modify EGaIn nanoparticles, and their Scanning Transmission Electron Microscopy (STEM) figures were illustrated (**Figure 2**a). The arrows next to the structural formulas indicate their dipoles can affect the working function of the metal core, and further control the oxide growth. 2,3,4,5,6-pentafluorothiophenol (FTP) shows the optimized oxide inhibition effect with increased work function, since the dipole of the molecule delocalizes electrons out of the metal surface. Each research shows that the SAM ligand structure can be engineered for different purposes. Farrell also explored the effect of SAM formation pathways on oxide layer thickness, involving modifying the nanoparticle with thiols, phosphate acids (PAs), and a mix of thiols and PA[80]. The thickness and their respective STEM images and XPS spectra of Ga 3d are shown in **Figure 2b**; the result indicates the inhibition effect of thiols and PA SAM

on oxidation. In addition, a hybrid SAM shows better solubility since the tail-groups of the ligands are complementary to each other.

Apart from probe sonication, the liquid metal bulk can also be dispersed by bath sonication in a solution of thiols. Although probe sonication was commonly used for high power and efficiency, it may induce overheat which leads to oxidation, dealloying, and phase transformation[22, 81-82]. Guo used 1-dodecanethiol (C12) to modify the EGaIn particles by bath sonicating for high dispersion and chemical stability in the lubricating oil. The liquid metal bulk was dispersed in a bath sonicator with a cooling system that maintained the temperature at 20 °C (**Figure 2c**)[83]. The nanoparticles possess great stability and dispersibility in the PAO10 oil, which enabled further applications. Tang combined bath sonication and polydimethylsiloxane (PDMS) microchannel to fabricate and modify EGaIn nanoparticles (**Figure 2d**)[84]. The sonication wave broke the bulk liquid metal into nanoparticles at the exit of the microchannel, and the nanoparticles were only exposed to ultrasonic waves for a short time before exiting, which reduced the chance of overheat. The medium was an aqueous solution of trithiocarbonate-functionalized brushed polyethylene glycol (bPEG) which improves the stability and biocompatibility of the nanoparticles. Furthermore, the addition of trisodium citrate was found to reduce the oxidation. The result shows that EGaIn nanoparticles fabricated in a solution of bPEG and trisodium citrate have the optimized dispersity and stability (**Figure 2e**)[84].

As mentioned before, phosphonic acid (PA) also has an affinity toward the particle surface of Ga-based liquid metal and SAM can be formed in one-pot fabrication process. Unlike thiols, the attachment of PAs is longevity, irreversible and transforms from physisorption to covalent bonding[85]. Farrell utilized decylphosphonic acid (DPA) to modify the EGaIn nanoparticle[85]. The result shows that process conditions could alter the binding mode of PAs with the oxide layer. This approach provides a new direction to form colloidal EGaIn with PA molecules and gives more possibilities for functionalization and further applications. It is worth mentioning that the performance of colloidal EGaIn is different from the bulk liquid metal modified with DPA[86], potentially due to higher surface energy and surface area for colloidal[85].

In addition, tannic acid (TA) is an emerging material to modify liquid metals. For surface modification surfactant, they are widely used for their intrinsic properties such as universal adhesion, self-assembly, metal coordination, redox, and antioxidants, etc.[87] TA was chosen in the

first place to modify LMNPs because it has catechol functional groups, which could form coordination bonds as well as increase the adsorption on the substrate together with gallol groups. After the modification, the TA-enabled direct-writing method has been successfully developed, providing essential insights into the interfacial chemistry of LM nanoparticles. [88].

Probe sonication is mostly used due to its high energy and efficiency. However, it has a limitation in achieving smaller particle sizes, typically in the range of hundreds of nanometers. To overcome this limitation and obtain a smaller size range of liquid metal particles, lasers were been employed to assist in the scission of the liquid metal, and the diameter of the nanoparticle can be controlled by the laser fluences[89-91]. Bo fabricated Galinstan nanoparticles with pulsed laser irradiation and probe sonication and the average diameter goes as low as 15.67 nm (laser fluences of 300 mJ pulse^{-1} cm^{-2})[89]. Li also adopted the combined method to fabricate Galinstan nanoparticles with an average particle size of 5.49 nm at a laser fluence of 150 mJ pulse^{-1} cm^{-2} (**Figure 2f**)[90]. These two types of nanoparticle materials have been applied for anisotropic conductive adhesives and carbon-based perovskite solar cells respectively.

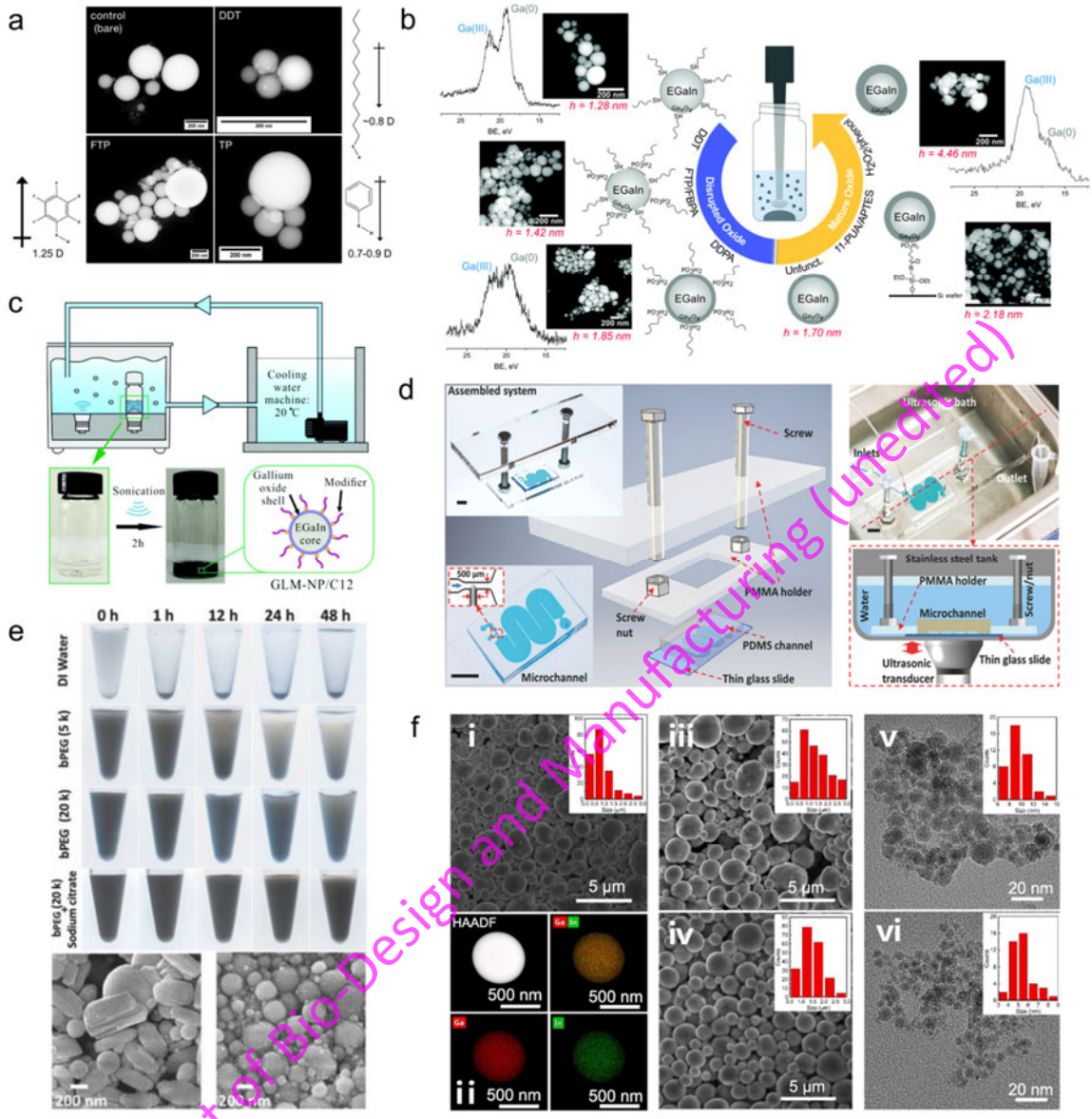

Figure 2. Thiolate molecules modified LMNPs. (a) STEM figures of thiolate molecules modified EGaIn nanoparticle.[38] (b) Different molecules to modify LMNP with associated STEM images and XPS spectra of the Ga 3d transition region.[80] (c) Fabrication process of LMNP-C12.[83] (d) Exploded schematic of the platform for on-chip production of LMNPs; The assembled system was placed in a sonication bath; Schematic of the cross-sectional view of the entire system.[84] (e) Comparison of the stability of nanoparticle suspensions obtained in different solutions; SEM images for the nanoparticles without and with the presence of trisodium citrate.[84] (f) i, SEM and ii, TEM images and size distributions of laser fabricated EGaIn particles with a laser fluence of 50, 75, 100 and 150 mJ pulse^{-1} cm^{-2} (iii-iv).[90]

2.1.2 Polymers

Polymers were usually modified on liquid metals by the affinity of hydroxyl groups or carboxyl acid groups with the help of sonication. One of the common polymer molecules for modification of liquid metal was dopamine (DA). Gan modified polydopamine (PDA) on LMNPs by sonicating bulk liquid metal in DA solution followed by self-polymerization (**Figure 3**a)[92]. The photothermal conversion property under laser irradiation of LMNPs was also explored. The PDA-modified nanoparticles had higher stability (Figure 3b)[93] and unique chemical properties. When exposed to the laser, PDA shells transferred the light energy into thermal energy and locally heat the LM nanoparticles, which would cause the spherical nanoparticles to become ellipsoidal. This property enabled PDA-coated LM nanodroplets to be further applied in soft nanorobotics, aqueous conductive inks and nanomedicines. Recently, Xu modified Ga–In–Sn alloy nanoparticles with PDA in a similar process as Gan[94]. However, the material was further modified with urease enzyme which gives good photothermal properties, asl well as dual-mode ultrasonic and photoacoustic imaging signals ability for drug delivery and imaging applications. In addition, the positive chemotaxis of the nanoparticles enabled directed transportation along a concentration gradient of urea. DA can also be modified on the LMNPs after sonication. Zhang modified Galinstan nanoparticles by distributing them in Tris-HCl solution with dopamine, carrying out the modification and polymerization of dopamine simultaneously[95]. The modified nanoparticles were further connected with graphite-like carbon nitride nanosheets (g-C_3N_4) by covalent bonds, being applicable in exosomes electrogenerated chemiluminescence biosensing (Figure 3c). Due to the excellent characteristics of the Galinstan NPs in facilitating electron transfer and suppressing the g-C_3N_4 passivation, the antibody-modified g-C_3N_4@Galinstan-PDA could recognize the exosomes specifically and exhibit stable and strong ECL signals.

Comparing with dopamine which is based on the affinity of liquid metals and hydroxyl groups, polymers can also be modified by the carboxyl groups on the monomers. Liu fabricated poly(vinyl pyrrolidone) (PVP) modified EGaIn nanoparticles by simply sonicating liquid metal droplets in an aqueous solution of PVP (Figure 3d, i), the color of modified nanoparticles was lighter than bare ones (Figure 3d, ii) and the particle size was smaller and more uniform after modification (Figure 3d, iii and iv)[96]. The stability of EGaIn nanoparticles in aqueous suspension was significantly improved, extending the durability in water from two days to 30 days and to 60 days in ethanol. The flexibility and self-repairing ability enable the nanoparticles to be applied as a composite material for energy storage. Lin modified a hydrophilic coating of poly(1-octadecene-alt-maleic

anhydride) (POMA) on liquid metals by sonicating the mixture of EGaIn, POMA-toluene emulsion in water (Figure 3e)[54]. During sonication, the emulsion broke, and POMA coated the particles; toluene was evaporated by heating, leaving POMA-LMNP in the water. The stability of liquid metal in biological buffer was also improved to 60 days without oxidation. Different from the two studies above, Yan functionalized the EGaIn nanoparticles with polymers by both one-pot synthesis and stepwise synthesis pathway[71]. In the two-step synthesis pathway, the 12-(2-bromoisobutyramido)dodecanoic acid (BiBADA) (Figure 2.3f (i)), which is an initiator that allows surface-initiated atom transfer radical polymerization (SI-ATRP), was firstly modified on the nanoparticle for polymer synthesis, followed by polymerization of monomers, while in the one-pot method, the EGaIn, BiBADA and monomers are sonicated together (Figure 3f (ii)). In addition, it is also possible to polymerize the monomer prior to the synthesized polymer coating on the liquid metal particles[97]. Fan reported a method of functionalization of LMNPs via the reversible addition-fragmentation chain transfer (RAFT) process (Figure 3g)[98]. 4-cyano-4-(((dodecylthio)carbonothioyl)thio)pentanoic acid (CDPA) is used in this process. It could stabilize EGaIn nanoparticles under ultrasonication and initiate well-controlled polymerization afterwards to achieve precise weight polymer chains.

The LMNPs themselves can also trigger polymerization reactions as initiators. Ma, J. sonicated the liquid metal and vinyl monomers in an aqueous solution, triggering a free radical polymerization which creates physical gels composed of high-molecular-weight polymers (Figure 3h)[99]. The oxide shell got ruptured during sonication, exposing the liquid metal to the monomers and triggering the polymerization. The grafted polymers can be further isolated from the nanoparticles by strong acid or base.

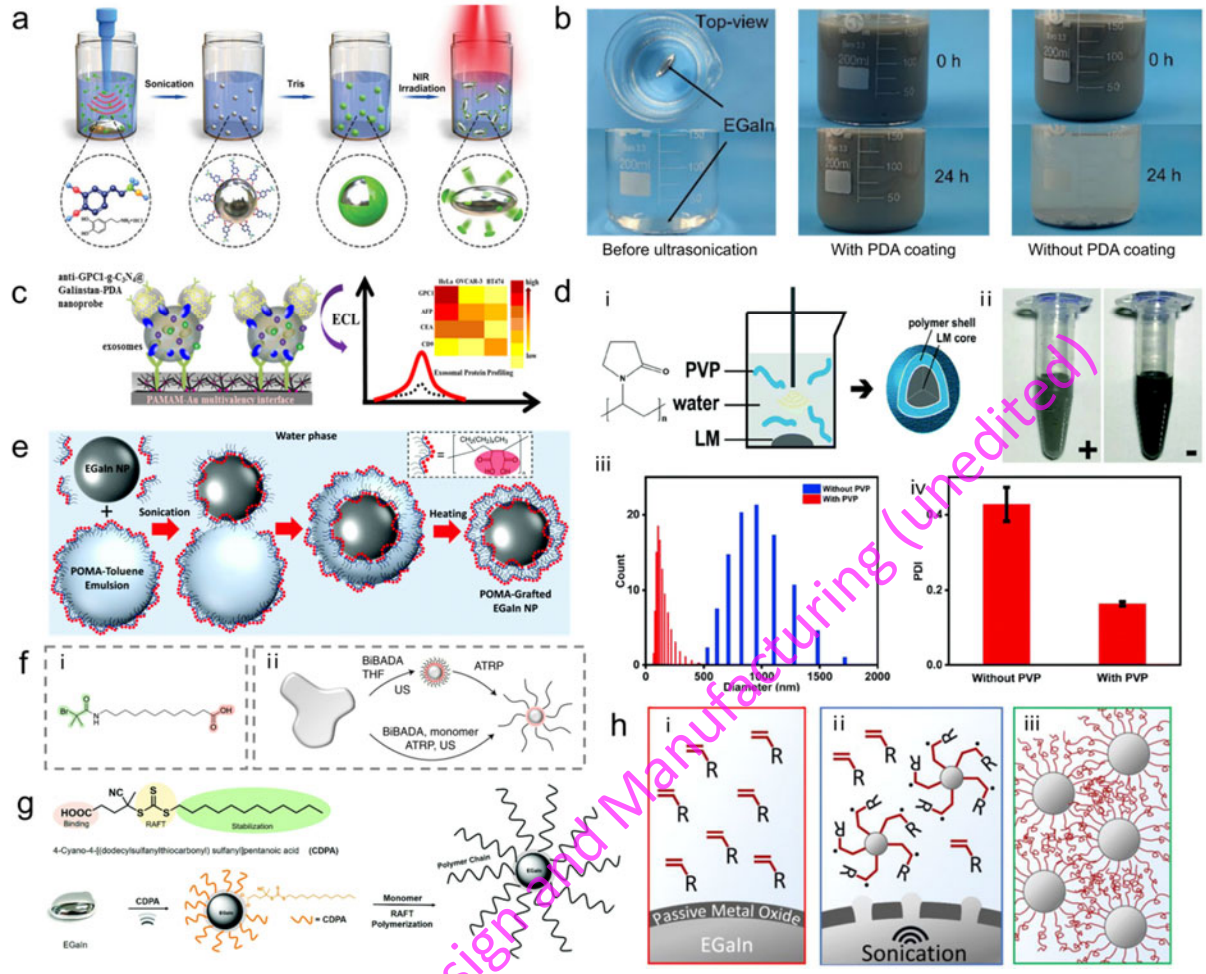

Figure 3. LMNPs modified with polymers. (a) Preparation process of PDA-coated LM nanodroplets with light-induced shape transformation.[92] (b) Comparison of the EGaIn droplet (before sonication, with/without PDA coating).[93] (c) Schematic illustration of the ECL biosensor.[95] (d) Schematic illustration of the synthesis procedure and the produced LMNP with (+) and without (−) PVP; Hydrodynamic size distribution and polydispersity index (PDI) of LMNPs produced in water and a PVP solution.[96] (e) Fabrication process of POMA-LMNP.[54] (f) i, Structure of BiBADA. ii, Stepwise functionalization of EGaIn or SI-ATRP.[71] (g) The structure of the RAFT agent–CDPA and fabrication process of CDPA-EGaIn.[98] (h) Schematic illustration of the polymerization.[99]

