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Liquid Metal Micro- and Nanodroplets: Characteristics, Fabrication Techniques, and Applications

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Liquid Metal Micro- and Nanodroplets: Characteristics, Fabrication Techniques, and Applications

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Abstract

Gallium-based liquid metal micro- and nanodroplets are being extensively explored in innumerable emerging technologies. Although many of these systems involve the interfaces of liquid metal with a continuous phase liquid (*e.g.*, microfluidic channels and emulsions), the static or dynamic phenomena at the interface have been scarcely discussed. In this study, we begin by introducing the interfacial phenomena and characteristics observed at the interface between liquid metal and continuous phase liquids. Based on these results, we can employ various methods to fabricate liquid metal droplets with tunable surface properties. Finally, we discuss how these techniques can be directly applied to a wide range of state-of-the-art technologies including microfluidics, soft electronics, catalysts, and biomedicines.

1. Introduction

Metals that exist in the liquid state near room-temperature belong to a class of materials known as liquid metals. Liquid metals exhibit superior electrical and thermal conductivities compared with non-metallic liquids. At the same time, their liquid properties can be employed for the design of interconnections, where external deformations such as bending or stretching are prone to damage solid materials. Liquid metal-based structures can overcome this lack of durability while simultaneously maintaining their electrical conductivity.¹ There are several types of liquid metals with low melting points: mercury, alkali metals, and gallium-based alloys. Mercury is known for its high toxicity and low vapor pressure. Alkali metals (*e.g.*, sodium, rubidium, caesium, and francium) ignite spontaneously and react vigorously with water. Rubidium and caesium are highly explosive, while francium is highly radioactive. Meanwhile, gallium is a nontoxic and environmentally friendly alternative that opens a door to a wide range of industrial applications. In particular, gallium-based micro- and nanodroplets have been employed for the design of systems that require both conductivity and flexibility.^{2,3} In this review, we summarize and discuss the interfacial properties, fabrication processes, and technological applications of gallium-based liquid metal droplets.

The metallic bonding forces of liquid metal contribute to their extremely high surface tension (500-700 mN/m).^{4,5} Although high-surface-tension liquids generally bead up into spheres, gallium-based liquid metal droplets tend to exhibit non-spherical geometries. This can be attributed to the effect of surface oxidation,^{5,6} which alters the mechanical and rheological properties of liquid metal. It is common for wrinkles to develop on the oxidized membrane, even for microscale droplets prepared by ultrasonication.⁵ While oxide-free liquid metal exhibits Newtonian behaviors with constant viscosity, oxidized liquid metal is known to be shear-thinning. However, different viscosities may be reported for liquid metal exposed in air, since the measured viscosity may be strongly affected by the oxide skin. Furthermore, the presence of the surface oxide makes it difficult to measure the interfacial energy of liquid metal via conventional techniques such as contact angle measurements or the pendant droplet method. While these methods depend on the equilibrium of a droplet's geometry at the liquid-liquid or liquid-gas interface, liquid metal surrounded by an oxide membrane can no longer be considered as an ideal liquid droplet. Since these droplets exhibit irregular geometries and non-constant curvature profiles, it is difficult to obtain accurate values of the corresponding interfacial properties.^{4,5}

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4 Therefore, investigating the various phenomena taking place on the surface of liquid
5 metal micro- and nanodroplets is crucial to utilizing their full potential. Identifying the effects
6 of ambient oxygen solubility⁵ and electric fields (e.g., electrocapillarity, continuous
7 electrowetting, electrowetting-on-dielectric, and electrochemically controlled capillarity)⁷ on
8 liquid metal droplets provides insight into how the metallic surface interacts with its
9 environment. The interface between liquid metal and its surrounding environment can be
10 further modulated by applying various surface functionalization techniques^{6,9,10,11}. When it is
11 required to merge the droplets into continuous networks, we may introduce additional
12 processes of thermal, laser, or mechanical sintering. Based on these characteristics, researchers
13 have sought a number of different methods to tailor the design of liquid metal droplets. Liquid
14 metal traveling through microfluidic channels can be separated into individual droplets of
15 particular dimensions or geometries. Droplets with tunable properties can also be achieved by
16 performing ultrasonication or mechanical agitation. We can incorporate these liquid metal
17 droplets to design structures with a higher degree of complexity, such as microfluidic systems,
18 soft robots/electronics, catalyst particles, and biomedicines/drug delivery.^{1,2,3,4}
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33 **2. Interfacial Properties of Liquid Metal Droplets in Fluid Systems**

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36 In gallium-based liquid metal, the oxide thickness depends on the ambient condition of
37 oxygen or water vapor concentration, as well as the surrounding chemical environment.^{4,5} The
38 surface properties of liquid metal droplets can be tuned by selecting an appropriate surrounding
39 fluid,⁵ by the means of electrochemical approaches,⁷ or by introducing different types of
40 surface functional groups.^{6,9,10,11}
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48 *2.1. Oxygen solubility of the ambient fluid*

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50 The morphology and surface energy of gallium-based liquid metal droplets exhibit a
51 strong correlation with the mole fraction of dissolved oxygen in the ambient fluid. In the case
52 of bulk liquid metal, the droplet's eccentricity (i.e., eccentricity of an ellipse with a moment of
53 inertia identical to the two-dimensional profile of the droplet) increases sigmoidally with
54 respect to the logarithm of the oxygen solubility. Compared with droplets present in liquids
55 with low oxygen solubility (e.g., water), droplets immersed in liquids with high oxygen
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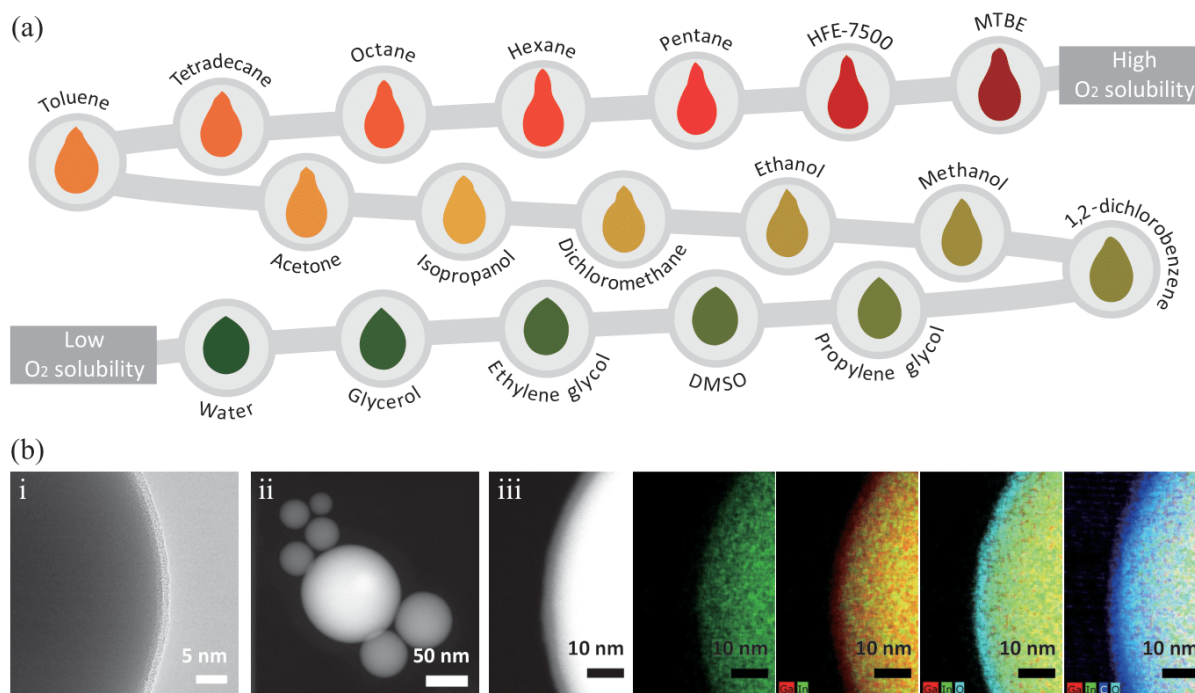


Figure 1: (a) Schematic of various bulk-scale pinch-off geometries of Galinstan droplets immersed in different liquids, in the order of high to low oxygen solubility. Reprinted with permission from *J. Colloid Interface Sci.* **2022**, *621*, 285–294.⁵ Copyright 2022 Elsevier. (b) Characterization of EGaIn (eutectic alloy of Ga and In) nanoparticles. i) Transmission electron microscope (TEM) image for EGaIn coating. The black core is the liquid metal and the thin and bright part is the gallium oxide layer. The surface of the oxide layer can be coated by an additional carbon layer. ii) Scanning transmission electron microscope (STEM) image of EGaIn nanodroplets. iii) Element mapping of the EGaIn coating on the leftmost picture, with elements colored respectively as Ga (red), In (green), O (cyan), and C (blue). From left to right, the four pictures show the mapping results for the EGaIn nanodroplet, adding the contribution of each element in sequence. Ga and In exist near the core of the droplet, which are surrounded by an oxide layer. The oxide layer is surrounded by an additional layer of carbon. Reprinted with permission from *Small* **2015**, *11*(48), 6397–6403.⁴ Copyright 2015 John Wiley & Sons.

