Advances in the Development of Liquid Metal-Based Printed Electronic Inks

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As a newly emerging additive manufacturing technology, printed electronics based on the printing principle has received more and more attention. Compared to conventional electronics manufacturing, such technique has many advantages such as speediness, flexibility, personalized customization, and low cost. Currently, there are three kinds of typical conductive inks used in printed electronics—conductive carbon ink, conductive polymer, and metal conductive ink. However, the electrical conductivities of the conductive carbon ink and the conductive polymer are typically lower than $10^5$ S/m, which impedes their application in high-sensitivity circuit fabrication. As to the metal conductive ink, post-treatments via long time curing process are often needed, which reduce the printing speed and improve the manufacturing costs. As an alternative, liquid metal is emerging as a new class of conductive ink and is thus becoming an important research focus. Such material has unique merits such as high electrical conductivity, simple preparation process, requiring no post-processing after printing, and so on.

To further push forward the research on liquid metal-based printed electronics, this article strives to present an overview on the related research advancement in recent years. Properties of liquid metal such as oxidation, wettability, and conductivity are discussed. Liquid metal techniques including tapping mode electronic printing, atomized spray printing, microcontact printing, laser sintering method of liquid metal nanoparticles, transfer printing, masked deposition, liquid metal corrosion sculpture method, colorful liquid metal circuit fabrication method, and hybrid rolling and transfer printing method are systematically expounded. Prospective direction worth pursuing is outlined.

Keywords: printed electronics, conductive ink, liquid metal, oxidation, wettability, electrical conductivity

INTRODUCTION

Printed electronics is a new advanced manufacturing technology in recent years, whose principle is fabricating electronic devices and systems through transferring conductive, dielectric, semiconductor materials on the substrate with conventional methods such as screen printing and inkjet printing (Cui, 2019; Gao et al., 2019). In comparison to traditional subtractive manufacturing, printed electronics has obvious advantages in large area, low cost, personalization, flexibility, low energy consumption, environmental protection, and so on. Various types of materials including inorganic nanoparticles, metal nanowires, conducting polymers, and carbon materials have been used as conductive ink in printed electronics (Kamyshny and Magdassi, 2019; Kim et al., 2019; Qiu et al., 2019).
The substrates used in printed electronics cover plastic, metal, glass, textile, ceramic, and paper. A variety of printing methods have been adopted, which include screen printing, gravure printing, flexographic printing, pad-printing, stamp-assisted transfer printing, piezoelectric printing, electrohydrodynamic (EHDI) inkjet printing, aerosol-jet printing, and so on (Khan et al., 2019). Printed electronics has extensive application prospect in the production of low-cost solar cells, flexible display devices, radio frequency identification (RFID) tags, robotics, and biocompatible implantable devices (Mohammed and Kramer, 2017). As an alternative, emergence of liquid metal printing technology accelerates the progress of such application study (Wang and Liu, 2016). The paper is dedicated to introducing the advances in investigating liquid metal printed electronics in recent years based on progress review about traditional conductive inks.

TRADITIONAL CONDUCTIVE INKS

According to different functional components, traditional conductive inks can be divided into three types: carbon-based, polymer, and metal-based conductive inks (Shan, 2013).