2.1.3 Carbon nanomaterials/Silica

One of the most frequently used materials for nanoparticle encapsulation is carbon nanomaterials, including graphene oxide (GO), reduced graphene oxide (rGO), carbon nanotubes (CNTs), graphene quantum dots (GQDs), etc. Unlike molecular ligands, carbon-based materials are larger and visible under an electron microscope. Similar to molecular ligands, carbon nanomaterials can stabilize and reduce the size of nanoparticles, and they also have the ability to influence the

mechanical and electrical properties of the nanoparticles. The fabrication process of carbon nanomaterials is also similar to the molecule ligand, involving probe sonication of liquid metal bulk in the solution of carbon nanomaterials. In addition, the decoration of metal nanoparticles on CNT is an effective strategy to enhance the electrochemical performance of various sensor applications[100-101], as the measured resistance to charge transfer of the materials is much lower after the modification[101].

Creighton explored the modification process of graphene-based nanomaterials, including GO, rGO, and thiolated GO on EGaIn particles and their influence on the stability, mechanical behavior and electrical performance of the material (**Figure 4**a)[72]. The surface of EGaIn nanoparticles capped by unmodified GO has characteristic wrinkled morphology, and GO sheets can be observed distinctly. The other two nanomaterials, rGO and thiolated GO do not show such affinity toward EGaIn nanoparticles as GO. rGO and the backbone have no affinity for EGaIn capsulation, although thiol groups have strong competitiveness with oxygen, they are anchored on the surface of GO which makes it slower to get to the surface of EGaIn than molecule ligands. Therefore, the unmodified GO has the best performance for LMNP encapsulation. In addition, GO-capped EGaIn nanoparticles showed great stability under a wide pH range from 3 and 11, and the stiffness of the nanoparticle was improved. Baharfar also utilized GO to encapsulate EGaIn nanoparticles by probe sonication. The surface morphology of the modified nanoparticles was also wrinkled, which is an evidence of successful modification (Figure 4b)[3]. Different from Creighton's research, it was unveiled that GO being reduced to rGO in the modification process, taking XPS, FTIR and ramen spectra results as evidence. The occurrence of redox reaction was attributed to the strong reducing property of EGaIn; and in this way, GO was immobilized to the nanoparticles forming an outer layer. The rGO-LM was further modified for dopamine detection and reached high sensitivity for both glass-carbon electrode and paper-electrode.

Lu encapsulated liquid metal materials with GQDs by applying ultrasound-based methods to bulk EGaIn in GQD aqueous solutions to generate transformable LMNPs (Figure 4c)[102]. A uniform nanospheres with GQD coated on the surface during this process. GQD not only reduces the particle size during the formation of nanoparticles, but also acts as a converter to absorb light energy and generate heat. Liquid metal can also be applied in the composite to improve conductivity and stability. Li utilized LMNPs to modify the $Ti_3C_2T_x$/PANI composite, a

lightweight electromagnetic shielding material[103]. A 3D conductive composite microsphere with LMNPs uniformly adsorbed onto the surface of $Ti_3C_2T_x$/PANI nanoflower is fabricated by controlling the LMNP concentrations (Figure 4d). In order to solve issues of poor connection between LMNPs and discontinuity of the $Ti_3C_2T_x$ MXene nanosheets, the $Ti_3C_2T_x$/PANI framework functions as a conductive bridge between LMNPs. The flexible, robust, conductive composite fabric with effective electromagnetic shielding was fabricated in this way.

As silanization was a common modification for any surface that possesses bound hydroxyls. Hu adopted a multifunctional mesoporous silica shell to improve the stability of liquid metal particles and develop an application for drug delivery (Figure 4e, i and ii)[104]. The silica coating not only ensured colloidal stability by preventing the aggregation and self-fusion of LMNP, but also experienced thermal stabilization based on the rigid silica shell. It can fix the shape, limit the morphological change of LMNP and reduce the contact with air and water to prevent the production of GaOOH. As shown in Figure 4e, iii, the tumor cells in the LM@MSN/DOX@HA + NIR group showed increased cell shrinkage and nuclei absence, indicating apparent cell damage. In addition, polymers can be immobilized on the oxide shell of EGaIn by silanization. The innate hydroxyl group on the surface of the oxide layer can form robust silane bonds with the alkoxysilane moieties of a substituted trialkoxysilane, leaving behind a tail group of the replaced functionality that faces outward (Figure 4f)[80]. Orthogonal functionalization to create chemically varied, and multifunctional hybrid liquid-metal nanoparticles served as a good example of the advantages of alkoxysilane ligands. Additionally, stretchy conductors with better electromechanical performance were created employing previously unattainable chemistries, known as polymerized liquid-metal networks.

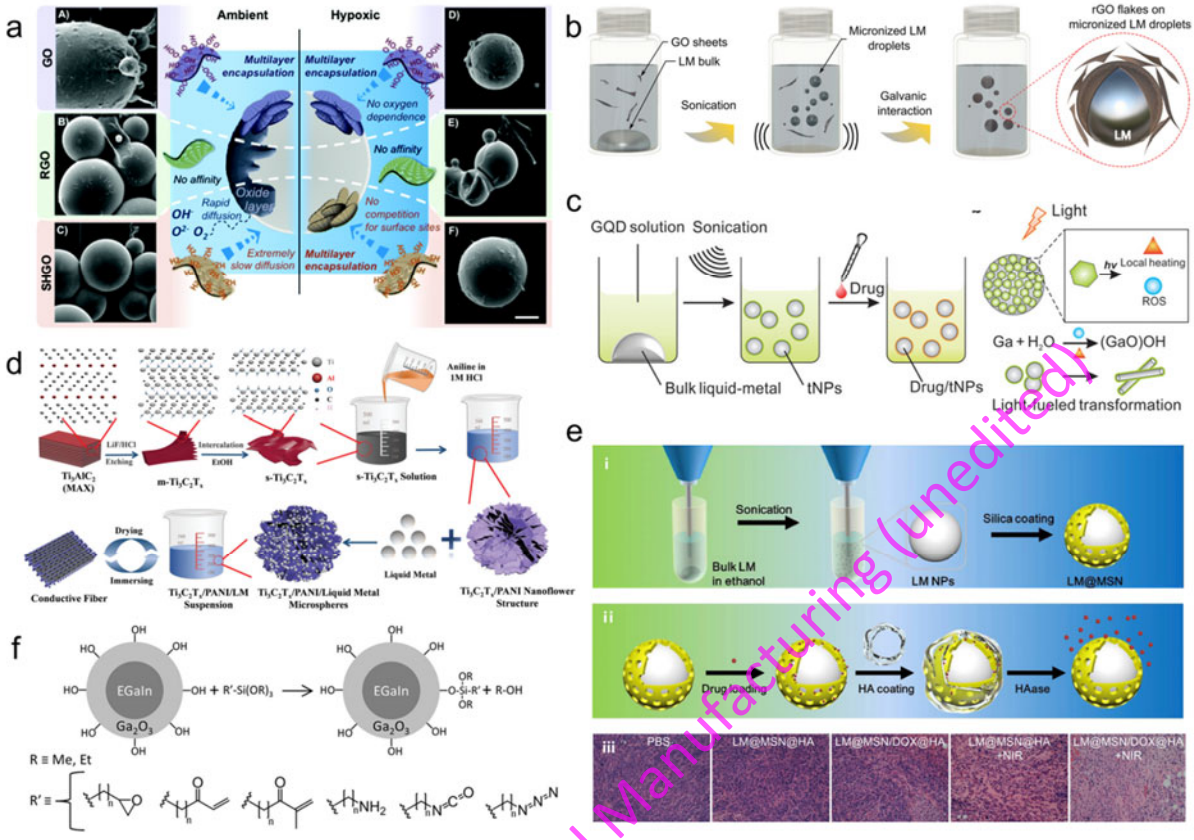

Figure 4. LMNPs modified with carbon nanomaterials/silica. (a) The morphology of EGaIn particles prepared in the presence of GO, rGO and SHGO in ambient and hypoxic environments (Scalebar is 2 μm).[72] (b) Synthesis process of LM–rGO nanocomposites.[3] (c) Synthesis process of the nanoparticle and the transition process from Ga to GaOOH.[102] (d) Schematic diagram of the synthesis of s-$Ti_3C_2T_x$, $Ti_3C_2T_x$/PANI nanoflower and $Ti_3C_2T_x$/PANI/LM microspheres.[103] (e) i and ii. Synthesis process of LM@MSN and LM@MSN/DOX@HA for effective photothermal and chemotherapy of tumors; iii. Tumor cells after different treatments (TUNEL immunofluorescence staining).[104] (f) Silanization process of EGaIn particles.[80]

2.1.4 Others

Silk is a natural flexible material that has been utilized as an engineering component for its biocompatibility, flexibility and biodegradability[105-107]. Zhang modified EGaIn with silk fibroin to increase the patterning performance for screen printing (**Figure 5**a)[108]. Silk fibroin is extracted from silkworm cocoons in advance, which enables the liquid metal to be modified by sonicating in an aqueous solution. Under sonication, the size of the liquid metal decreases, and the stability of the nanoparticle get enhanced. Microgels have been implied as an emerging material that is capable of combining with liquid metals with improved performance[109]. Different from the

polymer molecules introduced above (polymerization after immobilization of monomers), the microgel polymers are modified on the nanoparticle by cross-linking alginic acid on polymers and Ga^{3+} ions. In addition, the microgel polymers could cross-link with each other and form a sponge structure[22]. Recently, Wang designed a sponge composite based on alginate microgel encapsulated LMNP (Figure 5b)[22]. The encapsulated liquid metal possessed higher water stability, biocompatibility, drug-loading ability, etc. In addition, Wu also modified LMNPs with alginate microgel for printing (Figure 5c)[73]. The surface of the liquid metal droplets can be covered with microgels due to released Ga^{3+} during the mechanical stirring process (Figure 5d). These microgels exhibited shear-thinning performance as a result of the formation and rupture of hydrogen bonds under various stress conditions, offering the liquid metal ink with excellent printability and superior adhesion on a variety of substrates.

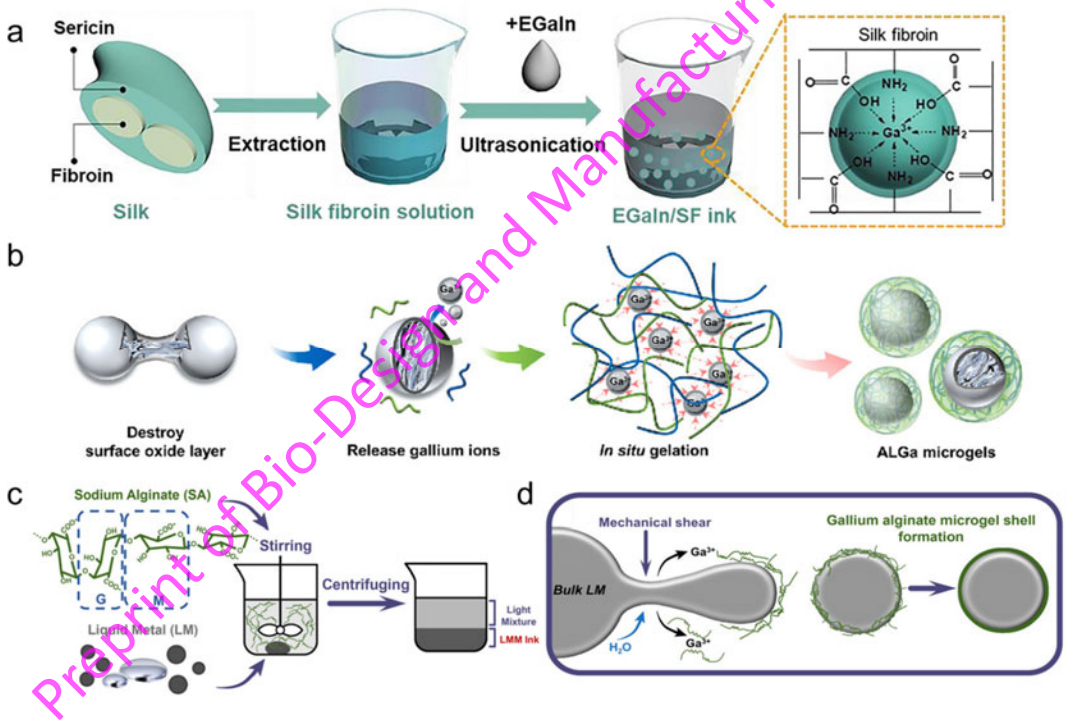

Figure 5. LMNPs modified with silk and microgel. (a) Synthesis process and chelation mechanism of EGaIn/SF ink.[108] (b) Synthesis process of alginate microgel-modified LMNPs.[22] (c) Synthesis process of LMM ink with mechanical stirring.[73] (d) Mechanical shearing is used in the formation of the LM-alginate core-shell structure.[73]

2.2 Galvanic Replacement Reaction

One simple pathway of modifying gallium-based liquid metal involves the replacement of Ga atoms in liquid metals with other metals, such as Au, Ag and Pt. In general, the reaction occurs in an aqueous solution containing a metal salt. Among the components of liquid metals, Ga has the lowest standard reduction potential. Therefore, Ag^{+}, Au^{+} and Pt^{2+} are more likely to replace Ga, rather than In or Sn. Usually, fabrication of metal decorated LMNP is achieved by two steps. After sonication in solution, the solution containing metal salt ions is added. The metal ions are reduced to metal nanoparticles which formed and decorated on the surface of liquid metals. These prepared liquid metal particles have a core (GaInSn/EGaIn)-shell (Ag, Au or Pt) structure, and remain stable in aqueous solutions.[72, 110-113] It is worth noting that Wang introduced two galvanic replacement patterns of LMNP, namely intracellular and extracellular replacement, based on the Gibbs free energy of the reaction[114]. Extracellular replacement pattern involves the replacement reaction at the surface of liquid metal, which is used to produce noble nanoparticles and multilayered nanoparticles. While intracellular replacement pattern extends the galvanic replacement reaction to the core of the liquid metal, extracellular replacement pattern provided a quick and easy procedure to create composite nanoparticles with fragile structures and noble metal nanoparticles. In this section, advances in extracellular replacement reaction in liquid metal was introduced.