solubility (e.g., alkanes and fluorinated liquids) tend to be encapsulated by a solid-like oxide membrane.⁵ Since liquid metal immersed in oxygenated environments readily form oxide layers, the resulting droplets display pear-shaped geometries [Figure 1 (a)].⁵

In the case of liquid metal emulsions in organic solvents, the oxygen solubility of the ambient fluid may additionally lead to varying degrees of molecular adsorption.⁵ While metallic components exist in the core of the drop, the surrounding oxide mainly consists of gallium and oxygen.^{4,6} High-resolution transmission electron microscope (TEM) images and element mapping results have proved that liquid metal micro- and nanoparticles sonicated in

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4 certain organic solvents tend to form an additional carbon coating surrounding the oxide layer
5 [Figure 1 (b)].⁴ This suggests that liquid metal droplets immersed in oxygen-rich environments
6 can additionally facilitate the adsorption of organic solvent molecules.⁵
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10 Likewise, adsorption is known to occur on liquid metal droplets dispersed in many
11 types of solvents, regardless of the polarity of the liquid media. When liquid metal
12 microdroplets are sonicated in different solvents, the carbon/oxygen and carbon/ gallium
13 atomic percent ratios on the surface of the oxide layer is known to increase with the solvent's
14 oxygen solubility.⁵ For instance, alkanes facilitate a large fraction of dissolved oxygen
15 molecules, which are conducive to the formation of the oxide layer. Therefore, Galinstan-
16 alkane emulsions contain large percentages of carbon atoms despite the relatively weak
17 interactions of alkanes with the surface groups (e.g., -OH) on the oxide layer. On the other
18 hand, acetone has a lower oxygen solubility compared with alkanes. In spite of the stronger
19 interactions between acetone and the oxide layer, the relative atomic percentage of carbon is
20 lower than what is measured for Galinstan-alkane systems.⁵ This suggests that the degree of
21 oxidation is the decisive factor in secondary adsorption, where the oxide layer serves as an
22 anchor for organic solvent molecules. Furthermore, the liquid metal layer's nonpolar surface
23 energy displays a logarithmic relationship with the oxygen solubility of the solvent used to
24 treat the liquid metal surface.⁵
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39 2.2. *Electrical control of interfacial tension*

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41 Voltage-driven control methods (e.g., electrocapillarity, continuous electrowetting,
42 electrowetting-on-dielectric, and electrochemically controlled capillarity) can be implemented
43 to manipulate liquid metal droplets at sub-mm length scales. In these techniques, charged
44 species or chemical species are driven towards the interface to lower the interfacial tension
45 between liquid metal droplets and their surrounding environment. Electrical approaches are
46 advantageous in that they require low power and are scalable to microsystems. Since one can
47 control the magnitude of the applied voltage, electrical methods facilitate the precise regulation
48 of interfacial tension.⁷
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56 Introducing either a positive or negative electrical potential at the boundary between
57 two fluids results in a change in interfacial tension. This is method known as electrocapillarity,
58 which is a classical approach for tuning the effective interfacial tension of a liquid metal droplet
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4 within an inert electrolyte. By applying a small electrical potential (≈ 1 V) to the droplet relative
5 to a counter electrode, we can change the density of charge in the electrical double layer at the
6 metal-solution interface. The surface area of liquid metal increases to reduce the capacitive
7 energy at the surface, concomitantly changing the effective interfacial tension. The presence of
8 an electrical potential flattens down the droplet's geometry, as gravitational effects come into
9 play.⁷
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15 The basic principles from electrocapillarity can be extended to electrowetting, which
16 refers to the change in wettability between a given liquid (e.g., liquid metal) and a specific
17 material. When the material is fluidic, we observe a continuous change in the wetting properties
18 (i.e., continuous electrowetting). Let us conceive of a microchannel framework containing an
19 aqueous solution, where a thin liquid layer exists between the metal droplet and the capillary
20 walls. Applying an external electric field to the liquid metal droplet allows continuous
21 electrowetting to take place; if we introduce a voltage difference between each end of the
22 microchannel, a potential drop develops through the liquid layer. Due to the asymmetry in the
23 electric double layer, a differential in surface tension builds up across the surface of the droplet.
24 Although continuous electrowetting is an effective method for the modulation of liquid metal-
25 liquid interfaces, applying an excessive voltage leads to electrolysis reactions. Electrolysis
26 accompanies the formation of hydrogen bubbles at the cathode, which can be problematic for
27 microfluidic systems. High voltages may additionally cause liquid metal droplets to split up
28 inside of microchannels.⁷
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40 On the other hand, we can consider the case where electrocapillarity changes the
41 wetting properties between a liquid and a solid. This phenomenon is known as electrowetting-
42 on-dielectric. As for electrowetting-on-dielectric techniques, an insulating layer is added
43 between the liquid and a conductive substrate. Unlike electrocapillarity, continuous
44 electrowetting, and electrochemically controlled capillarity, electrowetting-on-dielectric does
45 not require the usage of electrolytes. Moreover, while the three other methods only require a
46 small electric potential, a large voltage (>100 s of volts) must be supplied to overcome the large
47 surface tension of liquid metal. Applying a large voltage can theoretically the interfacial tension
48 of a liquid metal droplet on a substrate, thereby allowing the active control of its equilibrium
49 geometry. However, dielectric breakdown effects limit the magnitude of the electric field that
50 can be applied to the system. Another issue is that liquid metal droplets with oxide layers cannot
51 be effectively controlled via electrowetting-on-dielectric. Since conductive materials should
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4 not be introduced in electrowetting-on-dielectric techniques, it is undesirable to remove the
5 oxide via aqueous acids/bases.⁷
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8 Electrochemical approaches (e.g., galvanic replacement reactions) can be adopted to
9 reduce the surface tension of liquid metal. Electrochemically controlled capillarity is one
10 method that using surfactants to inject/withdraw liquid metal from electrolyte-filled capillaries
11 to selectively grow and remove the oxide membrane. This method is unique in that it utilizes
12 chemical reactions to modify the surface properties of liquid metal micro- and nanodroplets.
13 Notably, the interfacial energy between liquid metal droplets and the fluid environment can be
14 significantly reduced by electrochemically depositing oxide species. During the deposition
15 process, redox reactions in sodium hydroxide have been shown to effectively dissolve oxide
16 species.⁷ Using this idea, microfluidic systems composed of liquid metal droplets can control
17 the flow rate by adjusting the percentage of surface oxides. However, injecting liquid metal
18 inevitably leads to the formation of the surface oxide, which necessitates the continuous
19 introduction of acids/bases to the system. Neutral electrolytes also lead to the build-up of the
20 oxide membrane, which hinders the flow of the liquid metal droplet. In addition,
21 electrochemical reactions at the surface of liquid metal droplets accompany half reactions at
22 counter electrodes. This leads to the formation of bubbles that are undesirable for practical
23 applications.⁷
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39 2.3. *Surface functionalization*

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41 We have discussed how the oxide layer on the surface of liquid metal serves as an
42 anchor for organic solvent molecules.⁵ Likewise, specific functional groups can be anchored
43 to liquid metal droplets to alter their interfacial properties. For example, thiolated molecules
44 can functionalize the surface of liquid metal nanodroplets. Thiols tend to compete with oxygen
45 atoms on the empty sites of metallic surfaces. This property can be used to suppress the growth
46 of the oxide layer on the surface of liquid metal. We may also modulate the thermodynamics
47 of oxide growth by choosing different types of thiols to functionalize the surface.⁶
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55 Aggregation in colloidal systems occurs because the Gibbs free energy is reduced by
56 decreasing the total surface area. Such an aggregation of particles may be inhibited by
57 electrostatic repulsion or steric hindrance. While the zeta potential (i.e., electrostatic repulsion
58 between adjacent droplets in fluid media) of liquid metal droplets is affected by numerous
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4 factors (e.g., pH, temperature, and concentration of charged particles), a substantial portion of
5 the colloidal stability is governed by steric effects.^{4,5,10} The native oxide skin on the surface of
6 liquid metal is known to prevent the merging of droplets. In the case of liquid metal droplets
7 immersed in solvents with high oxygen solubility, it has been suggested that the carbon layer
8 plays a role similar to that of a surfactant; the thin solid layer acts to further stabilize the liquid
9 metal emulsions in the liquid medium.^{4,5} On the other hand, liquid metal droplets dispersed in
10 water often fail to maintain colloidal stability for longer periods of time. This can be partially
11 attributed to the relatively low oxygen solubility of liquid metal-water systems, as well as its
12 incapability of forming carbon adsorbates. Moreover, dispersing liquid metal in water for
13 longer periods of time may lead to additional chemical reactions. Since gallium is a strong
14 Bronsted acid, the metal is easily deprotonated, and exists as an ion in water. As
15 oligomerization occurs, metallic species can precipitate as hydroxide crystals.⁸ This may
16 significantly reduce the stability of liquid metal-water systems in the long term as presented in
17 Figure 2 (a).⁸