The conductive components of carbon-based inks include graphene, carbon nano-tube, fullerene, etc. For instance, graphene is widely regarded as an important candidate for fabricating flexible electronics due to its excellent mechanical, thermal, and electrical properties (Karagianlidis et al., 2017; Morales-Narvaez et al., 2017; Ji et al., 2018; Tran et al., 2018). Liquid-phase exfoliation is typically used to prepare high-quality graphene inks (Coleman et al., 2011). The process begins with peeling off the adjacent graphene layers on a bulk graphite with ultrasonication or under high shear rate, followed by adding the solvents and the surfactants to minimize the attraction between adjacent graphene sheets to obtain a stable, homogeneous graphene dispersion (Tran et al., 2018). Hyun et al. (2013) demonstrated a selective transfer printing method for fabricating foldable electronic circuits based on paper substrate with a dispersion of graphene nanoplates. The fabrication scheme can be depicted as follows (Figure 1A). Firstly, depositing a uniform layer of graphene nanoplates on a hydrophobic polytetrafluoroethylene (PTFE) membrane filter (pore diameter: 0.2 μm) by vacuum filtration of the graphene dispersion. Secondly, placing the membrane filter with the filtered graphene onto a paper substrate with the graphene side direct contact the paper. Thirdly, drawing a circuit diagram on the membrane filter with a pen and separate the filter from the paper. A graphene circuit is thus fabricated on the paper substrate through such transfer printing approach. To further improve the properties of carbon material, carbon-based composites such as graphene-silver ink (Karim et al., 2019), carbon nanotube/wax conductive ink (Chen et al., 2018), carbon nanotube/liquid metal ink (Park et al., 2019), and so on have also been tried for electronic applications.

Polymer conductive inks include poly (3,4-ethylenedioxythiophene) /poly(styrenesulfonate) (PEDT/PSS), polyaniline (PAN), polythiophene, polypyrrole (PPy), and so on. The corresponding printing methods can be direct writing (Aydemir et al., 2013), dip-pen nanolithography (Piner et al., 1999; Salaita et al., 2007), e-beam nanolithography (Yun et al., 2004), inkjet printing (Yoshioka and Jabbour, 2006; Yun et al., 2011), electrohydrodynamic printing (Chang et al., 2018), etc. Figures 1B,C show a conducting polymer pattern with direct laser writing method. A microfluidic chip with gold electrodes in the channel is fabricated first on a quartz glass substrate, and then the aqueous solution of pyrrole-3-carboxylic acid is injected in the microfluidic channel. Finally, a conductive polymer pattern with micro/nano structures in the aqueous solution is drawn by using a femtosecond laser (Agarwal et al., 2017).

Typical metal-based conductive inks include metal (e.g., Au, Ag, Pt, Cu) nanoparticle dispersion and metal compound precursor solution. Among them, Ag-based nanoink has gained special research interest due to its moderate price compared with Au and Pt (Lee et al., 2005; Rao et al., 2015), as well as its high electrical conductivity after sintering (Kwon et al., 2018; Glier et al., 2019). The typical sintering process lasts for up to 60 min at heating temperatures ranging between 125 and 250°C, which
limits the practical applications of the Ag-based nanoink on heat-sensitive flexible substrates (Mou et al., 2018). In recent years, infrared (NIR) sintering technology (Tobjork et al., 2012) has been widely used in flexible electronics, which greatly shortens the sintering time. The Ag nanoink could be selectively heated without substrate deformation due to the low NIR absorption of the polymer substrate (Gu et al., 2018). Figure 2A presents the conductivity variation of Ag nanoparticles (AgNP) sintered by NIR with the cross-sectional SEM images shown as insets of the sintered film at different sintering times. The flexible hybrid circuit presented in Figure 2B is fabricated through integrating the flexible circuit and the electrical components on a terephthalate (PET) substrate. The conductive circuit is made by screen printing, followed by sintering with NIR. Besides, Tavakoli et al. (2018) demonstrated a room temperature “sintering” method that could drastically improve the conductivity and mechanical deformability of the AgNP ink circuits printed on tattoo paper substrates. The circuit is fabricated through printing AgNP ink on tattoo substrate, followed by coating a layer of eutectic gallium-indium (EGaIn) liquid metal on the surface of the printed ink. Semisolid metal mixture composed of AgNP-Ga-In clusters surrounded by Ga-rich film is thus formed, which significantly improves the conductivity and the tolerance to tensile strain of the printed traces. Figure 2C presents a LED circuit with excellent flexibility, which is inkjet printed with AgNP-Ga-In ink on a soft brain-shaped toy.