Hoshyargar firstly conducted a comprehensive study of galvanic replacement of Galinstan[111]. The galvanic replacement reaction was testified with both bulk liquid metals and LMNPs. After incubation, a black Ag/Au layer was formed, and the metallic Ag and Au can be observed on the liquid metal bulk (**Figure 6**a). For the displacement reaction of the micro-Galinstan, the droplets were ultrasonically treated in an aqueous solution of $AgNO_3$ / $KAuBr_4$, and the nanocomposite was fabricated. The nanoparticles were in the shape of rice and the Energy dispersive X-ray (EDX) result indicated a 5 % doping in silver/gold nanoparticles. They discovered that the Au/Ag modified nanoparticle has a significantly improved catalytic activity toward degradation of Methylene blue. In addition, metallic modification could enhance the optical and photothermal conversion performance of liquid metals. It has also been found that the modification of Cu and Ni could enhance the optical properties of EGaIn nanoparticles by transforming the shape under laser (Figure 6b)[115]. It was demonstrated that under laser radiation, microparticles with optical tunability and rigidity could be strongly affected by the chemical composition. Recently, Guo modified EGaIn nanoparticles with Au nanoparticles by incubating sonicated nanoparticles in $HAuCl_4$ (Figure 6c)[116]. The nanoparticles fabricated in this way displayed a heterogeneous

structure with a litchi form (Figure 6d), comparing with the nano-rice shape. The nanocomposite showed an excellent performance in the photothermal conversion test (photothermal conversion efficiency is increased from 7% to 22.58% after modification) and was applied for photothermal therapy applications.

Oloye studied the galvanic replacement of liquid metal Galinstan with platinum/ copper for the synthesis of electrocatalytically active nanomaterials[110, 117]. A drop of Galinstan was dipped in the platinum salt for 24 hours. The appearance of bubbles generated from the mixture indicated the successful modification of platinum. The procedure was similar to copper modification, with platinum salt replaced by $CuSO_4$ aqueous solution. In this research, the materials demonstrate huge potential in environmental remediation applications, as it shows a degradation efficiency of 92% for methyl orange dye. Castilla-Amorós also explored the galvanic chemical reactivity of the gallium LMNP[118]. It was found that mushroom-like nanoparticles were synthesized, in which a spherical copper part was connected to a drop-shaped gallium domain (Figure 6e). Ghasemian introduced the galvanic replacement reaction as an inhibition method of oxidation[76]. In this reaction, MnO_4^- in aqueous solution was reduced to single-layer hydrated manganese dioxide nanosheets on the nanoparticle (Figure 6f). It was demonstrated that during this reaction, the exceptional gallium migrates from the metallic cores to the particle surfaces with solid indium cores left behind. They also employed nanoparticles as an effective photocatalyst to degrade an organic dye under simulated sun irradiation. Huang also functionalized LMNPs in chloroauric acid solution through galvanic replacement reaction[119]. The Au-modified nanoparticles demonstrated impressive electrical and thermal conductivity, indicating high potential of liquid metals for medical applications.

The effect of pH value on the galvanic replacement reaction between liquid metal bulk and $KAuBr_4$ was studied [75]. It is found that when pH is higher than 11.7, the galvanic reaction is oxide-free, and a more homogeneous thin film on the liquid metal would be formed (Figure 6g). Subsequently, a novel biphasic Au–$AuGa_2$/liquid metal framework was investigated, and the influence of pH leads to either intermetallic $AuGa_2$ or Au nanoparticles to encapsulate LM droplets. The large-size Ga alloy droplets were firstly ultrasonicated in an aqueous solution of surfactant to form submicron LM droplets; the droplets were then subjected to a galvanic replacement reaction in the alkaline $KAuBr_4$ solution, resulting in the formation of an encapsulated structure on its surface.

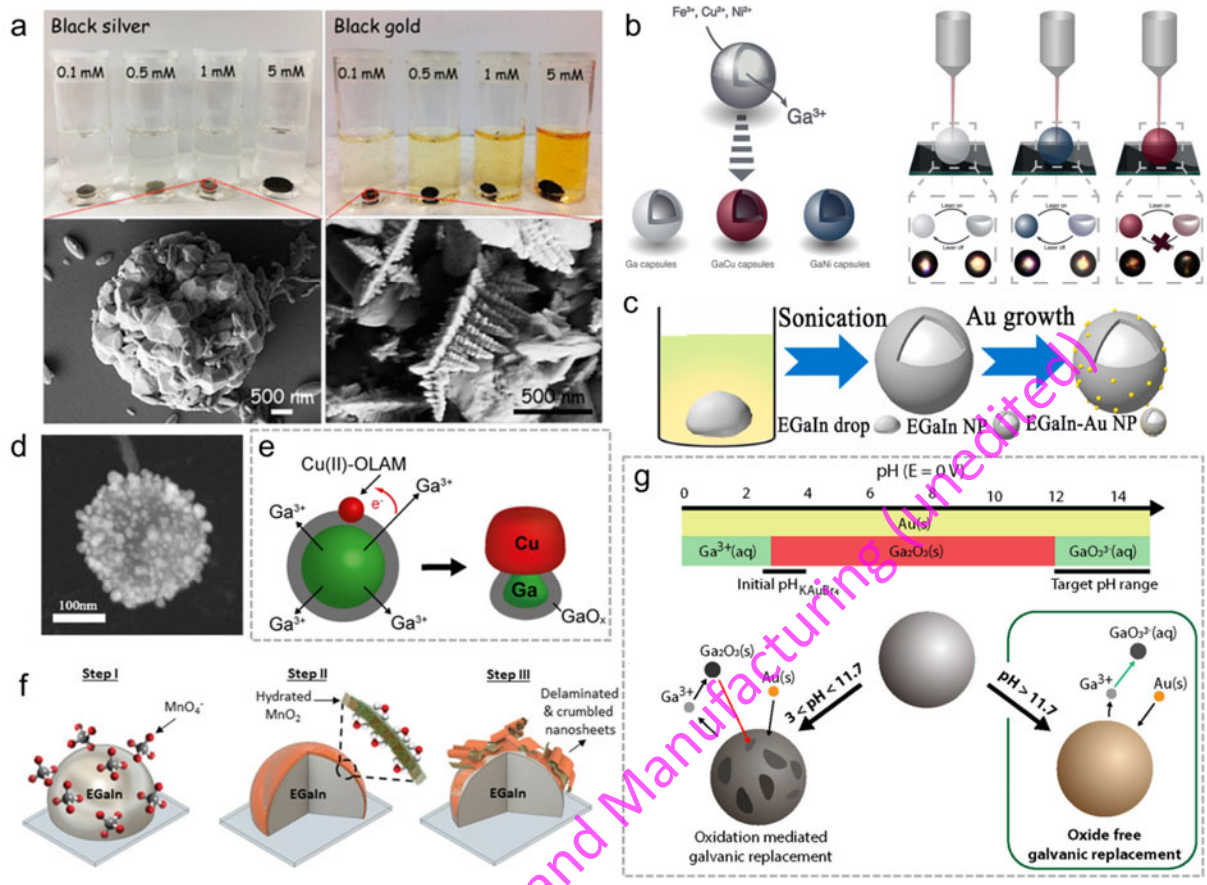

Figure 6. Modification of liquid metals by galvanic replacement reaction. (a) Liquid metal bulk after incubation in different concentrations of $AgNO_3$ or $KAuBr_4$ and morphology of silver or gold NPs.[111] (b) Schematic diagram of nanocomposite and concept of laser irradiation-induced shape change of the nanocomposites.[115] (c) Synthesis process of Au@EGaIn nanocomposites.[116] (d) High-angle annular dark-field-scanning TEM image of Au@EGaIn nanocomposites.[116] (e) Schematic diagram for the synthesis of Cu-Ga nanocomposites.[118] (f) Fabrication process of hydrated MnO_2 layer on liquid metals.[76] (g) Galvanic replacement pathways of liquid metals determined by pH in the reaction medium.[75]

2.3 Electroplating

In the process of electroplating, dissolved metal cations are reduced to the point where they coat an electrode with a fine, coherent layer of metal[120]. Similar to galvanic replacement modification, metal ion solution is utilized. However, instead of relying on galvani potential difference, electroplating involves applying a current to deposit the metal onto the surface, and the thickness and can be controlled by parameters like current density, time and temperature. Electroplating

modification has advantages such as oxidation inhibition, higher adhesion stability, and controllable wettability of the materials[64]. Copper, iron, and nickel are popular materials to be utilized for electroplating modification on liquid metals[77]. Liquid metal electroplated LMNPs could be applied in microfluidics, drug delivery and other applications as an intelligent soft robotics[77, 121]. For instance, Lim designed a multilayer nanocomposite deposition strategy for dopamine detection that involves Ga modification with CNTs, poly(diallyldimethylammonium chloride) and gold nanoparticles (**Figure 7**a) [9]. In this study, the thermal stretching method was firstly adopted to fabricate a core-shell electrode. Then a two-layer nanocomposite was modified to improve the biostability and electrochemical performance of the Ga electrodes (**Figure 7**b). The first layer is a CNT/polymer composite layer. CNT/polymer composite with a nonporous structure has excellent flexibility and electrochemical stability to improve the electrochemical performance and biostability of Ga alloys. After the deposition of the first layer of CNT composite, a second layer of AuNP deposition was used to improve the electrochemical properties for high-sensitivity applications. In addition, Zhang fabricated a liquid metal-based self-propelled motor that can proceed autonomous forward motion under the control of an applied electromagnetic field. After the nickel cap is electroplated onto a liquid metal droplet, an on-board fuel aluminum foil is added, which not only initiates independent movement, but also improves the adherence. The result shows that Ni/Al/EGaIn motor has the best stability and self-propulsion ability. Such micro-dynamic robotics can be used in drug delivery and medical imaging, etc. In the micro-dynamic robotic designs, self-driving is achieved using the unique properties of liquid metal; it is highly controllable and capable of navigating around after the drug release. Furthermore, experimental results indicate such route-controllable liquid metal micro-dynamic robotics are promising for a wide range of applications[121]. For example, Tang discovered a phagocytosis phenomenon that could describe the biomimetic cellular-eating of gallium-based liquid metal and particle internalization (**Figure 7**c)[78]. It is understood that this particle-eating behavior is principally caused by surface transition and the reactive nature of the intermetallic wetting between the two metallic phases, leading to a nonwetting-wetting transition. It is also found that a cathode voltage of 2.0 V could facilitate the phagocytosis phenomenon significantly, which implies that the electroplating modification can alter the wettability of the material.

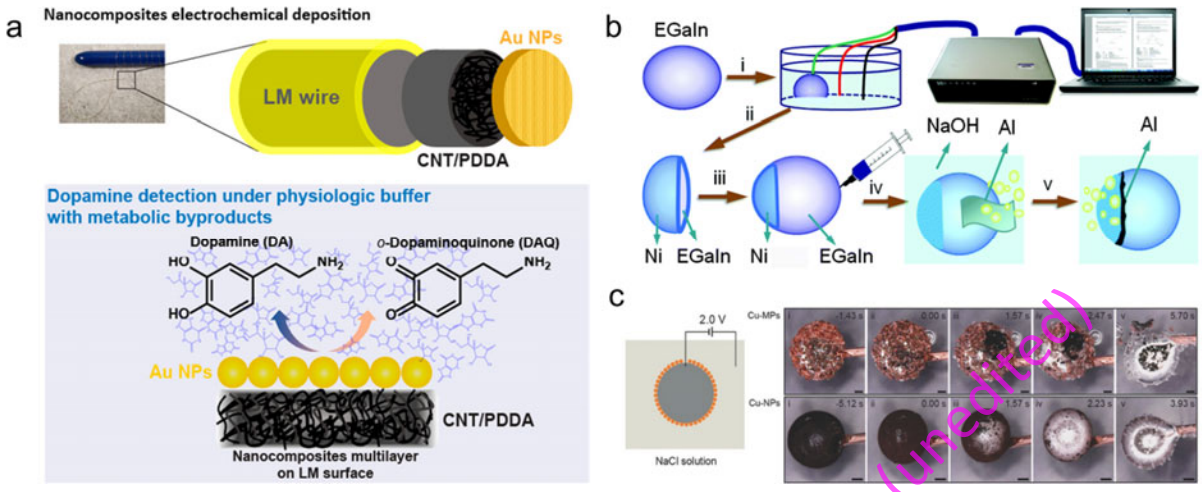

Figure 7. Modification of liquid metals by electroplating. (a) Nanocomposite multilayer electrochemical deposition and dopamine detection mechanism.[9] (b) Schematic diagram for the fabrication process of the magnetic soft motor.[121] (c) Liquid metal-phagocytosis in neutral solution with an assisting electrical polarization.[78]

3. Patterning methods of liquid metals

In order to produce flexible wearable devices, one method is to print conductive materials directly onto flexible substrates. Commonly used flexible substrates are polyethylene terephthalate[122], vinyl naphthalate[123], polyimide[124], polyurethane[125], ecoflex[126] and polydimethylsiloxane (PDMS)[127]. Ideal conductive materials need to maintain good conductivity and long-term durability under complex mechanical deformation, including conductive polymers[128], metal nanowires (NWS)/nanoparticles (NPS) (such as CuNWs/NPs and AgNWs/NPs)[129-133], carbon-based materials (graphene[134], carbon black[135], carbon nanotubes[136], etc.) and liquid metals[18, 137]. Liquid metal materials at room temperature are the most widely used in wearable sensors due to their excellent electrical conductivity and tensile properties. They possess a relatively low melting point and remain liquid state from room temperature to 2000 degrees Celsius. Liquid metal patterning remains one of the popular topics in the field, especially to expand to applications. Liquid metal materials possess the rheological and wetting properties as liquids, and can be controlled to enter the pipeline or adhere to different substrate surfaces. However, the high surface tension and the presence of surface oxide film make it impossible to generate liquid metal patterns through traditional printing or printing methods[138-140]. In the liquid metal manufacturing process, beyond the chemical modification,, patterning technology plays a vital role in reducing the surface tension of the liquid metal through various printing methods, enabling better adhesion to the substrate[141-142]. The liquid metal patterning methods can be systematically divided into four categories: printing technology, injection technology, additive technology and material reduction technology. Among them, printing lithography technology includes screen printing, template lithography, imprint lithography, etc.; Injection technology includes microfluidic injection, vacuum filling and other methods; additive technology includes micro-contact printing, 3D printing and other methods.

Table 2. Printing methods of liquid metals with advantages and disadvantages

Methods	Advantages	Disadvantages
Printing technology	Favorable writing resolution, attractive portability, digital control	High production cost, long cycle, and high operational

		requirements
Injection technology	Accurately control the shape and size of liquid metals	Relatively high cost, requiring mold manufacturing and maintenance during use
Additive technology	Easy to adjust the properties of liquid metals	The added substances will limit the performance of liquid metals
Material reduction technology	Manufacturing highly complex three-dimensional, structures suitable for various liquid metal products with varying degrees of complexity	The manufacturing process is quite complex and requires proper control of temperature and reaction conditions

3.1 Printing Technology

3.1.1 Direct writing

Liquid metal direct writing is a novel technique that involves using liquid metal materials as "ink" to directly write or draw conductive patterns on various substrates. When injecting liquid metal ink into the head of a ballpoint pen or other printing and writing tool, the pressure or mechanical force applied during the writing process may damage the oxide layer, causing it to separate from the metal surface and physically wear off the oxide layer. This method removes the oxide layer through the force of friction and scraping, exposing the metal surface. This method allows for the creation of customized electronic circuits, sensors, or other functional components with high precision and flexibility[143-144]. Inspired by daily handwriting, Liu[47] proposed a direct ink writing process called "liquid metal ball pen" (LMRP), which combines liquid metal ink with a ballpoint pen structure (**Figure 8**a). The ballpoint pen electronic device used room-temperature liquid metal ink to realize direct writing, so that the metal ink can be smoothly extruded on the flexible polymer substrate, forming conductive filaments and soft electronic devices. The stylus structure and the working principle were the same as that of the daily used ballpoint pen. With pure liquid metals used instead of ballpen inks, the tip ball rolled out of the base, bringing out the liquid metal in

continuous and uniform conductive filaments, forming straight lines, curves, and other complex patterns. With the help of auxiliary tools with different shapes and structures, it was also possible to draw even more complex conductive patterns in different situations.