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Polymer brushes are macromolecular structures with polymer chains that use bond linkages to tether to various surfaces. The addition of polymer brushes (e.g., polymeric surfactants or hydrophobic molecules) can further enhance the colloid and chemical stability of liquid metal micro/nanodroplets dispersed in various solvents.⁹ Bulk droplets generated by ultrasonication or mechanical agitation initially rupture and break down into smaller droplets. During this stage, the juvenile surfaces of liquid metal droplets tend to constantly disintegrate and redevelop. The addition of polymeric or molecular surfactants allows anchoring groups to attach in-situ during the fabrication process. In this process, the simplest method to enhance the colloidal stability of the droplets is to increase the number of anchoring groups.⁹

In general, high reaction temperatures are required to anchor polymer brushes to the surface of metallic particles. However, liquid metal micro- and nanodroplets allow similar interactions to occur at much lower temperature regimes. This means that the polymer-metal coordination is weaker than that of colloidal systems based on solid metal particles.⁹ Especially in the case of aqueous solvents, water molecules display a strong affinity towards the metal cations present in the system. When there is an excess of water in the liquid medium, the surface coating of stabilizing polymers may be affected by the attraction between water and metal ions.^{8,9} To resolve these issues, various methods have been established for the stabilization of liquid metal droplets in the emulsion state. In a recent study, researchers introduced

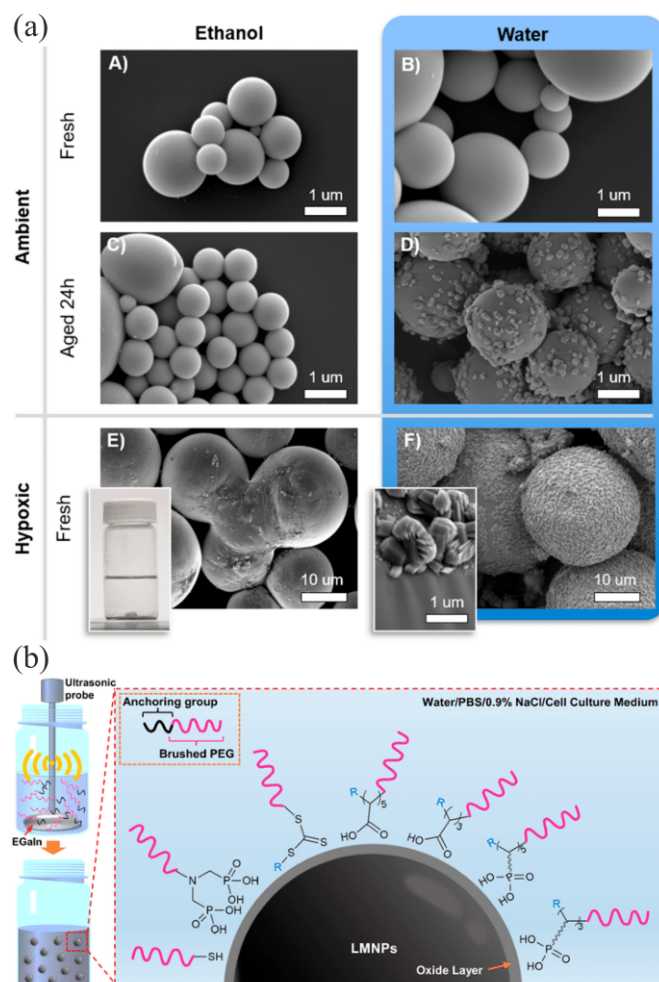


Figure 2: (a) Demonstration of solvent effects on liquid metal droplets. Suspensions of EGaIn liquid metal droplets, synthesized in ethanol or water under different conditions. Reprinted with permission from *Langmuir* **2020**, *36*(43), 12933–12941.⁸ Copyright 2020 American Chemical Society. (b) Production of polymer grafted liquid metal nanodroplets in polymer solutions via ultrasonication. The colloidal and chemical stabilities of liquid metal nanodroplets grafted by brushed polymers (bPEG) bearing a variety of anchoring groups were systematically investigated in biological buffers. Reprinted with permission from *ACS Appl. Nano Mater.* **2022**, *5*(5), 5959–5971.¹¹ Copyright 2022 American Chemical Society.

hydrochloric acid and polyvinylpyrrolidone (PVP) to a water-ethanol binary mixture containing liquid metal droplets.¹⁰ While the acid partially removed the oxide membrane, PVP could effectively suppress the coalescence of liquid metal droplets dispersed in the mixture. During solvent evaporation, the presence of PVP enhanced the steric forces between individual liquid metal droplets, which subsequently dried into a uniform layer.¹⁰

Attaching low concentrations of well-defined diblock copolymers to the oxide skin can

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4 form polymer brushes that are highly effective for the stabilization of liquid metal
5 nanodroplets.¹¹ Polymer brushes are especially useful in that blocks with multiple coordination
6 sites can attach to the surface of liquid metal droplets. These diblock copolymers can be
7 prepared via atom-transfer radical polymerization to establish flexible brush architectures,
8 controllable molecular weight, and narrow molecular weight distribution. Introducing even a
9 small concentration of polymer brushes can effectively prevent the agglomeration of
10 nanodroplets.^{9,10,11} Compared with small-molecule surfactants, block copolymer brushes at the
11 surface of liquid metal droplets are known to significantly improve the colloidal stability as
12 well as the yield of liquid metal droplets.¹¹

20 Reversible addition-fragmentation chain transfer is a common polymerization method
21 used to incorporate a wide variety of anchoring groups into brush polymers [Figure 2 (b)].⁹
22 Polymers bearing phosphonic acids can promote chemical stability by passivating the surface
23 of liquid metal droplets.^{9,11} When introduced in aqueous systems, they are also capable of
24 maintaining the morphology of liquid metal droplets at room temperature.⁹ Brushes with
25 multidentate phosphonic acid groups can effectively functionalize liquid metal interfaces with
26 complex fluids, such as those used for biological applications.¹¹ Liquid metal nanodroplets
27 grafted with non-phosphonic acid anchoring groups (e.g., trithiolcarbonates, thiols, and
28 carboxylic acids) are also widely used to stabilize liquid metal -based colloidal systems. For
29 instance, brushes based on carboxylic acids use multiple coordination interactions to firmly
30 attach onto oxides at the interface of liquid metal. However, such anchoring groups may be
31 unable to prevent the spontaneous shape transformation of liquid metal droplets at room
32 temperature.¹¹

3. Fabrication of Liquid Metal Droplets

46 Fabricating liquid metal micro- and nanodroplets is crucial for the design of liquid
47 metal-based polymer composites,^{1,2,3,12} microfluidic systems,^{13,14,18} and flexible/stretchable or
48 wearable devices.^{1,2,3,12} In this section, we present the various methods that can be exploited
49 for the fabrication of liquid metal micro- and nanodroplets.

3.1. Microfluidics

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4 A microfluidics platform can be used to mass-produce nanoparticles with tunable size
5 distributions on a chip [see Figure 3 (a)].¹³ Notably, monodispersed spherical liquid metal
6 droplets have been achieved by introducing a three-channel F-junction generator. By
7 employing this setup for dielectrophoresis, one of the branch channels could provide a flow of
8 sodium hydroxide to improve maneuverability.^{7,14} Considering that liquid metal-filled
9 microchannels serve as non-contact electrodes, the electrical field created throughout the liquid
10 metal droplet filled in the channel could automatically sort the liquid metal droplets.¹⁴ After
11 the liquid metal droplets are produced, such droplets can be hydrodynamically transferred
12 through a liquid-to-liquid interface into other fluidic components within a
13 microelectromechanical systems (MEMS) chip.
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25 3.2. *Ultrasonication*