**LIQUID METAL AND ITS PROPERTIES**

Liquid metal is a newly emerging class of conductive ink. Its types and applications have been first demonstrated by Zhang et al. (2012) and it is named as DREAM ink, which is an abbreviation of direct writing of electronics based on alloy and metal ink. The melting point of such ink is typically <300°C, and room temperature liquid metal is in liquid status at room temperature and atmospheric pressure. Liquid metal has the highest electrical conductivity and the highest thermal conductivity in all the fluid materials. It attracts more and more research interested ranging from chip cooling through neural function repairment and soft robot due to its fascinating properties. There are only three kinds of pure room temperature liquid metals in nature: mercury (Hg), gallium, and cesium (Cs), with their melting point respectively at −38.87, 29.78, and 28.65°C. Liquid alloys based on these elementary metals have been fabricated for the enrichment of liquid metal family. However, there exist safety or environmental pollution issues for partial members. Mercury and low melting point amalgam cannot easily be used for safety due to the volatility of mercury. A normal person will be poisoned immediately if the mercury concentration in ambient air is larger than 1.2 mg/m³. Mercury could cause damage to human beings and environment as it goes into the biological cycle (Wood, 1974; Trasande et al., 2005; Zabir et al., 2005). Alkalis such as sodium (Na), potassium (K), and cesium (Cs) are metals with the highest activity. Spontaneous combustion or explosions will occur as they meet with water. At present, gallium and its alloys are the most studied conductive liquid metal inks due to their usage safety. Table 1 lists the physical properties of several typical liquid metals compared with that of water. It can be seen that Ga, EGaIn (75% Ga, 25% In by weight), and Ga₇In₂₀.₅Sn₁₂.₅ have both metallic and fluid properties. The electrical conductivity of liquid metal is about 12 orders of magnitude higher than that of water. Its kinematic viscosity is about one third lower than that of water, indicating the good rheological property as well as the outstanding electrical property of liquid metal.

| Property                  | Ga   | EGaIn | Ga₇In₂₀.₅Sn₁₂.₅ | Water |
|---------------------------|------|-------|-----------------|-------|
| Melting point (°C)        | 29.8 | 15.5  | 10.5            | 0     |
| Density (g cm⁻³)          | 6.08 | 6.28  | 6.36            | 1     |
| Viscosity (mm²/s)         | 0.32 | 0.27  | 0.37            | 1.002 |
| Surface tension (N m⁻¹)   | 0.70 | 0.624 | 0.535           | 0.072 |
| Conductivity (10⁷ S m⁻⁻)  | 0.37 | 0.34  | 0.38            | 5.5 × 10⁻¹³ |
organometallic ink or carbon conductive ink, is rather low. The electrical performance of the printed circuit will be greatly improved to the level of bulk metals after post-treatments including drying, sintering, annealing, etc. The purpose of such post processes is to remove solvent, Dispersant, and stabilizer agent in the printing ink (Tai, 2012). However, long preparation time and complicated craft of the traditional inks limit their application in rapid circuit manufacturing. Compared to these traditional inks, liquid metal has many advantages such as simple preparation and no post-treatment processes. Table 2 lists a comparison of the electrical conductivities of several typical conductive inks. It can be seen that the electrical conductivities of the conductive carbon ink and the conductive polymer are about two to three orders of magnitude lower than that of liquid metal, which impedes their application development in high-sensitivity circuits fabrication. To the metal conductive ink, post-treatments are often needed to improve the electrical conductivity, reducing the printing speed while improving the manufacturing costs. In order to obtain enhanced performance, fabrication of composite conductive inks by adding liquid metal to carbon nanotube, polymer, AgNP, and so on has become a growing trend (Koh et al., 2018; Tavakoli et al., 2018; Park et al., 2019; Wang et al., 2019).