In addition, Boley proposed a novel direct-writing method, which complemented the previously explored printing method[145]. This approach was realized by flowing eutectic GA in (EGaIn) near the moving substrate with a blunt syringe nozzle (**Figure 8**b). As shown in Figure 8b, by carefully controlling the ink flow rate q, the nozzle moving speed V remained and the nozzle-substrate distance h_0, specified geometric shapes could be placed on the stage diagram. This method utilizes the strong adhesion between EGaIn and two silicon-based substrates. The formation of the gallium oxide skin during direct writing allows the written pattern to maintain its printed shape, even though the elastomer packaging process. The ball diameter of the ballpoint pen varies from 200 μm to 1,000 μm, and its writing accuracy is high, which will help to develop popular electronic products for pens for future daily use. The experimental results indicated that the structure of the nib can be clearly observed under an optical microscope, and the thickness of the conductive trace can be tuned up to 80 μm according to the SEM image. These fine structures reveal the highly acceptable writing precision of liquid metal-based ballpoint pen electronic devices, which is an important step forward from existing electronic writing resolutions.

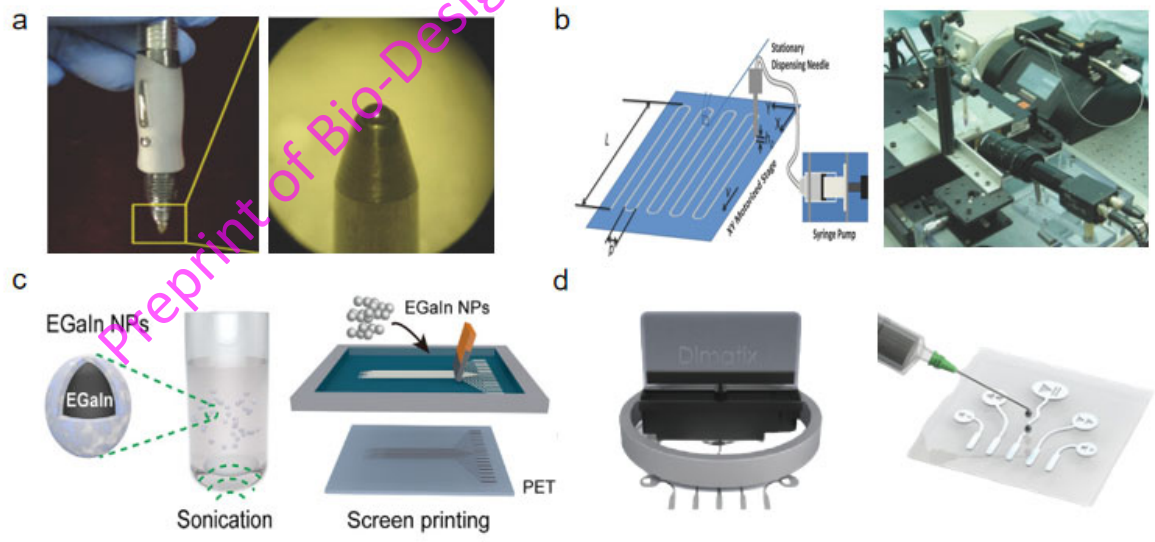

Figure 8. Printing lithography for liquid metal patterning. (a) Optical images of a rolling ball pen containing liquid metal ink and images of conductive trajectories written by LMRP[47]; (b) Schematic of direct writing system writing a serpentine pattern.[145]; (c) Schematic illustration of

the fabrication of stretchable electrode arrays (SEA) using screen printing[149]; (d) Stretchable circuit inkjet printing method and applications[151]

Compared with traditional direct drawing or writing, the mechanical direct writing method can achieve digital control and increase the accuracy of the liquid metal flexible electronic circuit. For example, the development of a desktop printer with intelligent control ability and high precision can realize the automation and direct printing of electronic products. Zheng have built a multifunctional desktop liquid metal printer and demonstrated the capabilities in printing planar circuits and 3D metal objects[47]. They designed a brush-like porous needle to print liquid alloy ink and identify matching substrate materials on different types of paper. Under the control of computer software, the prototype desktop printer can be easily operated to print various patterns on the selected substrates.

3.1.2 Screen printing

Screen printing is a popular technique that consists of five essential elements including screen printing plate, scraper, ink, printing stand and substrate. During the printing process, the ink was poured into one end of the printing plate; a certain pressure was applied, making the ink squeezed to the substrate. In general, the printing resolution depends on the size of the designed screen pattern. For the liquid metal based inks, the concentration needs to be adjusted to prevent blocking[146]. During the screen printing process, the mechanical force applied by the printing scraper will compress the surface of the liquid metal, thereby damaging or peeling off the oxide layer, in order to achieve a stable bonding between the liquid metal and the printing substrate. At present, there are dozens of publications regarding to patterning and application of screen-printing liquid metals[147, 148]. For example, Jiang developed a method for manufacturing highly scalable neural electrode arrays on polydimethylsiloxane plates, based on liquid metal conductor screen printings[149]. The flexible electrode array was composed of stretchable liquid metal interconnections, and a flexible PDMS substrate. The general procedure was to screen print EGaIn particle ink on polyethylene terephthalate (PET) substrate, bake it in an 80 ℃ oven, spin coat the printed pattern with PDMS prepolymer, and cure it at room temperature. The liquid metal pattern was then transferred from PET to the PDMS substrate, and the liquid metal circuit was sintered through shear stress (**Figure 8**c). The screen-printed electrode array showed a resolution of 50 μm,

which was ideal for neural interfaces. The integration of a liquid metal-polymer conductor enables the neural electrode array to maintain stable electrical properties and compliant mechanical properties under significant (≈ 108%) strain. Liquid metal electrode arrays have shown excellent performance in neurite growth and long-term implantation due to their high biocompatibility. The retractable electrode array can spontaneously keep contact with the brain surface and record high-throughput electrocorticography signals.

However, screen printing still has its limitations. Due to high surface tension and limited pressure provided by the doctor blade, it is difficult to disassemble the liquid metal into particles and pass through the grid. At the same time, due to individual differences, screen printing cannot provide a uniform force, which leads to disparity in the uniformity. In addition, current screen printing is confined to straight lines or simple shapes; it will be much more difficult when it comes to complex shape printing, such as polylines or grid patterns.

3.1.3 Inkjet printing

Inkjet printing is a non-contacting, pressure-free and substrate-free printing technique. The inkjet printing machine is composed of a system controller, an inkjet controller, a nozzle and substrate drive mechanism.[150] The ink pump ejects the ink from the nozzle at a certain pressure to form a continuous ink flow. This ink flow obtains static electricity in the metal tube filled with high voltage in the printing head and becomes an orderly ink drip. Adjusting the pressure and voltage range of the ink pump leads to the generation of micro ink drops. When the ink drops flow through the high-voltage electrical pipeline, the micro ink drops will be charged instead of the large ink drops. Once the charging signal is removed, the charged micro ink drops will be deflected under the effect of the DC electric field to form a printing ink beam and eject on the substrate to complete printing. When using liquid metals as the ink, the heating mechanism in inkjet printing equipment can provide heat, which helps to soften and damage the oxide layer, promoting better adhesion of liquid metal dyes. The non-charged ink drops are not deflected and will be recycled by the ink system. It is worth mentioning that Tavakoli printed high-resolution circuits on optical transparent polyurethane (PU) substrates[151]. This process includes ink-jet printing AgNP ink on a polyvinyl alcohol-coated substrate, the depositing of Galinstan, and follows by the selectively wetting to the printed AgNP circuit (**Figure 8**d). This novel ink-jet printing technology greatly simplifies the manufacturing process of liquid metal-based circuits.

3.2 Injection Technology

3.2.1 Microfluidic injection

Microfluidics refers to the system that apply micro pipes to process or manipulate micro fluids. Due to its capabilities in miniaturization and integration, microfluidic devices were named as microfluidic chips. With the emergence of such unique fluid phenomena, microfluidics can realize a series of micromachining and micromanipulation which are difficult to accomplish with conventional methods. Microfluidics technology integrates functional fluids into compact chip-like systems with low energy consumption in a portable manner, and it shows great prospects in the fields of drug/cell screening, sensing, health monitoring and micro-manufacturing. Replacing conventional fluids with liquid metals will bring additional functions to the microfluidic system, and expand the application from bioengineering to micro-electronics. Microfluidic technology utilizes the movement of microchannels and microfluidics to control the transportation and distribution of liquid metals. This microscale operation can help to destroy or remove the oxide layer on the surface of liquid metals.

On the basis of microfluidics, Li developed an innovative microfluidic-based system to effectively form patterned liquid metals[110]. They used soft lithography technology to make SU-8 photoresist mold. Then, the uniformly mixed Ecoflex 00-30 was carefully poured into the mold and being heated with a plate., The patterned substrate was stripped from the microchannel chip after the liquid elastomer being cured. Thin films were prepared by spinning the same mixed liquid elastomers. In order to better bond the two flexible parts, a small amount of liquid Ecoflex 00-30 was spin-coated on the film to form another film. Furtherly, EGaIn was injected into the microfluidic channel when the thin layer was semi-cured.. Finally, thin wires were inserted at both ends of the microchannel to fabricate a microfluidic flexible sensor.Such sensors could restrain the viscoelasticity of the microchannel and effectively improve the hysteresis performance.

3.2.2 Vacuum filling

Due to its simplicity, high resolution and repeatability, microfluidic injection has been widely used in the liquid metals patterning. However, microfluidic injection still has some disadvantages that cannot be ignored: 1) Considerable differential stress is required to inject liquid metal to break oxides and induce the liquid metal to flow into the channel; 2) The air discharged from liquid metal

get compressed during the injection, thus the microfluidic channel with a dead end tends to leave irremovable air-bubbles; 3) Injections usually require inlets and outlets to be connected the ends of microchannels, while complex microfluidic structures usually require multiple outlets.

Vacuum filling is an alternative solution to solve the above problem and fill the channel with liquid metal. Most vacuum-filling methods focuses on aqueous solution. Liquid metals are different from conventional aqueous solutions. Aqueous solution usually prevents with Newtonian rheological behavior, while liquid metal has an yield stress and behaves as non-Newtonian fluids. Since the vapor pressure of liquid metal can be ignored, it can also be processed in a vacuum environment without worrying about evaporation. Vacuum filling technology reduces the possibility of oxide layer formation by removing oxygen and other oxidizing substances from the air. The formation of an oxide layer is limited in anaerobic or low oxygen environments. In 2017, Dickey proposed a method of vacuum-filling complex microchannels with liquid metals[152]. It started with covering a single PDMS microchannel inlet with liquid metal. The entire structure was placed in the vacuum chamber; After the vacuum was released, the atmospheric pressure was restored to create a positive differential pressure, forcing EGaIn to flow into the microchannel. When the liquid metal filled the channel, the elastomer channel wall absorbed the residual air. Therefore, this liquid metal can fill the dead end with features and branch structures as small as micron level in a few seconds without any outlet. In this way, liquid metal can be used to build highly dense while unique soft electronic devices.

3.3 Additive Manufacturing Technology

3.3.1 Photolithography

Photolithography refers to the technology that transfer patterns on the mask to the substrate with a photoresist under the effect of light. The main process is as follows: firstly, ultraviolet light shines on the substrate surface with a layer of photoresist film through the mask, causing the photoresist in the exposed area to react chemically; Secondly, the photoresist in the exposed area or unexposed area (the former is called positive photoresist, and the latter is called negative photoresist) is dissolved and removed by the development technology so that the patterns on the mask are copied to the photoresist film; Finally, the pattern is transferred to the substrate by etching technology. For liquid metals, during the photolithography process, the photosensitive material coated on the

surface of the liquid metal will be exposed to ultraviolet light. These rays of light can alter or degrade photosensitive materials, thereby damaging the oxide layer. The subsequent etching step will remove the portion that has not been cured by light based on the pattern on the lithography plate, exposing the liquid metal surface below. This process also helps to remove and destroy the oxide layer.

Zhou further simplified the process of liquid metal patterning on the basis of template lithography[153]. They combined laser-induced selective metallization and selective wetting to prepare copper templates on the surface of elastomer, and painted Galinstan on copper templates (in alkaline solution) for fabricating high-resolution liquid metal circuits. This method illustrates stronger adhesion between the circuit and the substrate, and can be further used to fabricate 2D and 3D liquid metal circuits directly.

3.3.2 Micro-contact printing

As for the manufacturing of microelectronics and optical devices, the key process is to fabricate micrometer/nanometer scale patterns. Micro-contact printing is another method beyond photolithography; it prints graphics on the substrate through an elastic seal and self-assembled monolayer. The template is usually obtained by optical or electron beam lithography. The precursor of the molding material is solidified in the template and then being separated from the template after polymerization.

In comparison with other manufacturing technologies, the advantage of liquid metal micro-printing lies in the fact that it can fully provide the required precision, repeatability, and size/geometry capabilities, especially the scalability required, in order to achieve commercially applicable soft and scalable electronic products based on gallium based liquid metals. Meanwhile, during the micro contact printing process, templates made of silicone or other elastic materials will apply a certain degree of contact force and pressure to the surface of the liquid metal. This force can help destroy or remove the oxide layer, making it easier for the pattern to be printed on the metal surface. Ozdoganlar demonstrated the manufacturing of soft and scalable electronics based on EGaIn by using a micro-contact printing process[154]. In particular, they developed a photolithographic manufacturing method to functionalize the sparse/surface of EGaIn with reusable rigid (Si) and soft (PDMS) seals(**Figure 9a**). The photolithography stamps were firstly

made with N-[3-(trimethoxysilyl) propyl] ethylenediamine (NTPE) fictionization, and the printing substrate was surface functionalized with EGaIn. The printing process was as follows: EGaIn droplets were placed on the donor surface, and the roller surface was covered with EGaIn. The stamp was connected to the three-axis motion system and loaded by a roller until the extrusion mode is completely covered by EGaIn. After aligning the seal with the substrate surface, the seal was pushed onto the PDMS substrate under constant load. Then the seal was pulled back to complete the transfer of the EGaIn pattern. Finally, the printed circuit was sealed with a PDMS layer to complete the manufacturing of flexible components.

3.3.2 3D printing

3D printing technology is a method that involves generating three-dimensional solid objects using an additive deposition process. This technique involves adding and superposing materials layer by layer to build up the desired object.[155]. Firstly, the computer is used to design 3D models of required parameters. Secondly, the model is discretized into a series of ordered elements according to the process requirements, turning the original 3D CAD model into consecutive collections of slices; Based on the contour information of each slice, processing parameters is set up and the system automatically generates the G-code; Finally, consecutive layers of materials are deposited and automatically added up a 3D physical entity.

In the context of liquid metals, 3D printing technology can be used to create complex and precise structures by selectively depositing the liquid metals , following the same principle as described above. During the 3D printing process, heating and deposition both help to damage or remove the oxide layer, making it easier for the printed material to bond with the metal surface. Liquid metal 3D printing uses low melting point inks, and it allows the entire manufacturing process to be printed alternately with non-metallic materials; this therefore achieves rapid prototyping of various electronic circuit functional devices such as wearable devices. PVA is a common nonmetallic material for alternating printing with liquid metal. For example, Sun [156] introduced PVA solution as a "bridge" to connect the substrate and the surface oxide film of liquid metal, which solves the problem of poor wettability between pure liquid metal and various materials(Figure 9b). Such ink was printed on the polyacrylamide (PAAm) hydrogel with various patterns and high resolution; the patterns do not gather and became well combined with the substrate. In addition, the liquid metal can be recycled from the printed patterns.