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27 Ultrasonication uses sound to generate vapor cavities which can nebulize bulk liquid
28 metal within the aqueous media [see Figure 3 (b)].¹⁵ The competition between breakup and
29 coalescence of liquid metal droplets can be controlled by precise monitoring of the process.
30 Droplets of diverse geometries can be obtained by controlling the chemical environment,
31 temperature, and power supply during sonication.¹⁵ While droplet atomization continues to
32 occur, the surface oxide layer on liquid metal droplets can be removed by adding a small
33 concentration of acids or bases. On the other hand, polymeric/molecular surfactants or rheology
34 additives (e.g., colloidal clays such as laponite) interact with the metallic surface to stabilize
35 the droplets from coalescence during ultrasonication.^{10,15}
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43 Ultrasonication generates a substantial amount of heat, which may act as a double-
44 edged sword. The use of a highly volatile solvent or poor sealing can lead to evaporation of the
45 liquid medium during sonication. To minimize the effects of excess heat, it is generally
46 required to turn on a chiller to modulate the temperature of the liquid media. However, in
47 certain instances, inducing a change in temperature can be used as a viable method to precisely
48 control the fabrication process.¹⁶ A temperature cycling process during ultrasonication was
49 reported as an effective method to transform gallium-alloy-based nanodroplets into solid Janus
50 nanoparticles [see Figure 3 (c)]. Such results could be achieved by inducing phase separation
51 of gallium and other metallic species within the eutectic alloy.¹⁶
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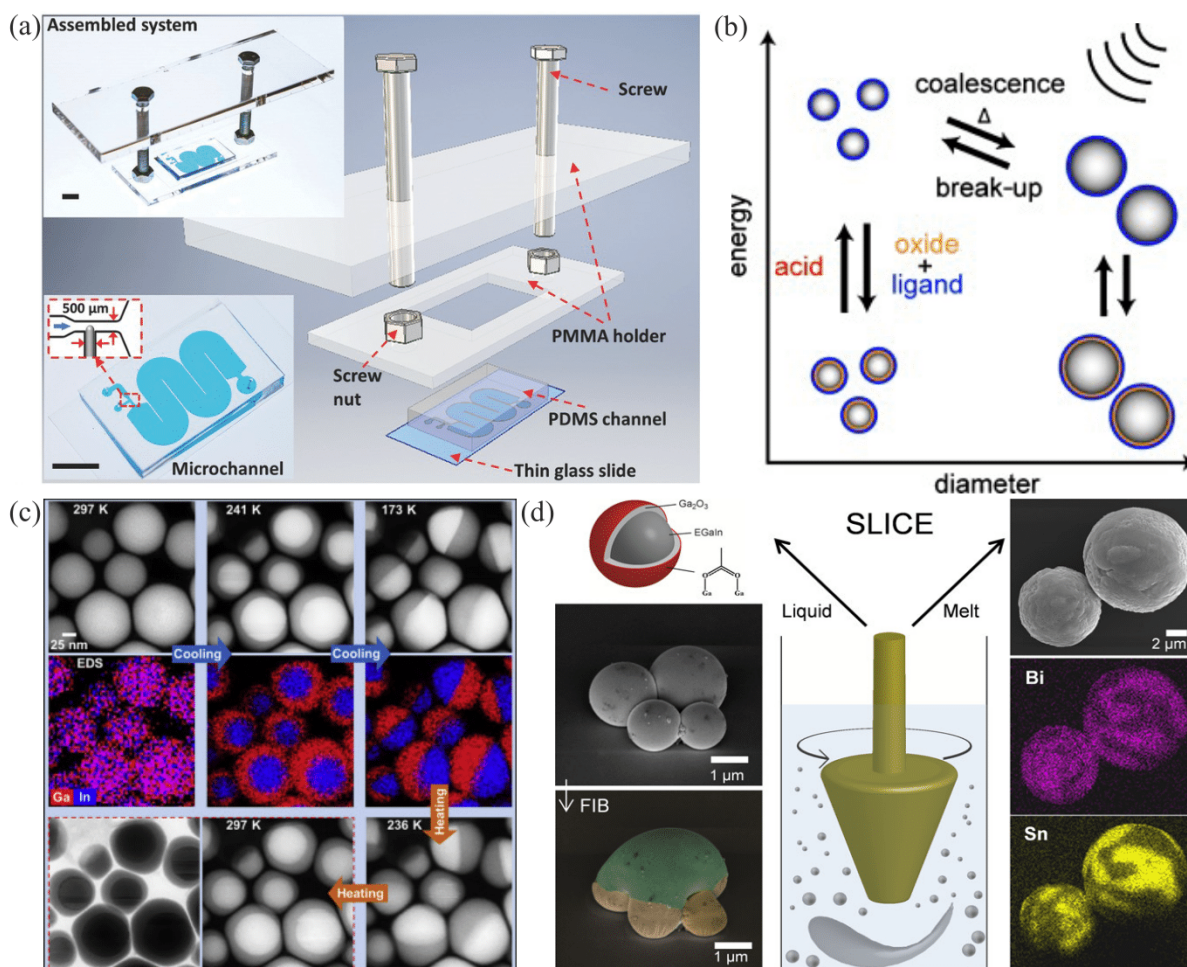


Figure 3: (a) Exploded schematic representation of the platform for on-chip production of liquid metal nanodroplets. The upper inset shows the assembled system, while the lower inset shows the microfluidic chip with a T-junction. Reprinted with permission from *Small* **2018**, *14*(21), 1800118.¹³ Copyright 2018 John Wiley & Sons. (b) An ultrasonication method for reversibly tuning the size of gallium nanodroplets. Reprinted with permission from *Angew. Chem.* **2015**, *127*(43), 12809-12813.¹⁵ Copyright 2015 John Wiley & Sons. (c) Phase separation behavior of gallium-based liquid metal nanodroplets. The particles transform into solid Janus nanoparticles after temperature cycling. Reprinted with permission from *Matter* **2019**, *1*(1), 192–204.¹⁶ Copyright 2019 Elsevier. (d) Synthesis of liquid metal core-shell particles via shearing liquids into complex particles (SLICE). Reprinted with permission from *Langmuir* **2014**, *30*(47), 14308–14313.¹⁷ Copyright 2014 American Chemical Society.

3.3. Mechanical agitation

The droplet emulsion technique has been introduced as a tunable method for the design of metallic particles. By shearing molten metals in the presence of a carrier fluid, researchers have been able to design a variety of complex micro- and nanoparticles (e.g., core-shell, hard/soft, and smooth/patchy).¹⁷ As a column of liquid metal is locally elongated, it breaks up into

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4 uniform satellite droplets, where oxidation and additional functionalization produces droplets
5 with tunable morphologies [see Figure 3 (d)]. When emulsion shearing is performed within an
6 acidic carrier fluid environment, surface tension effects drive the phase segregation of the
7 elements constituting the liquid metal alloy.¹⁷ By controlling the process of phase separation,
8 it is possible to fine-tune the surface composition and morphology of droplets. Optimal
9 shearing speeds and carrier fluids may be chosen to design particles of desired sizes or shapes.¹⁷
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18 **4. Applications of Liquid Metal Droplets**

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20 In the previous sections, we have investigated systems involves the interfaces of micro-
21 and nanoscale liquid metal droplets with a continuous phase, as can be seen in the case of
22 microfluidics, emulsions, or droplets with surface modification. Such droplets are being widely
23 explored for the fabrication of state-of-the-art devices, such as flexible/stretchable
24 electronics,^{1,4} polymer composites,^{1,2,3} and soft robotics.² Liquid metal droplets can also serve
25 as the basic building blocks for the design of novel materials, such as catalytic particles or
26 nanocarriers in biomedical applications. Owing to their high surface-to-volume ratios, micro-
27 and nanodroplets can be utilized as a platform to fabricate catalytic materials directly from the
28 liquid phase.^{22,23} The low toxicity of liquid metal droplets allows them to be incorporated in
29 biological applications, including biomedicines or drug delivery systems.^{24,25}
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41 *4.1. Microfluidics*

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43 While bulk-scale liquid metal (i.e., scales of several millimeters or centimeters) can be
44 utilized for device applications, liquid metal in the form of micro- and nanodroplets
45 accompanies a variety of merits. To begin with, the ultrahigh surface tension (500-700
46 mN/m)^{4,5} and oxide membrane makes it challenging to control metallic liquids at the bulk scale.
47 Liquid metal streams ejected through nozzles readily destabilize due to oxidation and surface
48 tension effects. For patterning or microfluidic/MEMS applications, it is difficult to fit bulk-
49 scale liquid metal through smaller grooves or channels. Despite the high surface tension of
50 liquid metal, micro- or nanodroplet suspensions may alleviate the difficulties of fitting bulk
51 liquid metal into the grooves of microchannels.¹⁸ In the form of micro- or nanodroplets, it is
52 easier to control volumes of liquid metal with higher degrees of precision and
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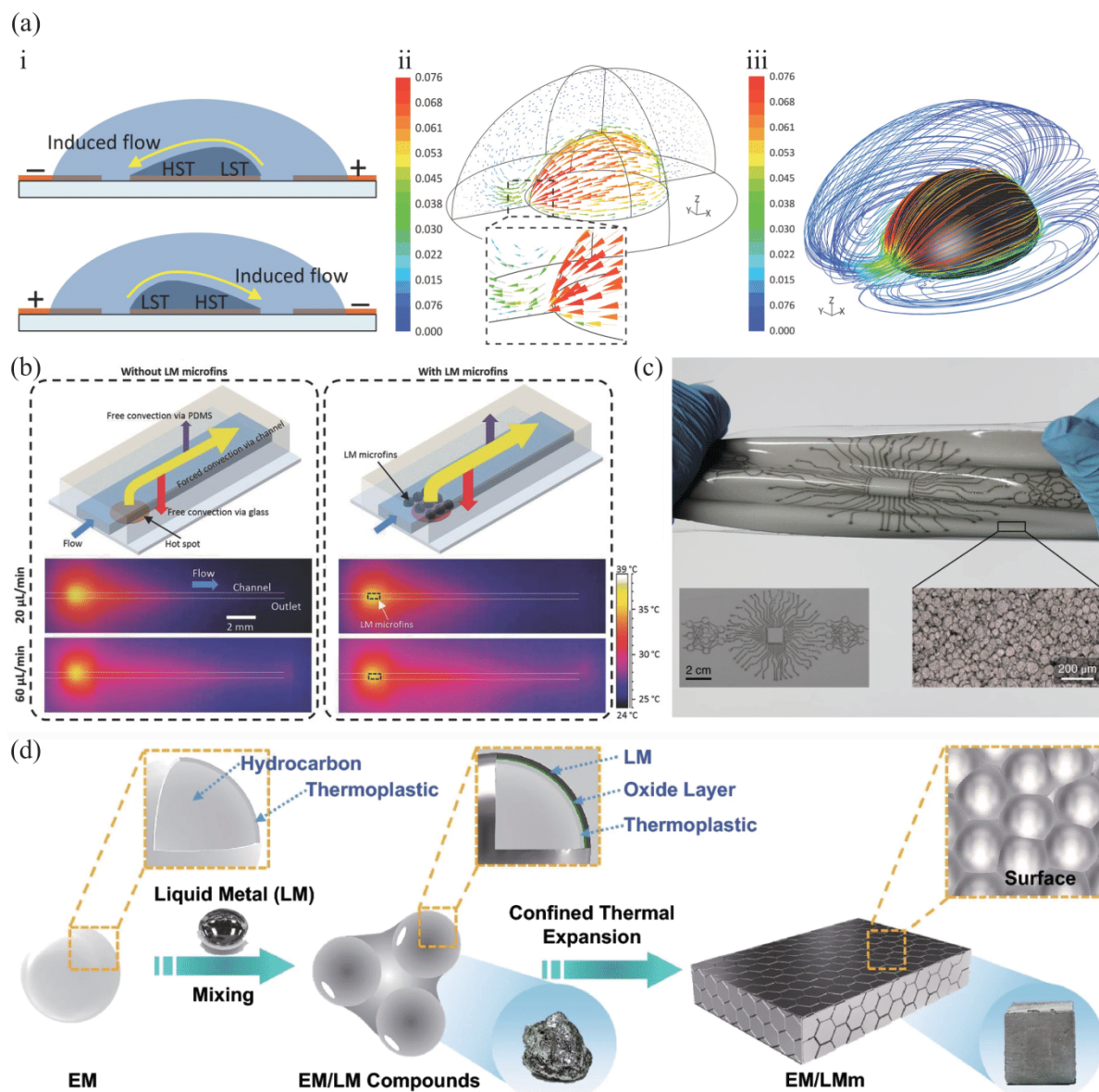


Figure 4: Applications using liquid metals for microfluidics and soft electronics. (a) i) Liquid metal actuator. ii) Flow velocity vectors (m/s) along the Galinstan surface. iii) Formation of vortices within the surrounding liquid colored by magnitude of flow velocity (m/s). Reprinted with permission from *Adv. Funct. Mater.* **2014**, *24*(37), 5851–5858.¹⁹ Copyright 2014 John Wiley & Sons. (b) 3D Galinstan microstructures for heat dissipation from a hot spot. Comparison of temperature contours for the microfluidic platform in the channel with liquid metal components. Reprinted with permission from *Adv. Funct. Mater.* **2015**, *25*(28), 4445–4452.²⁰ Copyright 2015 John Wiley & Sons. (c) Liquid metal-elastomer composites being stretched and twisted with an intricate design of electrically conductive traces. The lower left inset shows the undeformed sample and the lower right inset is an optical micrograph showing the liquid metal microdroplets in the elastomer. Reprinted with permission from *Nat. Mater.* **2018**, *17*(7), 618–624.² Photograph courtesy of Eric Markvicka. Copyright 2018 Springer Nature. (d) Illustration of the fabrication process of expandable microsphere/liquid metal monoliths for EMI shielding. Reprinted with permission from *Nano-Micro Lett.* **2022**, *14*(1), 1–15.³ Copyright 2022 Springer Nature.

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4 controllability.^{18,19,20}
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7 Micro- and nanoparticle-laden systems are effective carrier fluids due to their high
8 thermal and electrical conductivity.¹⁸ By modulating the oxide layer, we can also tune the
9 interfacial and rheological properties of liquid metal droplets for miniaturized microfluidics
10 (e.g., pumps, valves, heaters, and electrodes).^{18,19,20} For instance, inducing a charge gradient on
11 the surface of the liquid metal droplet is known to generate surface-tension-driven Marangoni
12 flows. Since the metal spheres are fixed in space, it is possible to create a pump when
13 electrolytes travel across the spherical surface.¹⁹ One study succeeded in creating harmonic
14 Marangoni flows by inputting a sinusoidal signal into a solution with liquid metal droplets. By
15 generating vortices, the resulting chaotic advection allowed a highly efficient mixing process
16 within the microfluidic system, as shown in Figure 4 (a).¹⁹
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24 Liquid metal droplets can also be used to trap suspended particles or enhance
25 convective heat transfer processes within a microfluidic channel. In one study,
26 dielectrophoresis was used to immobilize Galinstan microstructures on planar microelectrode
27 pads.²⁰ This method allowed researchers to fabricate patterns of three-dimensional
28 microstructures of various dimensions and aspect ratios, which could be further tuned to trap
29 nanoparticles flowing through a microfluidic channel. In a separate demonstration, three-
30 dimensional liquid metal microfin arrays could be placed over a hot spot to dissipate heat within
31 the channel [see Figure 4 (b)].²⁰ The microstructures could enhance the convective heat transfer
32 process by directing more heat into the liquid stream traveling through the channel.²⁰ Such
33 microfluidic systems can be integrated into mechanically adaptive materials for the design of
34 soft diodes, transient circuits, and biomedical sensing chips.
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47 *4.2. Soft electronics and robotics*