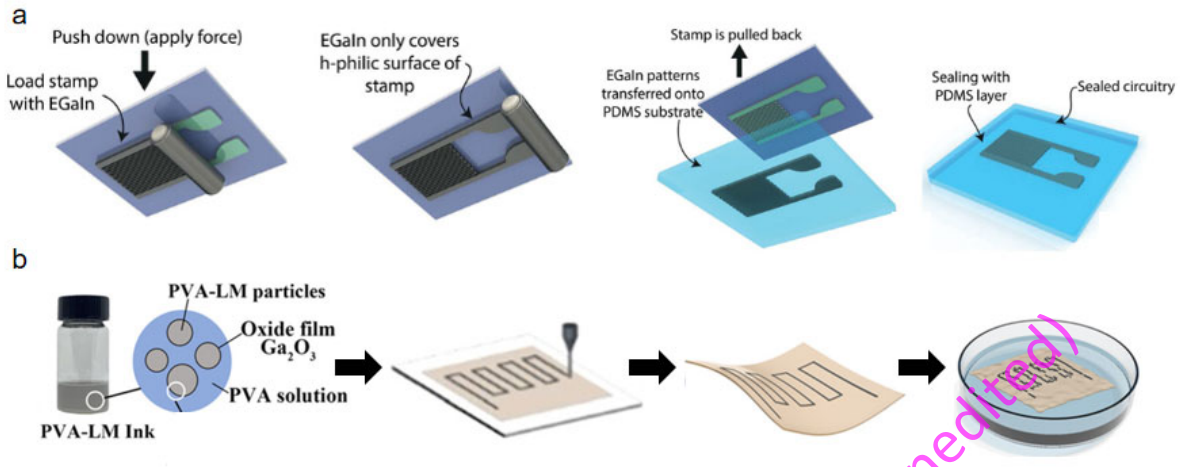

Figure 9. Additive manufacturing technology for liquid metal patterning. (a) Graphical diagram showing fabrication steps of the complete μCP process[154]; (b) The process of printing the PVA-LM ink including fabrication, printing, and recycling[156].

3.4 Other Patterning Technologies

In addition to the above patterning technologies, magnetic field-guided printing[157] is also an emerging option. By adding magnetic particles to the liquid metal, the magnetic particles could be fully mixed with the liquid metal under the effect of the magnetic field and gathered in the liquid metal under the capillary effect. Then, the magnetic liquid metal droplets can be guided to move directionally through the movement of the magnet, and to achieve patterned spreading on the surface of the substrate. This method not only controls the line width of liquid metal by adjusting the doping concentration of magnetic particles and the volume of droplets, but also overcomes the limitation of printing substrate. Graphic printing can also be achieved on either a paper surface or a three-dimensional ultra-sparse liquid metal curved surface, providing opportunities for manufacturing of the liquid metal wearable devices.

4. Typical biomedical applications

Liquid metals as emerging categories of biomaterials possess unique advantages, including their biocompatibility[158], high elasticity and flexibility[159], as well as excellent conductivity[160] and thermal conductivity[161]. With the functionalization of liquid metal, specific properties and

functions can be endowed to meet the requirements of specific fields. Bioengineers, with more complex and stringent material demands, has also focused on the application of liquid metals.

The biomedical applications of liquid metals have existed long before. For instance, as early as two centuries ago, the formation of amalgams by combining mercury with other metals was employed as dental fillings, without any direct adverse reactions occurring. Sodium-potassium alloy, an exceptionally reactive liquid metal, has been utilized as a targeted heat source for tumor therapy, producing a micro-explosion effect, and the resulting alkaline solution can enhance tumor ablation. Moreover, cationic reaction products including sodium ions and potassium ions are crucial in bodily fluids, exhibiting no side effects on human body. In the face of evolving health challenges and frontier disease research, liquid metal (LM) is becoming a key element. In recent years, gallium-based liquid metal alloys have demonstrated enormous potential in areas such as drug delivery[162], tumor therapy[163], and tissue repair[164-165] to biosensors[9, 166]. Early groundbreaking work primarily employed liquid metal biomaterials as injectable multifunctional fluid materials for a diverse range of in vivo applications. However, the chemical modification and patterning of liquid metal brought further possibilities for its application in bioengineering and regenerative medicine. And the chemical modification and functionalization of LMs endow them with enhanced functions, such as improved targeting ability and stimulus responsiveness, enabling them to achieve better and even multifunctional synergistic therapeutic effects [167-168].

4.1 Drug delivery system

Liquid metal can be used to prepare controlled release drug delivery systems, making it possible to slowly release drugs in the body. Due to its low viscosity and high surface tension, liquid metal can easily transport drugs through small holes or tubes. This flowability makes liquid metal particularly suitable for drug delivery in microdevices. At the same time, liquid metal can be combined with other materials to enhance drug stability and regulate drug release rate and duration. This enables personalized therapy and improved drug efficacy. Gu [169] have used liquid metal to prepare a transformable liquid metal nanomedicine consisting of a core-shell nanoparticle composed of a liquid-phase eutectic gallium-indium core and a polythiol polymer shell (**Figure 10**a). They employed a simple ultrasound-assisted emulsion-like ligand-mediated method at room temperature. The self-assembly of the nanoscaled liquid metal spheres could be easily achieved and tailored. These liquid metal nanoparticles generated are capable of fusion to promote drug

release and eventual degradation in a mild acidic environment. After fusion, these nanoparticles also exhibit enhanced contrast for X-ray imaging, indicating their potential as theranostic agents.

4.2 Tumor therapies

Given the widespread interest in tumor treatment, the direct injection of liquid metal (LM) into the living body, as well as the printing of conductive LM materials on the skin surface, indicating great potential as new treatment options. Liquid metals has high densities and can be used as a radiographic enhancer in radiation therapy, increasing the dose delivery to the tumor area. Additionally, liquid metal exhibits excellent thermal conductivity, allowing for tumor treatment through thermal therapy methods. Here, Zhang [170] designed tumor acid-responsive spherical nanocomposites called LMGC (liquid metal glucose oxidase [GOx] and mineralized calcium carbonate). They attached glucose oxidase (GOx) and mineralized calcium carbonate on the surface of liquid metal nanoparticles. The GOx was coated with amorphous calcium carbonate ($CaCO_3$) to prevent its deactivation. LMGC nanocomposites were developed to integrate adenosine triphosphate (ATP) depletion and photothermal therapy (PTT) for enhanced tumor treatment (**Figure 10**b). The LMGC nano-system effectively oxidized glucose, leading to the decomposition of amorphous calcium carbonate in the tumor microenvironment (TME), as well as the generation of hydrogen peroxide (H_2O_2) and gluconic acid (GA). Furthermore, the generated GA can stimulate the release of calcium ions (Ca^{2+}), interfere with mitochondrial function, reduce ATP production, and downregulate the expression of heat shock proteins (hSP). Such results further decreased heat tolerance of tumor cells and improved PTT therapeutic outcomes.

The good deformability, elasticity, and pseudo biological effects of liquid metal droplets may potentially inhibit the elimination of phagocytic immune cells and prolong blood circulation, enhance their ability to cross blood vessels and penetrate tumor parenchyma, and provide additional small capillary transport pathways. Therefore, Xu et al. utilized a simple ultrasound chemistry method to introduce a mechanically degradable ligand to promote the synthesis of water-soluble liquid metal nanodroplets below 30 nm[171]. The droplets demonstrated excellent tumor penetration and biocompatibility, and could activate tumor selective carrier drug conversion while it synchronously consumed Cu^{2+} ions, and generated Ga^{3+} ions through galvanic substitution. Simultaneously, along with the abundant reactive oxygen species generated in situ, anti-tumor activity was selectively triggered both *in vivo* and *in vitro*.

4.3 Tissue repairs

Liquid metal materials can also be prepared into three-dimensional tissue scaffolds for tissue engineering and regenerative medicine. These scaffolds have good biocompatibility and mechanical properties, which support cell growth and tissue repair, and promote the formation of new tissue. For example, Zhao [172] used photolithography to transform the LM pattern into a W-shaped conductive guide rail, which were then encapsulated into microneedles. The microneedle patch consisted of two inclined hydrogel portions and a breathable gauze. The claw-like structure formed by the pointed tips of the microneedles allowed the patch to adhere to the skin and secure the wounded area (**Figure 10**c), preventing secondary splitting. When the embedded W-patterned LM was connected to the tip of each microneedle portion and linked to an external power source, the microneedle patch could provide a stable electric field around the wound, guiding cell migration and accelerating wound healing.

Because the exudation of tissue fluid at the wound, bacterial infection and other factors will delay the healing of the wound, the traditional wound dressing is mainly composed of gauze and bandages, but lacks of active wound treatment. Therefore, Ren et al. have developed a liquid metal based intelligent wound dressing[173]. The wearable wound dressing consisted of a wound patch (WP) and a liquid metal flexible circuit. The liquid metal heating coil and drug loaded thermosensitive hydrogel were integrated into the wearable WP, which could achieve effective collaborative wound exudate management and on-demand wound treatment. The dressing adheres to the wound site and the wound exudate spontaneously pumped into the microfluidic channel for storage. At the same time, wound dressings could detect the state of the wound through temperature and humidity sensors, as the feedback to control the liquid metal heater through smart phones, so as to achieve on-demand drug release from hydrogels.

4.4 Biosensors

In recent years, liquid metal has emerged as one of the most popular options in develping wearable medical biosensors. Due to its excellent conductivity and deformability, liquid metal can be used to produce various wearable medical biosensors, allowing the biosensors to comfortably adhere to the surface of the human body to monitor different physiological signals. Its high sensitivity and stability allows it to detect weak biological signals and ensure long-term stability of the biosensors'

operation. Kim [174] achieved this by using EGaIn as a reducing agent for the graphene oxide (GO), forming a core-shell structure of EGaIn encapsulated in reduced graphene oxide (RGO) (**Figure 10**d). The RGO-encapsulated EGaIn (REG) and the metal-coated REG (M-REG) exhibited strong interfacial adhesions with EGaIn current collectors, preventing delamination during and after mechanical deformation. Furthermore, scientists found that reduced RGO-encapsulated interdigitated electrodes (RIDE) and metal-coated RIDE (M-RIDE), which took advantage of the tunable surface of REG, demonstrated excellent electrochemical sensing performance. Such advances provide feasibility for simultaneous detection of ascorbic acid, dopamine, and uric acid, as well as enzymatic detection of glucose.

In addition to common wearable sensors that detect body fluids adhered to the skin surface, implantable wearable sensor devices are also a common area of application for liquid metal. Neural electrodes are sensors used to detect neural signals, but conventional metal wire electrodes have excessive background noise, making it difficult to detect faint single-cell signals. Both neurological research and its clinical treatments require neural electrodes to remain in the body as long as possible, presenting a significant challenge. Traditional neural electrodes are made from glass, silicon, and solid metal materials, and are often too rigid and incompatible with the naturual biological neural tissues. On one hand, rigid neural electrodes can easily damage nerve cells; on the other hand, human body's immune response can stimulate the growth of scar tissues around the electrode, hindering its connection with nerve cells. The emergence of liquid metal offers hope for addressing these challenges.

Liquid metal materials possess both fluidity and conductivity, which is suitable for fabricating flexible and stretchable peripheral nerve electrodes, especially when combined with other flexible insulating materials such as silicone rubber. This furtherly reduces mechanical damage to biological tissues after the electrode implantations. Liquid metal peripheral nerve electrodes also exhibit excellent conductivity, surpassing conductive hydrogels, ionic liquids, and conducting polymer PEDOT:PSS, approaching the conductivity level of platinum. Due to the presence of liquid phase under room temperature, liquid metal maintains excellent conductivity even after stretching, a unique advantage compared to rigid electrodes like platinum. Peripheral nerve electrodes made from liquid metal can adapt to the repeated stretching or twisting movements of

the body while maintaining stable and effective bidirectional transmission of high signal-to-noise ratio neural signals.

Zheng et al. utilized photolithography to embed electronic circuits on a fibrous polymer matrix, and developed an category of electrodes suitable for implantable biomedical devices[175]. Such devices possess unprecedented flexibility, stretchability and permeability. The key step of this technology involves placing a fibrous polymer onto a silver microcircuit pattern using electrospinning to create liquid metal microelectrodes (referred to as "μLME"). These μLMEs enable ultra-high-density circuit patterning, achieving 75,500 electrodes per square centimeter, surpassing previous techniques by thousands of times. These μLMEs exhibit long-term biocompatibility and comfortable wearability on human skin. During manufacturing, circuits made with EGaIn are placed on a permeable "fibrous pad," electrospun from styrene-butadiene-styrene (SBS) copolymer, making the electronic devices soft, stretchable, and suitable for comfortable wearing and implantation. The μLMEs possess mechanical properties which is similar to brain tissue, allowing precise recording of neural signals by closely adhering to the cortical surface. When dormant mice exhibit characteristic identifiable brainwaves during non-rapid eye movement sleep, the μLME array can accurately detect somatosensory evoked potentials generated in response to electrical stimulation applied to various parts of the body. The unique properties exhibited by liquid metals make them promising for biomedical and clinical applications. However, significant gaps still exist in the translation of LM biomaterials from laboratory settings to clinical use. Core challenges faced by LM biomaterials in biomedical applications include concerns regarding biocompatibility, material stability, and ethical considerations. With the advancemes of technology and the continuous deepening of research, coping and solving these challenges will become future priorities, and liquid metals will also bring more possibilities in benefiting the biomedicine field.

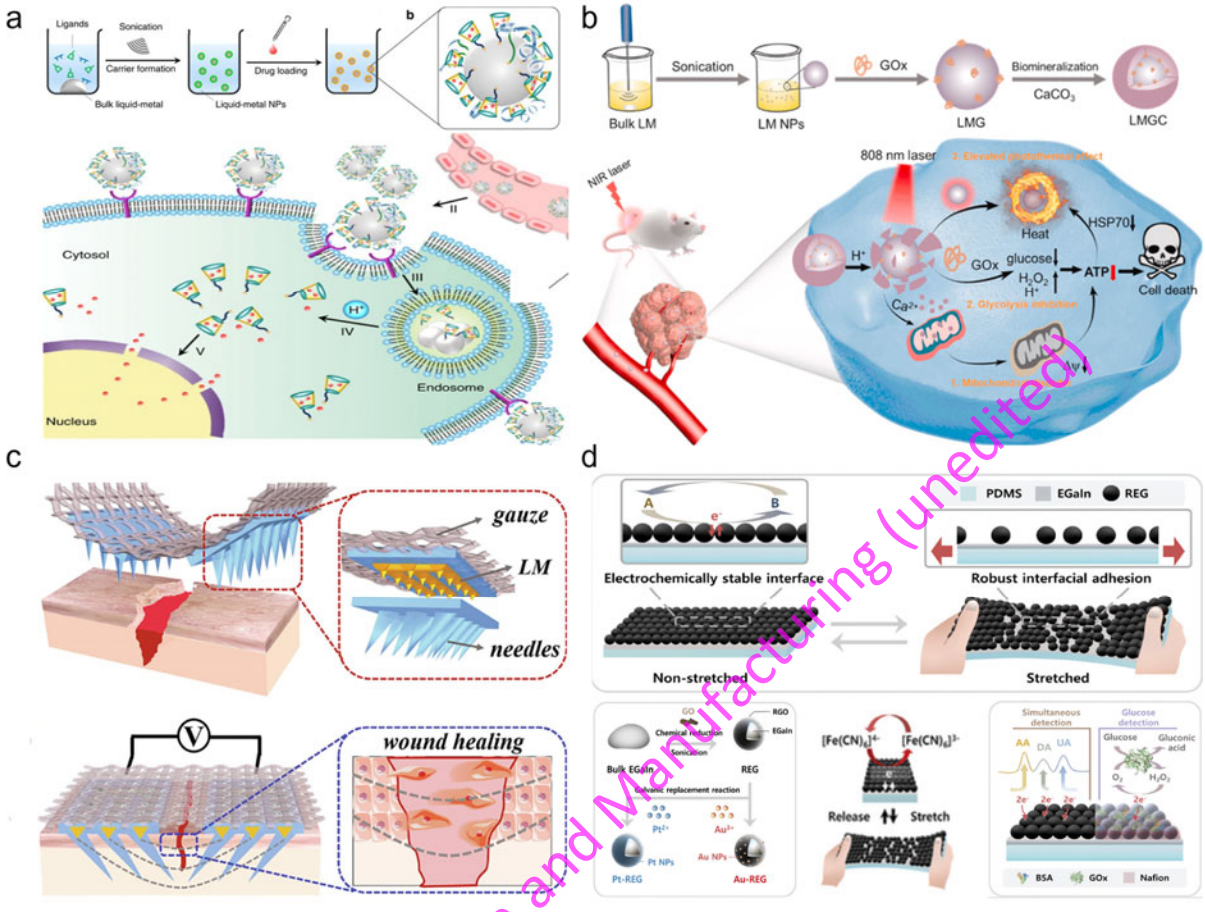

Figure 10. Biomedical applications of LMNPs. (a) Preparation of drug loaded mesoporous silica hybrid (DOX-MS/LM) and pH-responsive delivery of Dox by LM-NP/Dox-L to the nuclei for the targeted cancer therapy[169]; (b) Schematic illustration of the fabrication process of LMGC and the LMGC-mediated antitumor synergistic therapy by combining dual ATP inhibition and enhanced PTT [170]; (c) Schematic illustration of the claw-inspired microneedle patch with liquid metal encapsulation and its wound healing application[171]; (d) Functionalized EGaIn electrode with RGO assembled EGaIn core-shell particles for the soft and deformable electrochemical biosensor.[172].