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49 Introducing liquid metal into the system does not degrade the general properties (e.g.,
50 stretchability, elastic compliance, and dielectric breakdown strength) required for soft-matter
51 engineering.^{1,2,4,10} Since liquid metal exhibits both electrical conductivity and fluidity, it is
52 possible to construct conductive networks of liquid metal droplets with dynamic responses.
53 While external deformations such as bending or stretching are prone to damaging solid
54 materials, the usage of liquid metal can overcome this lack of durability.^{1,4} This means that
55 liquid metal-based structures can undergo continuous changes in cross-sectional area,
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4 maintaining their electrical conductivity at the same time. Likewise, liquid metal-based
5 electrodes patterned over a polymer structure can resist considerable strain without
6 destabilizing into shorter ligaments.^{2,10} Post-fabrication treatments allow liquid metal droplets
7 to further merge into percolated networks.^{4,12} Based on these micro- and nanoscale building
8 blocks, we can design complex systems involving the interfaces of liquid metal with a
9 continuous phase (e.g., liquid metal-based inks, emulsions, and soft composites). It is possible
10 to configure a wide range of material properties from the different combinations of liquid
11 metal-solvent or liquid metal-polymer interfaces that can exist; this feature highlights the
12 versatility of liquid metal micro- and nanodroplets.
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21 In this regard, liquid metal-elastomer nanocomposites with dielectric properties are
22 highly promising for flexible and stretchable devices. Conventional liquid metal–elastomer
23 systems (e.g., microfluidic circuits, liquid metal embedded elastomers through dispersions,
24 drop-cast films, and backfilled cellular structures) may often lead to electrical shorting due to
25 unintended activation. Employing liquid metal droplets dispersed in an elastomeric phase
26 allowed researchers to design high-performance electric circuits/soft robotic devices with
27 autonomous and instantaneous self-healing characteristics [see Figure 4 (c)].² By dispersing
28 liquid metal droplets dispersed in an elastomeric phase, the composite exhibited a significant
29 level of stress shielding that was effective in preventing electrical shorting issues. Even when
30 subject to spatially random damage, the self-healing architecture helped the electrical wiring
31 to maintain its functionality. An additional elastomeric sealing layer or selective patterning
32 techniques could be applied to protect the liquid metal circuit and inhibit inadvertent activation
33 between adjacent pathways. Liquid metal droplets have also gained much attention as
34 composite fillers for electromagnetic interference shielding applications.³ In order to construct
35 conductive networks, expandable microspheres with thermal self-expanding properties were
36 incorporated with liquid metal droplets [see Figure 4 (d)]. A mechanical mixing process
37 continuously generated a new oxide membrane, which allowed the microspheres to be coated
38 with liquid metal. The self-healing properties of these networks are expected to resolve the
39 leakage issues of conventional electromagnetic sealing interfaces.³
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54 However, the oxide membrane can act as an insulating barrier between individual liquid
55 metal droplets. This means that additional manufacturing processes may be required to create
56 electrically conductive pathways between individual droplets. Various sintering methods have
57 been proposed for the design of soft and deformable circuit interconnects based on liquid metal
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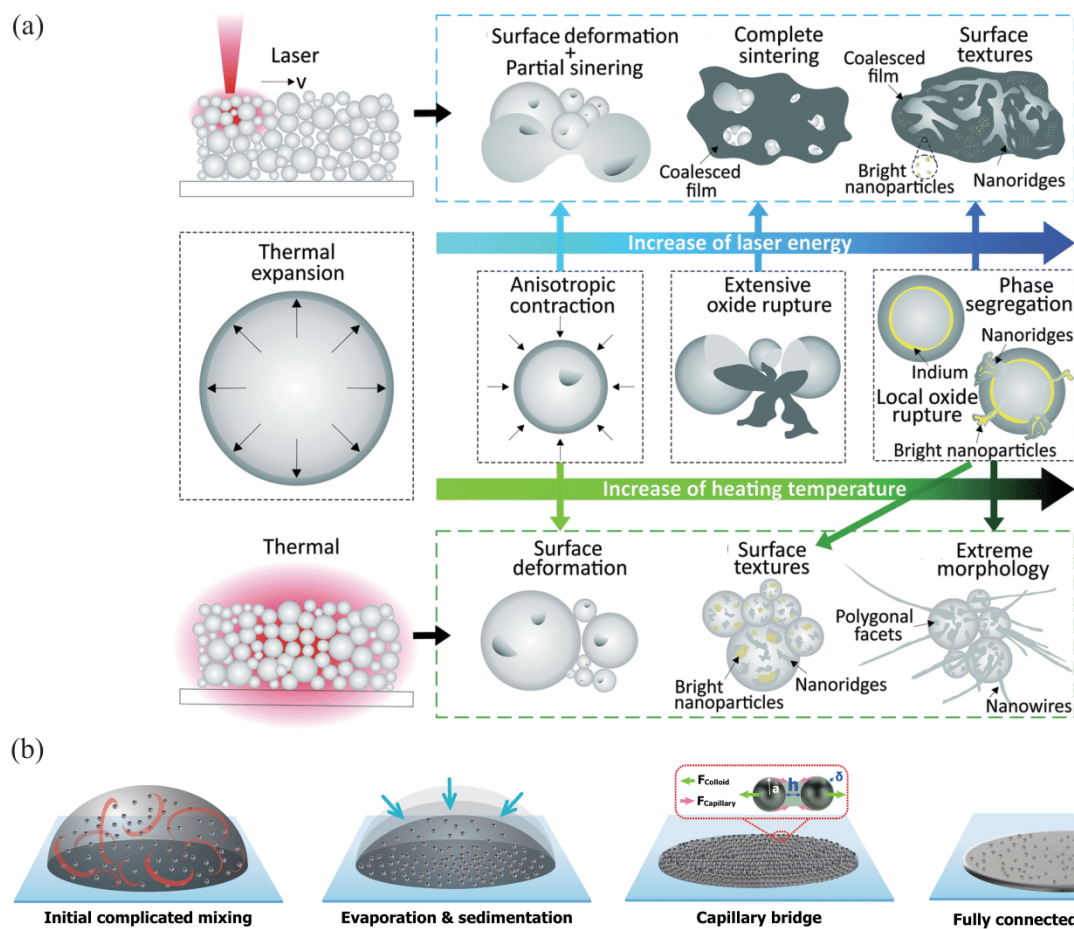


Figure 5: (a) Schematic for mechanisms of laser and thermal sintering liquid metal nanoparticle films. Reprinted with permission from *Nanoscale*, **2019**, *11*(38), 17615–17629.²¹ Copyright 2019 Royal Society of Chemistry. (b) Formation of a self-sintered uniform liquid metal pattern using sintering-free ink. The dried pattern is fully connected after the avalanche coalescence of liquid metal particles due to capillary adhesion. Reprinted with permission from *Adv. Mater. Interfaces*, **2022**, *9*(35), 2201693.¹⁰ Copyright 2022 John Wiley & Sons.

inks.⁴ Since liquid metal droplets can be easily merged under sufficient pressure, mechanical sintering allows the fabrication of self-healing electronic devices. For example, we can consider a polymer composite containing droplets of liquid metal. When this composite is sliced in half, the droplets will initially be smeared along the side walls, later creating a conductive path to restore their intrinsically high conductivity.¹² These droplets can rupture to form new connections with neighboring droplets and effectively re-route electrical signals.^{2,12}

Thermal and laser sintering methods have also been proposed to rupture the oxide membrane and reconnect the liquid metal droplets [see Figure 5 (a)].²¹ In the case of thermal sintering, only a small portion of the oxide layer is affected by thermal stress. This local rupture

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4 is followed by a strong phase segregation process, which contributes to the formation of solid-
5 like particle films.²¹ Meanwhile, laser sintering accompanies an extensive rupture of the oxide
6 membrane. This allows the cores of liquid metal particles to interconnect and coalesce into
7 conductive networks.²¹ In recent years, sintering-free liquid metal inks have been successfully
8 prepared by adding a certain volume of acids and polymers into the continuous phase.¹⁰ Such
9 inks can be suspended in soft elastomers to design composites with spontaneous self-repairing
10 characteristics.¹⁰ Even when the matrix is significantly damaged, liquid metal droplets can
11 rupture to form interconnections with neighboring droplets. Without additional manual
12 reapplying or heating processes, electronic signals can be reconfigured to achieve an
13 electronically robust network as shown in Figure 5 (b).^{2,10} This percolated path is created
14 throughout the elastomeric matrix due to the merging of liquid metal droplets.⁴
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26 *4.3. Catalysts*

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29 Compared with bulk materials, micro- and nanoparticles exhibit high surface areas and
30 high surface-to-volume ratios. This makes small-scale structures particularly useful for catalyst
31 applications that tend to be highly dependent on surface reactions. Liquid metal micro- and
32 nanodroplets are effective platforms for designing such catalytic materials. Liquid metal-based
33 particles are especially unique in that they originate from the liquid phase; the methods for
34 controlling their surface morphologies and catalytic reactions are different from those applied
35 to conventional solid particles.^{22,23} Micro- and nanosized liquid metal droplets can be combined
36 with nanosized metal oxides to create liquid metal/metal oxide frameworks. Studies have
37 shown that it is possible to actively control the diameter and stoichiometry of these spherical
38 structures. When metallic droplets are prepared in the form of liquid suspensions, we can
39 specifically tune the plasmon resonance wavelength of the catalytic frameworks to be designed.
40 The resulting spheres display high sensitivity toward heavy metal ions and excellent
41 photocatalytic properties.²²
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52 In one study concerning photochemical catalysts, researchers focused on the
53 photocatalytic performance of stoichiometric gallium oxides (Ga_2O_3) that could decompose
54 different pollutants and organic dyes under ultraviolet (UV)/visible-light irradiation.²³ The
55 researchers developed a novel fabrication method to directly synthesize the oxide from liquid-
56 state gallium droplets. The self-limiting oxide skin of liquid gallium was implemented as a
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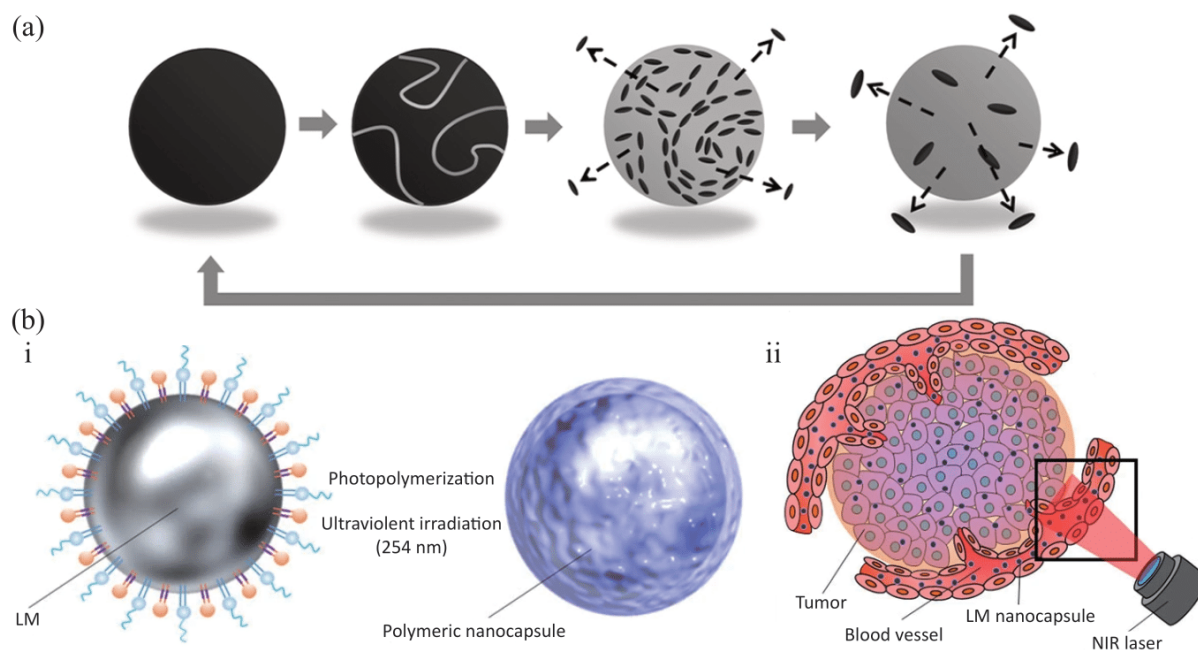


Figure 6: Applications using liquid metals for catalysts and biomedicines. (a) Sketch of transformation of liquid metal/metal oxide spherical structures during sonication. Grey shapes, black shapes, and black ovals stand for Galinstan spheres, oxide layers, and nanoplatelets, respectively. Reprinted with permission from *Adv. Funct. Mater.* **2014**, *24*(24), 3799–3807.²² Copyright 2014 John Wiley & Sons. (b) i) Polymeric core-shell structure encapsulating liquid metal photopolymerized using functional phospholipids with 254 nm ultraviolet irradiation. ii) Schematic for laser-triggered liquid metal transformation in a blood vessel model. Reprinted with permission from *Nat. Commun.* **2017**, *8*(1), 1–19.²⁵ Copyright 2017 Springer Nature.

precursor for suspensions of gallium oxide nanoparticles. After sonicating gallium in water, annealing the liquid metal-water suspension produced rods/nanoflakes of gallium oxide as presented in Figure 6 (a). The harvested nanoflakes were shown to contain trap states under the conduction band minimum, thereby effectively reducing the energy bandgap. Under irradiation of solar light, such structures could be used as photocatalysts for the decomposition of organic model dyes.²³

4.4. Biomedicines

In the field of biomedicines and drug delivery, many types of inorganic nanocarriers exhibit systemic toxicity while lacking in biodegradability. Moreover, it is difficult to tailor their physicochemical properties to satisfy the conditions required for target delivery and efficient elimination. Due to their low toxicity, gallium-based liquid metal micro- and

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4 nanodroplets are being implemented for various healthcare applications.^{24,25} In addition, the
5 transformable and degradable nature of liquid metal nanocapsules enables them to effectively
6 regulate the drug release process.²⁴ In this regard, novel methods are being explored to attach
7 biopolymers and enzymes onto the activated surfaces of liquid metal nanodroplets.
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12 Nanomedicines based on liquid metal droplets carry distinct advantages: droplets are
13 simple to fabricate, allow the bioconjugation of functional molecules, and are capable of
14 fusing/degrading in mildly acidic environments. One group of researchers created a liquid
15 metal-based drug delivery platform for anticancer therapy.²⁴ By using ultrasonication, drug-
16 loaded nanodroplets of liquid metal could be formed via ligand-mediated self-assembly. In
17 mildly acidic cellular environments, these liquid metal nanodroplets were shown to easily
18 degrade by fusing with one another. After cellular internalization, the loaded chemical could
19 be released at the opportune moment. Data from X-ray images also suggested that the fused
20 nanospheres could serve as theranostic reagents.²⁴ Additional properties intrinsic to liquid
21 metal droplets (e.g., mechanical flexibility, electrical conductivity, and the ability to dissolve
22 other metallic species) may be investigated for the development of new materials/scaffolds for
23 drug delivery and tissue engineering.
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34 With proper functionalization, liquid metal droplets can facilitate the design of
35 nanocapsule configurations. Photopolymerized liquid metal droplets prepared with functional
36 phospholipids were shown to produce nanocapsules with low toxicity and high dispersibility
37 in water.²⁵ Under near-infrared (NIR) light, these capsules were capable of generating heat,
38 simultaneously producing reactive oxygen species. NIR laser irradiation could disrupt the
39 surface of these capsules, which consequently transforms their equilibrium geometry.²⁵ This
40 configuration allowed the contactless release of loaded drugs with exceptional controllability.
41 The study further demonstrated the chemotherapeutic capability of liquid metal nanodroplets
42 functionalized with a tumor-targeting ligand [Figure 6 (b)].²⁵ By inhibiting the formation of
43 tumors, these droplets are expected to serve as non-toxic theranostic drug delivery systems.
44 Such liquid metal nanodroplets have been utilized as markers for spatiotemporal targeting for
45 the X-ray-enhanced imaging of biological organs. These nanostructures can also be beneficial
46 when optical manipulation is required for microfluidic blood vessel systems. Moreover, the
47 researchers demonstrated that liquid metal droplets could be used to eliminate cancer cells and
48 control the calcium ion flux between cells.²⁵
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5. Future Outlook

Liquid metal is a truly unique material in that it exhibits a metallic nature while simultaneously displaying fluidic properties. Unlike conventional liquids, the metallic nature of liquid metal droplets gives rise to a number of unique characteristics. The metallic bonding forces in liquid metal contribute to extremely high values of surface tension.^{1,5} This surface is prone to interact with oxygen/adsorbate molecules, which subsequently alter the geometry, chemistry, and surface energy of liquid metal droplets.⁵ Therefore, a thorough understanding of liquid metal surfaces is critical in designing droplets with tunable interfacial, morphological, and rheological properties. Liquid metal droplets of specific geometries or surface wettabilities can be achieved by subjecting them to acid/base treatment^{3,10}, making use of electric fields⁷, or performing experiments in vacuum environments. Such droplets can be further incorporated into electrodes/microchannels that are elemental for the fabrication of various emerging technologies. For example, liquid metal micro- and nanodroplets are promising materials for future-generation soft composites,^{1,2,3} printable circuits,⁴ micro/nanofluidics,^{13,14,18} catalysts,^{22,23} and biomedicines.^{24,25} Despite the multitude of papers focused on the potential applications of liquid metal droplets, much remains to be explored about the fundamental physicochemical aspects of liquid metal interfaces. The behavior of liquid metal droplets in various fluid environments⁵ and surface-functionalization conditions^{9,11} have only recently been investigated. Employing these characteristics, researchers must constantly look out for novel approaches to fabricate liquid metal droplets in various environments.

In order to fully appreciate the nature of liquid metal droplets, contemporary researchers are to develop a comprehensive perspective across different fields. For one, chemists must seek effective methods for the production of spherical liquid metal droplets and functionalization of liquid metal-based nanoconjugates. The next milestone will be to improve the synthesis and chemical modification procedures of future-generation structures and complexes based on liquid metal micro- and nanodroplets. At the same time, one may find it thought-provoking to review the classical papers in the field of metallurgy; the well-known material/physical properties of molten metals of historic importance can help gain insight into room-temperature liquid metal alloys. From the perspective of rheology and fluid dynamics, we must further explore the non-Newtonian properties of metallic inks/suspensions prepared at different shear rates, temperatures, and chemical conditions. Understanding the dynamics of liquid metal droplets and their flow characteristics in various microchannel configurations will also be

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4 essential for practical applications. This directly connects to the role of mechanical and
5 electrical engineers who must devise effective MEMS platforms and soft/stretchable circuits
6 that can embody these novel materials. By incorporating the self-healing properties and
7 sintering methods of liquid metal droplets, we must continue to design liquid-metal based soft
8 electronic systems with electrical stability. As for biologists, it would be critical to examine the
9 behavior of liquid metal-based nanocomplexes in physiological environments through assays
10 and imaging techniques. Evaluating the biocompatibility, spatiotemporal controllability, and
11 bioactive functionalization of these novel materials remains a quest for liquid metal droplets in
12 biomedical/healthcare applications.
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7. Brief Biography of authors

Gaabhin Ryu is a summa cum laude graduate of KAIST (Korea Advanced Institute of Science and Technology), where she received dual degrees in Mechanical Engineering (B.S.) and Material Science Engineering (B.S.) in 2023. Her current studies are focused on the understanding of novel phenomena and unconventional materials (e.g., liquid metal, nanopalm frameworks, and salt balls) from a physicochemical/geometric perspective.