5. Conclusions

In conclusion, liquid metal surface modification offers a transformative direction for advancing printing technology, as well as the subsequent applications in biomedical engineering. When it comes to printing in biological contexts, such as bioelectronics or tissue engineering, the significance of surface modification becomes paramount. Liquid metals, for instance, require precise surface modifications to ensure antioxidation, biocompatibility, and enhanced properties. By tailoring the surface properties of liquid metals through chemical treatments, functional

coatings, or electroplating, the stability, adhesion, and overall performance of the liquid metal could be enhanced. This enables the seamless integration of liquid metals into patterning techniques, allowing precise deposition of relevant biomaterials. Therefore, surface modification has been acting as a bridge between the versatility of liquid metals and the intricate demands of fabrication strategies, enabling breakthroughs in biomedical engineering.

Through meticulous manipulation of liquid metal properties, scientists have been able to revolutionize the way to approach liquid metal printing on various substrates. The ability to precisely tailor liquid metal characteristics, such as adhesion, conductivity, and wettability, has led to substantial improvements in printing quality and precision. In this way, the integration of modified liquid metals into patterning opens up further possibilities for their application. However, challenges also remain scaling up production methods, improving biocompatibility, ensuring long-term stability and uniformity of modified materials, and addressing potential safety concerns. Prioritizing research into the development of innovative surface modifications and encapsulation techniques are possible solutions to enhance the biocompatibility and stability of liquid metal biomaterials. Nevertheless, the combination of advanced materials science and patterning technology has also broadened the path for biomedical applications of liquid metals. The development of composite drugs and flexible devices based on liquid metals with better biocompatibility and more precise treatment is still worth in-depth explorations.

Acknowledgements

The work was financially supported by the National Natural Science Foundation of China (Grant 22174121, 22211530067, T2250710180), 2022 Natural Science Foundation of Guangdong Provincial Basic and Applied Basic Research Fund (Guangdong Hybribio), Guangdong Peral River Talent Program (2021CX02Y066), Shenzhen Bay Open Laboratory Fund 2021 by Shenzhen Bay Laboratory, CUHKSZ-Boyalife Joint Laboratory Fund, the University Development Fund (UDF01002012), and Shenzhen Key Laboratory of Functional Aggregate Materials (ZDSYS 20211021111400001).

Conflict of interest

The authors declare that they have no conflict of interest.

Author contributions:

G.L, Z.H. and Z.B conceive the concept of this study. Z.H. and Z.B investigated and summarized the literature, and wrote the original draft. G.L. conducted deep review, revise and editing, supervised the work, and provided the funding. D.Z. conducted review, revise and editing. All authors have revised, read and approved this manuscript for publication.

Copyright delaration:

All pictures included in this literature review are either the original work of the author or used with permission. Copyright for these pictures belongs to their respective owners.

References

[1] K. Kalantar-Zadeh, M. A. Rahim, J. Tang, Low melting temperature liquid metals and their impacts on physical chemistry. *Acc. Mater. Res.* **2021**, 2, 577.

[2] J. Ye, Z.-R. Xing, J.-Y. Gao, J. Liu, Liquid metal coil. *Mater. Today Commun.* **2022**, 32, 104120.

[3] M. Baharfar, M. Mayyas, M. Rahbar, F.-M. Allioux, J. Tang, Y. Wang, Z. Cao, F. Centurion, R. Jalili, G. Liu, K. Kalantar-Zadeh, Exploring interfacial graphene oxide reduction by liquid metals: Application in selective biosensing. *ACS Nano* **2021**, 15, 19661.

[4] S. Chen, H.-Z. Wang, R.-Q. Zhao, Liquid metal composites. W. Rao, J. Liu, *Matter* **2020**, 2, 1446.

[5] Z. Ma, Q. Huang, Q. Xu, Q. Zhuang, X. Zhao, Y. Yang, H. Qiu, Z. Yang, C. Wang, Y. Chai, Z. Zheng, Permeable superelastic liquid-metal fibre mat enables biocompatible and monolithic stretchable electronics. *Nat. Mater.* **2021**, 20, 859.

[6] S. Houshyar, A. Rifai, R. Zizhou, C. Dekiwadia, M. A. Booth, S. John, K. Fox, V. K. Truong, Liquid metal polymer composite: Flexible, conductive, biocompatible, and antimicrobial scaffold. *J. Biomed. Mater. Res. Part B* **2022**, 110, 1131.

[7] L. Mou, J. Qi, L. Tang, R. Dong, Y. Xia, Y. Gao, X. Jiang, Highly stretchable and biocompatible liquid metal-elastomer conductors for self-healing electronics. *Small* **2020**, 16, 2005336.

[8] N. Ning, W. Huang, S. Liu, Q. Zhao, H. Zou, B. Yu, M. Tian, L. Zhang, Highly stretchable liquid metal/polyurethane sponge conductors with excellent electrical conductivity stability and good mechanical properties. *Compos. B: Eng.* **2019**, 179, 107492.

[9] T. Lim, H. Zhang, Multilayer carbon nanotube/gold nanoparticle composites on gallium-based liquid metals for electrochemical biosensing. *ACS Appl. Nano Mater.* **2021**, 4, 12690.

[10] M. Zhang, X. Wang, Z. Huang, W. Rao, Liquid metal based flexible and implantable biosensors. *Biosensors* **2020**, 10, 170.

[11] Y. Liu, S. Lu, Z. Zhang, Z. Yang, X. Cui, G. Liu, Printable biosensors towards next-generation point-of-care testing: paper substrate as an example. *Lab Chip* **2023**, 23, 3328.

[12] Y. Lu, Q. Hu, Y. Lin, D. B. Pacardo, C. Wang, W. Sun, F. S. Ligler, M. D. Dickey, Z. Gu, Transformable liquid-metal nanomedicine. *Nat. Commun.* **2015**, 6, 10066.
[13] D. Kim, J. Hwang, Y. Choi, Y. Kwon, J. Jang, S. Yoon, Effective delivery of anti-cancer drug molecules with shape transforming liquid metal particles. J. Choi, *Cancers* **2019**, 11, 1666.
[14] K. Khoshmanesh, S.-Y. Tang, J. Y. Zhu, S. Schaefer, A. Mitchell, K. Kalantar-zadeh, M. D. Dickey, Liquid metal enabled microfluidics. *Lab Chip* **2017**, 17, 974.
[15] L. Zhu, B. Wang, S. Handschuh-Wang, X. Zhou, Liquid metal-based soft microfluidics. *Small* **2020**, 16, 1903841.
[16] Y. Yu, J. Guo, B. Ma, D. Zhang, Y. Zhao, Liquid metal-integrated ultra-elastic conductive microfibers from microfluidics for wearable electronics. *Sci. Bull.* **2020**, 65, 1752.
[17] Y.-G. Park, G.-Y. Lee, J. Jang, S. M. Yun, E. Kim, J.-U. Park, Liquid metal-based soft electronics for wearable healthcare. *Adv. Healthcare Mater.* **2021**, 10, 2002280.
[18] E. J. Markvicka, M. D. Bartlett, X. Huang, C. Majidi, An autonomously electrically self-healing liquid metal–elastomer composite for robust soft-matter robotics and electronics. *Nat. Mater.* **2018**, 17, 618.
[19] K. Kalantar-Zadeh, J. Tang, T. Daeneke, A. P. O'Mullane, L. A. Stewart, J. Liu, C. Majidi, R. S. Ruoff, P. S. Weiss, M. D. Dickey, Emergence of liquid metals in nanotechnology. *ACS Nano* **2019**, 13, 7388.
[20] R. R. Moskalyk, A. Alfantazi, Review of copper pyrometallurgical practice: today and tomorrow. *Miner. Eng.* **2003**, 16, 893.
[21] D. Caplin, J. Cooper, P. Ford, J. Loram, Bryan Randell Coles. *Philos. Mag. B* **1992**, 65, 1113.
[22] D. Wang, W. Rao, Alginate sponge assisted instantize liquid metal nanocomposite for photothermo-chemotherapy. *Appl. Mater. Today* **2022**, 29, 101583.
[23] G. Li, D.-W. Lee, An advanced selective liquid-metal plating technique for stretchable biosensor applications. *Lab Chip* **2017**, 17, 3415.
[24] P. S. Banerjee, D. K. Rana, S. S. Banerjee, Influence of microstructural alterations of liquid metal and its interfacial interactions with rubber on multifunctional properties of soft composite materials. *Adv. Colloid Interface Sci.* **2022**, 308, 102752.
[25] P. Duwez, R. H. Willens, W. Klement, Jr., Metastable Electron Compound in Ag-Ge Alloys. *J. Appl. Phys.* **2004**, 31, 1137.
[26] S. Handschuh-Wang, T. Gan, T. Wang, F. J. Stadler, X. Zhou, Surface tension of the oxide skin of gallium-based liquid metals. *Langmuir* **2021**, 37, 9017.
[27] I. Egry, E. Ricci, R. Novakovic, S. Ozawa, Surface tension of liquid metals and alloys—Recent developments. *Adv. Colloid Interface Sci.* **2010**, 159, 198.
[28] K. Foremny, S. Nagels, M. Kreienmeyer, T. Doll, W. Deferme, Biocompatibility testing of liquid metal as an interconnection material for flexible implant technology. *Nanomaterials (Basel)* **2021**, 11.
[29] S. Chen, R. Zhao, X. Sun, H. Wang, L. Li, J. Liu, Toxicity and biocompatibility of liquid metals. *Adv. Healthcare Mater.* **2023**, 12, 2201924.
[30] N. B. Morley, J. Burris, L. C. Cadwallader, M. D. Nornberg, GaInSn usage in the research laboratory. *Rev. Sci. Instrum.* **2008**, 79, 056107.
[31] M. Zhang, S. Yao, W. Rao, J. Liu, Transformable soft liquid metal micro/nanomaterials. *Mater. Sci. Eng.: R: Rep.* **2019**, 138, 1.

[32] M. D. Dickey, R. C. Chiechi, R. J. Larsen, E. A. Weiss, D. A. Weitz, G. M. Whitesides, *Adv. Funct. Mater.* **2008**, 18, 1097.
[33] J. Kalová, R. Mareš, *Int. J. Thermophys.* **2015**, 36, 2862.
[34] T. Liu, P. Sen, C. J. Kim, Characterization of nontoxic liquid-metal alloy galinstan for applications in microdevices. *J. Microelectromech. Syst.* **2012**, 21, 443.
[35] D. Kim, P. Thissen, G. Viner, D.-W. Lee, W. Choi, Y. J. Chabal, J.-B. Lee, Recovery of nonwetting characteristics by surface modification of gallium-based liquid metal droplets using hydrochloric acid vapor. *ACS Appl. Mater. Interfaces* **2013**, 5, 179.
[36] X. Zhang, T. Li, Y. Li, Y. Duan, H. Li, How do different liquid metal films coalesce on carbon substrates?. *J. Phys. Chem. C* **2018**, 122, 7702.
[37] Y. Liu, M. Gao, S. Mei, Y. Han, J. Liu, Ultra-compliant liquid metal electrodes with in-plane self-healing capability for dielectric elastomer actuators. *Appl. Phys. Lett.* **2013**, 103.
[38] Z. J. Farrell, C. Tabor, Control of gallium oxide growth on liquid metal eutectic gallium/indium nanoparticles via thiolation. *Langmuir* **2018**, 34, 234.
[39] M. G. Mohammed, R. Kramer, All-printed flexible and stretchable electronics. *Adv. Mater.* **2017**, 29, 1604965.
[40] Y. Khan, A. Thielens, S. Muin, J. Ting, C. Baumbauer, A. C. Arias, A new frontier of printed electronics: flexible hybrid electronics. *Adv. Mater.* **2020**, 32, 1905279.
[41] B. Deng, G. J. Cheng, *Adv. Mater.* **2019**, 31, 1807811.
[42] A. Kamyshny, S. Magdassi, Conductive nanomaterials for 2D and 3D printed flexible electronics. *Chem. Soc. Rev.* **2019**, 48, 1712.
[43] M. M. Hamedi, A. Ainla, F. Güder, D. C. Christodouleas, M. T. Fernández-Abedul, G. M. Whitesides, Integrating electronics and microfluidics on paper. *Adv. Mater.* **2016**, 28, 5054.
[44] N. C. Raut, K. Al-Shamery, Inkjet printing metals on flexible materials for plastic and paper electronics. *J. Mater. Chem. C* **2018**, 6, 1618.
[45] A. Sheng, S. Khuje, J. Yu, D. Petit, T. Parker, C.-G. Zhuang, L. Kester, S. Ren, Ultrahigh Temperature Copper-Ceramic Flexible Hybrid Electronics. *Nano Lett.* **2021**, 21, 9279.
[46] J. Ma, F. Krisnadi, M. H. Vong, M. Kong, O. M. Awartani, M. D. Dickey, Shaping a soft future: patterning liquid metals. *Adv. Mater.* **2023**, 35, 2205196.
[47] Yi, Zheng, Qin, Zhang, Jing, Liu, Pervasive liquid metal based direct writing electronics with roller-ball pen. *AIP Adv.* **2013**, 3, 112117.
[48] L. Tang, J. Mou, W. Zhang, X. Jiang, Large-scale fabrication of highly elastic conductors on a broad range of surfaces. *ACS Appl. Mater. Interfaces* **2019**, 11, 7138.
[49] X. Xu, G. Han, H. Yu, X. Jin, J. Yang, J. Lin, C. Ma, Resistance change of stretchable composites based on inkjet-printed silver nanowires. *J. Phys. D: Appl. Phys.* **2020**, 53, 05LT02.
[50] D. Foresti, K. T. Kroll, R. Amissah, F. Sillani, K. A. Homan, D. Poulikakos, J. A. Lewis, Acoustophoretic printing. *Sci. Adv.* **2018**, 4, eaat1659.
[51] L. Teng, L. Zhu, S. Handschuh-Wang, X. Zhou, Robust, multiscale liquid-metal patterning enabled by a sacrificial sealing layer for flexible and wearable wireless powering. *J. Mater. Chem. C* **2019**, 7, 15243.
[52] L. Ren, J. Zhuang, G. Casillas, H. Feng, Y. Liu, X. Xu, Y. Liu, J. Chen, Y. Du, L. Jiang, S. X. Dou, Nanodroplets for stretchable superconducting circuits. *Adv. Funct. Mater.* **2016**, 26, 8111.