Prof. Inkyu Park received his B.S., M.S., and Ph.D. from KAIST (1998), UIUC (2003) and UC Berkeley (2007), respectively, all in mechanical engineering. He has been with the department of mechanical engineering at KAIST since 2009 as a faculty and he is currently a full professor, vice department head, and KAIST Endowed Chair Professor. His research interests are micro/nanofabrication, smart sensors for healthcare, environmental and biomedical monitoring, and flexible & wearable electronics.

Prof. Hyoungsoo Kim received his Ph.D. from Delft University of Technology (2013) in Mechanical Engineering. He joined the Department of Mechanical Engineering at KAIST in 2017 as a faculty and he is currently an associate professor. His research interests are experimental fluid mechanics, soft matter hydrodynamics, fluid-fluid interfacial instabilities.

8. References

- (1) Dickey, M. D. Stretchable and Soft Electronics using Liquid Metals. *Adv. Mater.* **2017**, *29*(27), 1606425.
- (2) Markvicka, E. J.; Bartlett, M. D.; Huang, X.; Majidi, C. An autonomously electrically self-healing liquid metal–elastomer composite for robust soft-matter robotics and electronics. *Nat. Mater.* **2018**, *17*(7), 618–624.
- (3) Xu, Y.; Lin, Z.; Rajavel, K.; Zhao, T.; Zhu, P.; Hu, Y.; Sun, R.; Wong, C.P. Tailorable, lightweight and superelastic liquid metal monoliths for multifunctional electromagnetic interference shielding. *Nano-Micro Lett.* **2022**, *14*(1), 1–15.
- (4) Lin, Y.; Cooper, C.; Wang, M.; Adams, J. J.; Genzer, J.; Dickey, M. D. Handwritten, soft circuit boards and antennas using liquid metal nanoparticles. *Small* **2015**, *11*(48), 6397–6403.
- (5) Ryu, G.; Park, K.; Kim, H. Interfacial properties of liquid metal immersed in various liquids. *J. Colloid Interface Sci.* **2022**, *621*, 285–294.
- (6) Farrell, Z. J.; Tabor, C. Control of gallium oxide growth on liquid metal eutectic gallium/indium nanoparticles via thiolation. *Langmuir* **2017**, *34*(1), 234–240.
- (7) Eaker, C. B.; Dickey, M. D. Liquid metal actuation by electrical control of interfacial tension. *Appl. Phys. Rev.* **2016**, *3*(3), 031103.
- (8) Creighton, M. A.; Yuen, M. C.; Susner, M. A.; Farrell, Z.; Maruyama, B.; Tabor, C. E. Oxidation of gallium-based liquid metal alloys by water. *Langmuir* **2020**, *36*(43), 12933–12941.
- (9) Lin, Y.; Genzer, J.; Li, W.; Qiao, R.; Dickey, M. D.; Tang, S. Y. Sonication-enabled rapid production of stable liquid metal nanoparticles grafted with poly(1-octadecene-alt-maleic anhydride) in aqueous solutions. *Nanoscale* **2018**, *10*(42), 19871–19878.
- (10) Park, K.; Pyeon, J.; Jeong, S. H.; Yoon, Y. -J.; Kim, H. Avalanche coalescence of liquid metal particles for uniform flexible and stretchable electrodes. *Adv. Mater. Interfaces.* **2022**, *9*(35), 2201693.
- (11) Huang, X.; Xu, T.; Shen, A.; Davis, T. P.; Qiao, R.; Tang, S. Y. Engineering polymers via understanding the effect of anchoring groups for highly stable liquid metal nanoparticles. *ACS Appl. Nano Mater.* **2022**, *5*(5), 5959–5971

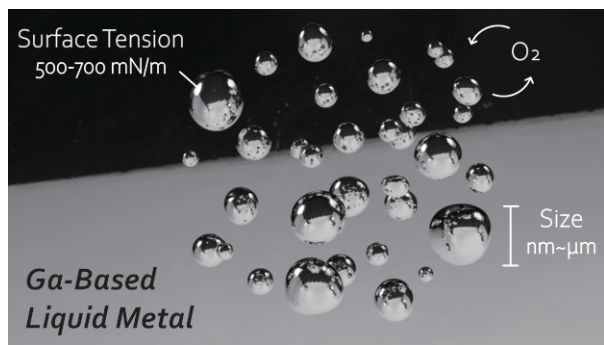
- 1
2
3
4 (12) Blaiszik, B. J.; Jones, A. R.; Sottos, N. R.; White, S. R. Microencapsulation of gallium–
5 indium (Ga–In) liquid metal for self-healing applications. *J. Microencapsul.* **2014**, *31*(4),
6 350–354.
7
8
9
10 (13) Tang, S.; Qiao, R.; Yan, S.; Yuan, D.; Zhao, Q.; Yun, G.; Davis, T. P.; Li, W.
11 Microfluidic mass production of stabilized and stealthy liquid metal nanoparticles. *Small*
12 **2018**, *14*(21), 1800118.
13
14
15 (14) Tian, L.; Gao, M.; Gui, L. A microfluidic chip for liquid metal droplet generation and
16 sorting. *Micromachines* **2017**, *8*(2), 39.
17
18
19 (15) Yamaguchi, A.; Mashima, Y.; Iyoda, T. Reversible size control of liquid-metal
20 nanoparticles under ultrasonication. *Angew. Chem.* **2015**, *127*(43), 12809–12813.
21
22
23 (16) Tang, S. Y.; Mitchell, D. R.; Zhao, Q.; Yuan, D.; Yun, G.; Zhang, Y.; Qiao, R.; Lin, Y.;
24 Dickey, M. D.; Li, W. Phase separation in liquid metal nanoparticles. *Matter* **2019**, *1*(1), 192–
25 204.
26
27
28 (17) Tevis, I. D.; Newcomb, L. B.; Thuo, M. Synthesis of liquid core–shell particles and solid
29 patchy multicomponent particles by shearing liquids into complex particles (SLICE).
30 *Langmuir* **2014**, *30*(47), 14308–14313.
31
32
33 (18) Khoshmanesh, K.; Tang, S. Y.; Zhu, J. Y.; Schaefer, S.; Mitchell, A.; Kalantar-zadeh,
34 K.; Dickey, M. D. Liquid metal enabled microfluidics. *Lab Chip* **2017**, *17*(6), 974–993.
35
36
37 (19) Tang, S. Y.; Sivan, V.; Petersen, P.; Zhang, W.; Morrison, P. D.; Kalantar-zadeh, K.;
38 Mitchell, A.; Khoshmanesh, K. Liquid metal actuator for inducing chaotic advection. *Adv.*
39 *Funct. Mater.* **2014**, *24*(37), 5851–5858.
40
41
42 (20) Tang, S. Y.; Zhu, J.; Sivan, V.; Gol, B.; Soffe, R.; Zhang, W.; Mitchell, A.;
43 Khoshmanesh, K. Creation of liquid metal 3D microstructures using dielectrophoresis. *Adv.*
44 *Funct. Mater.* **2015**, *25*(28), 4445–4452.
45
46
47 (21) Liu, S.; Reed, S. N.; Higgins, M. J.; Titus, M. S.; Kramer-Bottiglio, R. Oxide rupture-
48 induced conductivity in liquid metal nanoparticles by laser and thermal sintering. *Nanoscale*,
49 **2019**. *11*(38), 17615–17629.
50
51
52 (22) Zhang, W.; Ou, J. Z.; Tang, S. Y.; Sivan, V.; Yao, D. D.; Latham, K.; Khoshmanesh, K.;
53 Mitchell, A.; O’Mullane, A. P.; Kalantar-zadeh, K. Liquid metal/metal oxide frameworks.
54
55
56
57
58
59
60

1
2
3
4 *Adv. Funct. Mater.* **2014**, 24(24), 3799–3807.

5
6
7 (23) Syed, N.; Zavabeti, A.; Mohiuddin, M.; Zhang, B.; Wang, Y.; Datta, R. S.; Atkin, P.;
8 Carey, B. J.; Tan, C.; van Embden, J.; Chesman, A. S. R.; Ou, J. Z.; Daeneke, T.; Kalantar-
9 zadeh, K. Sonication-assisted synthesis of gallium oxide suspensions featuring trap state
10 absorption: test of photochemistry. *Adv. Funct. Mater.* **2017**, 27(43), 1702295.
11

12
13
14 (24) Lu, Y.; Hu, Q.; Lin, Y.; Pacardo, D. B.; Wang, C.; Sun, W.; Ligler, F. S.; Dickey, M. D.;
15 Gu, Z. Transformable liquid-metal nanomedicine. *Nat. Commun.* **2015**, 6(1), 1–10.
16

17
18 (25) Chechetka, S. A.; Yu, Y.; Zhen, X.; Pramanik, M.; Pu, K.; Miyako, E. Light-driven
19 liquid metal nanotransformers for biomedical theranostics. *Nat. Commun.* **2017**, 8(1), 1–19.
20
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