[53] S. Peng, Y. Li, L. Wu, J. Zhong, Z. Weng, L. Zheng, Z. Yang, J.-T. Miao, 3D printing mechanically robust and transparent polyurethane elastomers for stretchable electronic sensors. *ACS Appl. Mater. Interfaces* **2020**, 12, 6479.
[54] Y. Lin, J. Genzer, W. Li, R. Qiao, M. D. Dickey, S.-Y. Tang, Sonication-enabled rapid production of stable liquid metal nanoparticles grafted with poly (1-octadecene-alt-maleic anhydride) in aqueous solutions. *Nanoscale* **2018**, 10, 19871.
[55] D. Wang, C. Gao, W. Wang, M. Sun, B. Guo, H. Xie, Q. He, Shape-transformable, fusible rodlike swimming liquid metal nanomachine. *ACS Nano* **2018**, 12, 10212.
[56] C. Zhang, F.-M. Allioux, M. A. Rahim, J. Han, J. Tang, M. B. Ghasemian, S.-Y. Tang, M. Mayyas, T. Daeneke, P. Le-Clech, R. B. Kaner, D. Esrafilzadeh, K. Kalantar-Zadeh, *CNucleation and growth of polyaniline nanofibers onto liquid metal nanoparticles. hem. Mater.* **2020**, 32, 4808.
[57] S.-Y. Tang, R. Qiao, Y. Lin, Y. Li, Q. Zhao, D. Yuan, G. Yun, J. Guo, M. D. Dickey, T. J. Huang, T. P. Davis, K. Kalantar-Zadeh, W. Li, Functional Liquid Metal Nanoparticles Produced by Liquid-Based Nebulization. *Adv. Mater. Technol.* **2019**, 4, 1800420.
[58] P. Lin, Z. Wei, Q. Yan, J. Xie, Y. Fan, M. Wu, Y. Chen, Z. Cheng, Capillary-based microfluidic fabrication of liquid metal microspheres toward functional microelectrodes and photothermal medium. *ACS Appl. Mater. Interfaces* **2019**, 11, 25295.
[59] Q. Hu, T. Jiang, H. Jiang, Numerical simulation and experimental validation of liquid metal droplet formation in a Co-flowing capillary microfluidic device. *Micromachines* **2020**, 11, 169.
[60] H. Bark, P. S. Lee, Surface modification of liquid metal as an effective approach for deformable electronics and energy devices. *Chem. Sci.* **2021**, 12, 2760.
[61] Y. Lin, J. Genzer, M. D. Dickey, Attributes, fabrication, and applications of gallium-based liquid metal particles. *Adv. Sci.* **2020**, 7, 2000192.
[62] K. S. Suslick, Sonochemistry. *Science* **1990**, 247, 1439.
[63] T. R. Lear, S.-H. Hyun, J. W. Boley, E. L. White, D. H. Thompson, R. K. Kramer, Liquid metal particle popping: Macroscale to nanoscale. *Extreme Mech. Lett.* **2017**, 13, 126.
[64] Y. Lin, C. Cooper, M. Wang, J. J. Adams, J. Genzer, M. D. Dickey, Handwritten, soft circuit boards and antennas using liquid metal nanoparticles. *Small* **2015**, 11, 6397.
[65] A. Yamaguchi, Y. Mashima, T. Iyoda, Reversible size control of liquid-metal nanoparticles under ultrasonication. *Angew. Chem. Int. Ed.* **2015**, 54, 12809.
[66] J. W. Boley, E. L. White, R. K. Kramer, Mechanically sintered gallium-indium nanoparticles. *Adv. Mater.* **2015**, 27, 2355.
[67] D. Kim, J.-B. Lee, Magnetic-field-induced liquid metal droplet manipulation. *J. Korean Phys. Soc.* **2015**, 66, 282.
[68] Z. Huang, S. Zou, G. Liu, Surface Modification of Liquid Metal with p-Aniline Derivatives toward Bioapplications: Biosensing as an Example. *ACS Appl. Mater. Interfaces* **2022**, 14, 56429.
[69] J. N. Hohman, M. Kim, G. A. Wadsworth, H. R. Bednar, J. Jiang, M. A. LeThai, P. S. Weiss, "Directing substrate morphology via self-assembly: Ligand-mediated scission of gallium–indium microspheres to the nanoscale. *Nano Lett.* **2011**, 11, 5104.
[70] Y. Yu, E. Miyako, Manipulation of Biomolecule-Modified Liquid-Metal Blobs. *Angew. Chem. Int. Ed.* **2017**, 56, 13606.

[71] J. Yan, M. H. Malakooti, Z. Lu, Z. Wang, N. Kazem, C. Pan, M. R. Bockstaller, C. Majidi, K. Matyjaszewski, Solution processable liquid metal nanodroplets by surface-initiated atom transfer radical polymerization. *Nat. Nanotechnol.* **2019**, 14, 684.
[72] M. A. Creighton, M. C. Yuen, N. J. Morris, C. E. Tabor, Graphene-based encapsulation of liquid metal particles. *Nanoscale* **2020**, 12, 23995.
[73] P. Wu, J. Fu, Y. Xu, Y. He, Liquid metal microgels for three-dimensional printing of smart electronic clothes. *ACS Appl. Mater. Interfaces* **2022**, 14, 13458.
[74] Y. Ding, X. Guo, Y. Qian, H. Gao, D. H. Weber, L. Zhang, J. B. Goodenough, G. Yu, In Situ Formation of Liquid Metals via Galvanic Replacement Reaction to Build Dendrite-Free Alkali-Metal-Ion Batteries. *Angew. Chem. Int. Ed.* **2020**, 59, 12170.
[75] R. David, N. Miki, Synthesis of sub-micrometer biphasic Au-$AuGa_2$/liquid metal frameworks. *Nanoscale* **2019**, 11, 21419.
[76] M. B. Ghasemian, M. Mayyas, S. A. Idrus-Saidi, M. A. Jamal, J. Yang, S. S. Mofarah, E. Adabifiroozjaei, J. Tang, N. Syed, A. P. O'Mullane, T. Daeneke, K. Kalantar-Zadeh, Self-limiting galvanic growth of MnO_2 monolayers on a liquid metal—applied to photocatalysis. *Adv. Funct. Mater.* **2019**, 29, 1901649.
[77] J. Gong, B. Liu, P. Zhang, H. Zhang, L. Gui, Copper-Electroplating-Modified Liquid Metal Microfluidic Electrodes. *Sensors* **2022**, 22, 1820.
[78] J. Tang, X. Zhao, J. Li, Y. Zhou, J. Liu, Liquid metal phagocytosis: intermetallic wetting induced particle internalization. *Adv. Sci.* **2017**, 4, 1700024.
[79] A. Yamaguchi, Y. Mashima, T. Iyoda, Reversible size control of liquid-metal nanoparticles under ultrasonication. *Angew. Chem. Int. Ed.* **2015**, 54, 12809.
[80] Z. J. Farrell, C. J. Thrasher, A. E. Flynn, C. E. Tabor, Silanized liquid-metal nanoparticles for responsive electronics. *ACS Appl. Nano Mater.* **2020**, 3, 6297.
[81] C. Chiew, M. J. Morris, M. H. Malakooti, Functional liquid metal nanoparticles: synthesis and applications. *Mater. Adv.* **2021**, 2, 7799.
[82] X. Li, X. Ding, Y. Du, C. Xiao, K. Zheng, X. Liu, X. Tian, X. Zhang, Controlled transformation of liquid metal microspheres in aqueous solution triggered by growth of GaOOH. *ACS Omega* **2022**, 7, 7912.
[83] J. Guo, J. Cheng, H. Jin, Q. Sun, J. Yang, W. Liu, Constructing a novel and high-performance liquid nanoparticle additive from a Ga-based liquid metal. *Nanoscale* **2020**, 12, 9208.
[84] S. Y. Tang, R. Qiao, S. Yan, D. Yuan, Q. Zhao, G. Yun, T. P. Davis, W. Li, Microfluidic mass production of stabilized and stealthy liquid metal nanoparticles. *Small* **2018**, 14, e1800118.
[85] Z. J. Farrell, N. Reger, I. Anderson, E. Gawalt, C. Tabor, Route to Universally Tailorable Room-Temperature Liquid Metal Colloids via Phosphonic Acid Functionalization. *J. Phys. Chem. C* **2018**, 122, 26393.
[86] N. Ilyas, A. Cook, C. E. Tabor, Designing liquid metal interfaces to enable next generation flexible and reconfigurable electronics. *Adv. Mater. Interfaces* **2017**, 4, 1700141.
[87] F. Centurion, M. M. Hassan, J. Tang, F.-M. Allioux, S. Chakraborty, R. Chen, G. Mao, N. Kumar, K. Kalantar-Zadeh, M. A. Rahim, *Nanoscale* **2022**, 14, 14760.
[88] M. A. Rahim, F. Centurion, J. Han, R. Abbasi, M. Mayyas, J. Sun, M. J. Christoe, D. Esrafilzadeh, F. M. Allioux, M. B. Ghasemian, *Adv. Funct. Mater.* **2021**, 31, 2007336.

[89] G. Bo, H. Yu, L. Ren, N. Cheng, H. Feng, X. Xu, S. X. Dou, H. Wang, Y. Du, Gallium-indium-tin liquid metal nanodroplet-based anisotropic conductive adhesives for flexible integrated electronics. *ACS Appl. Nano Mater.* **2021**, 4, 550.
[90] S. Li, Y. Li, K. Liu, M. Chen, W. Peng, Y. Yang, X. Li, Laser induced core–shell liquid metal quantum dots for high-efficiency carbon-based perovskite solar cells. *Appl. Surf. Sci.* **2021**, 565, 150470.
[91] J. Chen, J. Zhang, Z. Luo, J. Zhang, L. Li, Y. Su, X. Gao, Y. Li, W. Tang, C. Cao, Q. Liu, L. Wang, H. Li, Superelastic, sensitive, and low hysteresis flexible strain sensor based on wave-patterned liquid metal for human activity monitoring. *ACS Appl. Mater. Interfaces* **2020**, 12, 22200.
[92] T. Gan, W. Shang, S. Handschuh-Wang, X. Zhou, Light-induced shape morphing of liquid metal nanodroplets enabled by polydopamine coating. *Small* **2019**, 15, 1804838.
[93] J. Gao, Q. Yan, X. Tan, L. Lv, J. Ying, X. Zhang, M. Yang, S. Du, Q. Wei, C. Xue, H. Li, J. Yu, C. T. Lin, W. Dai, N. Jiang, Surface modification using polydopamine-coated liquid metal nanocapsules for improving performance of graphene paper-based thermal interface materials. *Nanomaterials (Basel)* **2021**, 11.
[94] D. Xu, J. Hu, X. Pan, S. Sánchez, X. Yan, X. Ma, Enzyme-powered liquid metal nanobots endowed with multiple biomedical functions. *ACS Nano* **2021**, 15, 11543.
[95] Y. Zhang, F. Wang, H. Zhang, H. Wang, Y. Liu, Multivalency interface and g-C3N4 coated liquid metal nanoprobe signal amplification for sensitive electrogenerated chemiluminescence detection of exosomes and their surface proteins. *Anal. Chem.* **2019**, 91, 12100.
[96] Y. Liu, Q. Wang, S. Bi, W. Zhang, H. Zhou, X. Jiang, Water-processable liquid metal nanoparticles by single-step polymer encapsulation. *Nanoscale* **2020**, 12, 13731.
[97] T. Liu, X. Wu, S. Zhu, F. Lorandi, L. Ni, S. Li, M. Sun, B. P. Bloom, D. H. Waldeck, V. Viswanathan, J. F. Whitacre, K. Matyjaszewski, Polymer-Stabilized Liquid Metal Nanoparticles as a Scalable Current Collector Engineering Approach Enabling Lithium Metal Anodes. *ACS Appl. Energy Mater.* **2022**, 5, 3615.
[98] B. Fan, J. Wan, Y. Liu, W. W. Tian, S. H. Thang, Functionalization of liquid metal nanoparticles via the RAFT process. *Polym. Chem.* **2021**, 12, 3015.
[99] J. Ma, Y. Lin, Y.-W. Kim, Y. Ko, J. Kim, K. H. Oh, J.-Y. Sun, C. B. Gorman, M. A. Voinov, A. I. Smirnov, J. Genzer, M. D. Dickey, Liquid metal nanoparticles as initiators for radical polymerization of vinyl monomers. *ACS Macro Lett.* **2019**, 8, 1522.
[100] X. Han, Y. Li, Z. Deng, DNA-wrapped single walled carbon nanotubes as rigid templates for assembling linear gold nanoparticle arrays. *Adv. Mater.* **2007**, 19, 1518.
[101] Z. Wang, H. Guo, R. Gui, H. Jin, J. Xia, F. Zhang, Simultaneous and selective measurement of dopamine and uric acid using glassy carbon electrodes modified with a complex of gold nanoparticles and multiwall carbon nanotubes. *Sens. Actuators, B* **2018**, 255, 2069.
[102] Y. Lu, Y. Lin, Z. Chen, Q. Hu, Y. Liu, S. Yu, W. Gao, M. D. Dickey, Z. Gu, Enhanced endosomal escape by light-fueled liquid-metal transformer. *Nano Lett.* **2017**, 17, 2138.
[103] J. Li, Y. Li, L. Yang, S. Yin, $Ti_3C_2T_x$/PANI/liquid metal composite microspheres with 3D nanoflower structure: preparation, characterization, and applications in EMI shielding. *Adv. Mater. Interfaces* **2022**, 9, 2102266.

[104] J.-J. Hu, M.-D. Liu, Y. Chen, F. Gao, S.-Y. Peng, B.-R. Xie, C.-X. Li, X. Zeng, X.-Z. Zhang, Immobilized liquid metal nanoparticles with improved stability and photothermal performance for combinational therapy of tumor. *Biomaterials* **2019**, 207, 76.
[105] D. N. Rockwood, R. C. Preda, T. Yücel, X. Wang, M. L. Lovett, D. L. Kaplan, Materials fabrication from Bombyx mori silk fibroin. *Nat. Protoc.* **2011**, 6, 1612.
[106] J. Liu, T. Kong, H.-M. Xiong, Mulberry-Leaves-Derived Red-Emissive Carbon Dots for Feeding Silkworms to Produce Brightly Fluorescent Silk. *Adv. Mater.* **2022**, 34, 2200152.
[107] H. M. Mousa, K. H. Hussein, M. M. Sayed, M. R. El-Aassar, I. M. A. Mohamed, H.-H. Kwak, H.-M. Woo, A. Abdal-hay, Development of biocompatible tri-layered nanofibers patches with endothelial cells for cardiac tissue engineering. *Eur. Polym. J.* **2020**, 129, 109630.
[108] Y. Zhang, Z. Cheng, C. Ni, Z. Wang, Y. Yu, X. Zhai, S. Xu, Z. Zhao, L. Hu, Y. Hu, Highly conductive EGaIn/silk fibroin ink for graphene 3D array structure micro-supercapacitors. *Chem. Eng. J.* **2022**, 428, 132084.
[109] B. He, P. Wang, Q. Lu, Y. Du, S. Liu, Q. Ye, F. Zhou, W. Liu, Zwitterionic microgel-functionalized gallium-based liquid-metal nanodroplets as aqueous lubricant additives. *Tribol. Int.* **2023**, 177, 107952.
[110] O. Oloye, C. Tang, A. Du, G. Will, A. P. O'Mullane, Galvanic replacement of liquid metal galinstan with Pt for the synthesis of electrocatalytically active nanomaterials. *Nanoscale* **2019**, 11, 9705.
[111] F. Hoshyargar, J. Crawford, A. P. O'Mullane, Galvanic replacement of the liquid metal galinstan. *J. Am. Chem. Soc.* **2017**, 139, 1464.
[112] M. Karbalaei Akbari, Z. Hai, Z. Wei, R. K. Ramachandran, C. Detavernier, M. Patel, J. Kim, F. Verpoort, H. Lu, S. Zhuiykov, Sonochemical functionalization of the low-dimensional surface oxide of Galinstan for heterostructured optoelectronic applications. *J. Mater. Chem. C* **2019**, 7, 5584.
[113] D. Desmaële, F. La Malfa, F. Rizzi, A. Qualtieri, M. De Vittorio, Including liquid metal into porous elastomeric films for flexible and enzyme-free glucose fuel cells: a preliminary evaluation. *J. Low Power Electron. Appl.* **2018**, 8, 45.
[114] Y. Wang, S. Wang, H. Chang, W. Rao, Galvanic replacement of liquid metal/reduced graphene oxide frameworks. *Adv. Mater. Interfaces* **2020**, 7, 2000626.
[115] A. S. Falchevskaya, N. K. Kulachenkov, S. V. Bachinin, V. A. Milichko, V. V. Vinogradov, Single Particle Color Switching by Laser-Induced Deformation of Liquid Metal-derived Microcapsules. *J. Phys. Chem. Lett.* **2021**, 12, 7738.
[116] Z. Guo, J. Lu, D. Wang, W. Xie, Y. Chi, J. Xu, N. Takuya, J. Zhang, W. Xu, F. Gao, H. Wu, L. Zhao, Galvanic replacement reaction for in situ fabrication of litchi-shaped heterogeneous liquid metal-Au nano-composite for radio-photothermal cancer therapy. *Bioact. Mater.* **2021**, 6, 602.
[117] O. Oloye, J. F. S. Fernando, E. R. Waclawik, D. Golberg, A. P. O'Mullane, Galvanic replacement of liquid metal Galinstan with copper for the formation of photocatalytically active nanomaterials. *New J. Chem.* **2020**, 44, 14979.
[118] L. Castilla-Amorós, D. Stoian, J. R. Pankhurst, S. B. Varandili, R. Buonsanti, Exploring the chemical reactivity of gallium liquid metal nanoparticles in galvanic replacement. *J. Am. Chem. Soc.* **2020**, 142, 19283.

[119] Z. Huang, M. Guan, Z. Bao, F. Dong, X. Cui, G. Liu, Ligand Mediation for Tunable and Oxide Suppressed Surface Gold-Decorated Liquid Metal Nanoparticles. *Small* **2023**, 2306652.
[120] A. S. Hamdy Makhlouf, R. Rodriguez, Advances in Smart Coatings and Thin Films for Future Industrial and Biomedical Engineering Applications. Elsevier **2020**, p. 407.
[121] J. Zhang, R. Guo, J. Liu, Self-propelled liquid metal motors steered by a magnetic or electrical field for drug delivery. *J. Mater. Chem. B* **2016**, 4, 5349.
[122] S. Kim, J. Han, M.-A. Kang, W. Song, S. Myung, S.-W. Kim, S. S. Lee, J. Lim, K.-S. An, Flexible chemical sensors based on hybrid layer consisting of molybdenum disulphide nanosheets and carbon nanotubes. *Carbon* **2018**, 129, 607.
[123] V. Zardetto, T. M. Brown, A. Reale, A. Di Carlo, Substrates for flexible electronics: A practical investigation on the electrical, film flexibility, optical, temperature, and solvent resistance properties. *J. Polym. Sci., Part B: Polym. Phys.* **2011**, 49, 638.
[124] Y. Zhao, J.-G. Song, G. H. Ryu, K. Y. Ko, W. J. Woo, Y. Kim, D. Kim, J. H. Lim, S. Lee, Z. Lee, J. Park, H. Kim, Low-temperature synthesis of 2D MoS 2 on a plastic substrate for a flexible gas sensor. *Nanoscale* **2018**, 10, 9338.
[125] V.-T. Nguyen, Q.-D. Nguyen, B. K. Min, Y. Yi, C.-G. Choi, $Ti_3C_2T_x$ MXene/carbon nanotubes/waterborne polyurethane based composite ink for electromagnetic interference shielding and sheet heater applications. *Chem. Eng. J.* **2022**, 430, 133171.
[126] D. Zhang, S. Xu, X. Zhao, W. Qian, C. R. Bowen, Y. Yang, Wireless monitoring of small strains in intelligent robots via a joule heating effect in stretchable graphene–polymer nanocomposites. *Adv. Funct. Mater.* **2020**, 30, 1910809.
[127] T. Q. Trung, S. Ramasundaram, B.-U. Hwang, N.-E. Lee, An all-elastomeric transparent and stretchable temperature sensor for body-attachable wearable electronics. *Adv. Mater.* **2016**, 28, 502.
[128] D. Zhang, Y. Tang, Y. Zhang, F. Yang, Y. Liu, X. Wang, J. Yang, X. Gong, J. Zheng, Highly stretchable, self-adhesive, biocompatible, conductive hydrogels as fully polymeric strain sensors. *J. Mater. Chem. A* **2020**, 8, 20474.
[129] S. Zhang, L. Cai, W. Li, J. Miao, T. Wang, J. Yeom, N. Sepúlveda, C. Wang, Fully Printed Silver-Nanoparticle-Based Strain Gauges with Record High Sensitivity. *Adv. Electron. Mater.* **2017**, 3, 1700067.
[130] L. Li, Z. Lou, D. Chen, K. Jiang, W. Han, G. Shen, Recent advances in flexible/stretchable supercapacitors for wearable electronics. *Small* **2018**, 14, 1702829.
[131] H. Li, H. Guo, K. Huang, B. Liu, C. Zhang, X. Chen, X. Xu, J. Yang, Carbon electrode with conductivity improvement using silver nanowires for high-performance supercapacitor. *Appl. Phys. A* **2018**, 124, 763.
[132] X. Xu, Z. Liu, P. He, J. Yang, Screen printed silver nanowire and graphene oxide hybrid transparent electrodes for long-term electrocardiography monitoring. *J. Phys. D: Appl. Phys.* **2019**, 52, 455401.
[133] Y. Zhang, P. He, M. Luo, X. Xu, G. Dai, J. Yang, Highly stretchable polymer/silver nanowires composite sensor for human health monitoring. *Nano Res.* **2020**, 13, 919.
[134] X. Xu, M. Luo, P. He, J. Yang, Washable and flexible screen printed graphene electrode on textiles for wearable healthcare monitoring. *J. Phys. D: Appl. Phys.* **2020**, 53, 125402.
[135] S. Jang, J. Kim, D. W. Kim, J. W. Kim, S. Chun, H. J. Lee, G.-R. Yi, C. Pang, Carbon-based, ultraelastic, hierarchically coated fiber strain sensors with crack-controllable beads. *ACS Appl. Mater. Interfaces* **2019**, 11, 15079.

[136] Y. Gao, X. Fang, J. Tan, T. Lu, L. Pan, F. Xuan, Highly sensitive strain sensors based on fragmentized carbon nanotube/polydimethylsiloxane composites. *Nanotechnology* **2018**, 29, 235501.
[137] X. Li, M. Li, L. Zong, X. Wu, J. You, P. Du, C. Li, Liquid metal droplets wrapped with polysaccharide microgel as biocompatible aqueous ink for flexible conductive devices. *Adv. Funct. Mater.* **2018**, 28, 1804197.
[138] T. Daeneke, K. Khoshmanesh, N. Mahmood, I. A. de Castro, D. Esrafilzadeh, S. J. Barrow, M. D. Dickey, K. Kalantar-zadeh, Liquid metals: fundamentals and applications in chemistry. *Chem. Soc. Rev.* **2018**, 47, 4073.
[139] B. Deng, G. J. Cheng, Pulsed laser modulated shock transition from liquid metal nanoparticles to mechanically and thermally robust solid–liquid patterns. *Adv. Mater.* **2019**, 31, 1807811.
[140] M. J. Ford, D. K. Patel, C. Pan, S. Bergbreiter, C. Majidi, Controlled assembly of liquid metal inclusions as a general approach for multifunctional composites. *Adv. Mater.* **2020**, 32, 2002929.
[141] J.-H. Kim, S. Kim, H. Kim, S. Wooh, J. Cho, M. D. Dickey, J.-H. So, H.-J. Koo, *Nat Commun.* **2022**, 13, 4763.
[142] Y.-G. Park, H. Min, H. Kim, A. Zhexembekova, C. Y. Lee, J.-U. Park, *Nano Lett.* **2019**, 19, 4866.
[143] Y.-G. Park, H. S. An, J.-Y. Kim, J.-U. Park, *Sci Adv.* **2019**, 5, eaaw2844.
[144] K. Yamagishi, W. Zhou, T. Ching, S. Y. Huang, M. Hashimoto, *Adv. Mater.* **2021**, 33, 2008062.
[145] J. W. Boley, E. L. White, G. T. C. Chiu, R. K. Kramer, Direct Writing of Gallium-Indium Alloy for Stretchable Electronics. *Adv. Funct. Mater.* **2016**, 26, 2405.
[146] D. A. Pardo, G. E. Jabbour, N. Peyghambarian, Application of screen printing in the fabrication of organic light-emitting devices. *Adv. Mater.* **2000**, 12, 1249.
[147] M. Wang, C. Ma, P. C. Uzabakiriho, X. Chen, Z. Chen, Y. Cheng, Z. Wang, G. Zhao, *Acs Nano* **2021**, 15, 19364.
[148] K. Zheng, F. Gu, H. Wei, L. Zhang, X. a. Chen, H. Jin, S. Pan, Y. Chen, S. Wang, *Small Methods* **2023**, 7, 2201534.
[149] R. Dong, L. Wang, C. Hang, Z. Chen, X. Liu, L. Zhong, J. Qi, Y. Huang, S. Liu, L. Wang, Y. Lu, X. Jiang, Printed stretchable liquid metal electrode arrays for in vivo neural recording. *Small* **2021**, 17, 2006612.
[150] M. Singh, H. M. Haverinen, P. Dhagat, G. E. Jabbour, Inkjet printing—process and its applications.*Adv. Mater.* **2010**, 22, 673.
[151] A. F. Silva, H. Paisana, T. Fernandes, J. Góis, A. Serra, J. F. J. Coelho, A. T. de Almeida, C. Majidi, M. Tavakoli, High resolution soft and stretchable circuits with PVA/liquid-metal mediated printing. *Adv. Mater. Technol.* **2020**, 5, 2000343.
[152] Y. Lin, O. Gordon, M. R. Khan, N. Vasquez, J. Genzer, M. D. Dickey, Vacuum filling of complex microchannels with liquid metal. *Lab Chip* **2017**, 17, 3043.
[153] C. Xiao, J. Feng, H. Xu, R. Xu, T. Zhou, Scalable strategy to directly prepare 2D and 3D liquid metal circuits based on laser-induced selective metallization. *ACS Appl. Mater. Interfaces* **2022**, 14, 20000.
[154] E. P. Yalcintas, K. B. Ozutemiz, T. Cetinkaya, L. Dalloro, C. Majidi, O. B. Ozdoganlar, Soft electronics manufacturing using microcontact printing. *Adv. Funct. Mater.* **2019**, 29, 1906551.

[155] B. Elder, R. Neupane, E. Tokita, U. Ghosh, S. Hales, Y. L. Kong, Nanomaterial patterning in 3D printing. *Adv. Mater.* **2020**, 32, 1907142.
[156] J. Xu, H. Guo, H. Ding, Q. Wang, Z. Tang, Z. Li, G. Sun, Printable and recyclable conductive ink based on a liquid metal with excellent surface wettability for flexible electronics. *ACS Appl. Mater. Interfaces* **2021**, 13, 7443.
[157] R. Xu, G. S. Cañón Bermúdez, O. V. Pylypovskyi, O. M. Volkov, E. S. Oliveros Mata, Y. Zabila, R. Illing, P. Makushko, P. Milkin, L. Ionov, Self-healable printed magnetic field sensors using alternating magnetic fields. *Nat. Commun.* **2022**, 13, 6587.
[158] Q. Zhuang, K. Yao, M. Wu, Z. Lei, F. Chen, J. Li, Q. Mei, Y. Zhou, Q. Huang, X. Zhao, Wafer-patterned, permeable, and stretchable liquid metal microelectrodes for implantable bioelectronics with chronic biocompatibility. *Sci Adv.* **2023**, 9, eadg8602.
[159] D. Pei, S. Yu, P. Liu, Y. Wu, X. Zhang, Y. Chen, M. Li, C. Li, Reversible wet-adhesive and self-healing conductive composite elastomer of liquid metal. *Adv. Funct. Mater.* **2022**, 32, 2204257.
[160] R. Fang, B. Yao, T. Chen, X. Xu, D. Xue, W. Hong, H. Wang, Q. Wang, S. Zhang, 3D Highly Stretchable Liquid Metal/Elastomer Composites with Strain - Enhanced Conductivity. *Adv. Funct. Mater.* **2023**, 2310225.
[161] H. Chathuranga, I. Marriam, Z. Zhang, J. MacLeod, R. Bai, Z. Lei, Y. Li, Y. Liu, H. Yang, C. Yan, Liquid metal incorporated graphene oxide films with enhanced through-plane thermal conductivity and flame resistance. *Applied Materials Today* **2022**, 29, 101617.
[162] F. Li, J. Shu, L. Zhang, N. Yang, J. Xie, X. Li, L. Cheng, S. Kuang, S.-Y. Tang, S. Zhang, Liquid metal droplet robot. *Applied Materials Today* **2020**, 19, 100597.
[163] X. Sun, T. Wu, M. Duan, B. Yuan, X. Zhu, H. Wang, J. Liu, Flexible Skin Patch Enabled Tumor Hybrid Thermophysical Therapy and Adaptive Antitumor Immune Response. *Adv. Healthc. Mater.* **2023**, 12, 2202872.
[164] J. Cheng, J. Shang, S. Yang, J. Dou, X. Shi, X. Jiang, Wet-Adhesive Elastomer for Liquid Metal-Based Conformal Epidermal Electronics. *Adv. Funct. Mater.* **2022**, 32, 2200444.
[165] Z. Ge, W. Guo, Y. Tao, H. Sun, X. Meng, L. Cao, S. Zhang, W. Liu, M. L. Akhtar, Y. Li, Wireless and Closed-Loop Smart Dressing for Exudate Management and On-Demand Treatment of Chronic Wounds. *Adv. Mater.* **2023**, 35, 2304005.
[166] M. Baharfar, M. Mayyas, M. Rahbar, F.-M. Allioux, J. Tang, Y. Wang, Z. Cao, F. Centurion, R. Jalili, G. Liu, Exploring interfacial graphene oxide reduction by liquid metals: Application in selective biosensing. *ACS nano* **2021**, 15, 19661.
[167] X. Sun, B. Cui, B. Yuan, X. Wang, L. Fan, D. Yu, Z. He, L. Sheng, J. Liu, J. Lu, Liquid metal microparticles phase change medicated mechanical destruction for enhanced tumor cryoablation and dual-mode imaging. *Adv. Healthc. Mater.* **2020**, 30, 2003359.
[168] J. Li, Z. Fu, Y. Liu, Encapsulation of liquid metal nanoparticles inside metal–organic frameworks for hydrogel-integrated dual functional biotherapy. *Chem. Eng. J.* **2023**, 457, 141302.
[169] Y. Lu, Q. Hu, Y. Lin, D. B. Pacardo, C. Wang, W. Sun, F. S. Ligler, M. D. Dickey, Z. Gu, Transformable liquid-metal nanomedicine. *Nat. Commun.* **2015**, 6, 10066.
[170] X.-L. Ding, M.-D. Liu, Q. Cheng, W.-H. Guo, M.-T. Niu, Q.-X. Huang, X. Zeng, X.-Z. Zhang, Multifunctional liquid metal-based nanoparticles with glycolysis and mitochondrial metabolism inhibition for tumor photothermal therapy. *Biomaterials* **2022**, 281, 121369.
[171] J. Yan, J. Wang, X. Wang, D. Pan, C. Su, J. Wang, M. Wang, J. Xiong, Y. Chen, L. Wang,

Adv. Mater. **2024**, 36, 2307817.
[172] X. Zhang, G. Chen, L. Sun, F. Ye, X. Shen, Y. Zhao, Claw-inspired microneedle patches with liquid metal encapsulation for accelerating incisional wound healing. *Chem. Eng. J.* **2021**, 406, 126741.
[173] Z. Ge, W. Guo, Y. Tao, H. Sun, X. Meng, L. Cao, S. Zhang, W. Liu, M. L. Akhtar, Y. Li, *Adv. Mater.* **2023**, 35, 2304005.
[174] D. Lee, S. Park, J. Seo, W. Y. Lee, M. g. Kim, J. Kim, Functionalized EGaIn Electrodes with Tunable Reduced-Graphene-Oxide Assembled EGaIn Core–Shell Particles for Soft and Deformable Electrochemical Biosensors. *Adv. Funct. Mater.* **2023**, 2311696.
[175] Q. Zhuang, K. Yao, M. Wu, Z. Lei, F. Chen, J. Li, Q. Mei, Y. Zhou, Q. Huang, X. Zhao, "Wafer-patterned, permeable, and stretchable liquid metal microelectrodes for implantable bioelectronics with chronic biocompatibility", *Sci. Adv.* **2023**, 9, eadg8602.

TOC