### Table 2 | A comparison of the electrical conductivities of several typical conductive inks.

| Ink type                 | Components          | Post-treatment     | Conductivity | References         |
|--------------------------|---------------------|--------------------|--------------|--------------------|
| Carbon conductive ink    | Graphene            | —                  | 4.3 × 10⁴ S/m | Huang et al., 2016 |
| Carbon nano-tube (CNT)¹  | —                   | —                  | (5.03 ± 0.05) × 10⁵ S/m | Pidcock and Panhuis, 2012 |
| Conductive polymer ink   | PEDOT/PSS²          | Plasma irradiation/10 s | 5.7 × 10⁴ S/m | Nitta et al., 2019 |
| Nano silver ink          | Ag-DDA³             | 140°C/60 min       | 3.45 × 10⁴ S/m | Mo et al., 2011    |
| Liquid metal             | EGaln               | —                  | 3.40 × 10⁵ S/m | Kramer et al., 2014 |
|                          | Ga₆₈.₅In₂₁.₅Sn₁₀   | —                  | 3.46 × 10⁵ S/m | Kramer et al., 2014 |
|                          | Bi₆₅In₄₈.₆Sn₁₂Zn₄.₄ | —                  | 7.3 × 10⁶ S/m | Wang and Liu, 2014 |

¹The mass fraction is 80%.
²The weight ratio of PSS to EDOT is 6.
³The protective agent is dodecylamine (DDA).
⁴The maximum electrical power density of the system is 360 kW/m².

OXIDATION CHARACTERISTICS OF LIQUID METAL

Gallium and Ga-based alloys are the representatives of room temperature liquid metal. As gallium is exposed to air, it is easy to react with oxygen to form gallium oxide, which in turn prevents gallium from further oxidation. Such characteristic of gallium is similar to that of aluminum (Regan et al., 1997). Contrary to gallium, indium is not easy to oxidize (Tostmann et al., 1999). The substance coated on the surface of Ga-based liquid alloys is mainly gallium oxide, which could increase the surface tension of the liquid metal. The oxide film could also alter the mechanical property of liquid metal, which behaves like an elastic ball in normal state and a liquid once the surface stress is larger than 0.5 N/m.

Zhang et al. (2013) disclosed that, oxidation of liquid metal played an extremely important role in realizing its printability and adhesion to various target substrates. Generally, large surface tension and poor adhesion between the liquid metal and the substrate often impede the flexible printing process including impact and spread (Figure 3A). To experimentally characterize the adhesion of the liquid metal ink, the surface tension and the contact angle of the droplets were both measured (Zhang et al., 2013). The EGaln alloy was oxidized through constantly stirring in air at room temperature, and the quantity of oxide can be calculated by weighing the weight difference between EGaln-based liquid metal with and without oxidization. As it is shown in Figure 3B, with the increase of oxygen content, the
Zheng et al. (2013) investigated the influence of oxidation on electrical reliability of liquid metal. Kramer et al., 2014 established a generalized way for pervasively and directly printing electronics on various substrates which were expected to be significant in a wide spectrum of electrical engineering areas. In that method, the liquid metal no longer needs to be pre-oxidized to guarantee its applicability on target substrates. One critical mechanism was found as that the atomized liquid metal droplets could be quickly oxidized in the air due to their large specific surface area, resulting in a significant increase of the adhesive capacity and thus firm deposition of the ink to the substrate.

WETTABILITY AND CONDUCTIVITY OF LIQUID METAL

Gao et al. (2012) investigated the influence of oxidation on wettability and conductivity of the liquid metal. The liquid metal was GaIn_{10}, while the substrate was, respectively, epoxy resin sheet, glass, plastic, silica gel sheet, paper, and cloth. It was found experimentally that with the increase of oxide content, the wettability of liquid metal was improved and the conductivity was thus reduced. Zheng et al. (2014), respectively, measured the contact angles between EGaIn droplets and polystyrene (PVC) and stainless steel, and paper substrates, respectively. It was discovered that with the increase of the applied pressure, the contact angle between EGaIn droplets and PVC reached the largest variation range. In general, PVC film serves as the best candidate substrate among the above three ones for liquid metal printing.

There is also an important relationship between the surface roughness and the wetting property of liquid metal. Kramer et al. (2014) measured the contact angles of EGaIn and GaIn_{8.5}Sn_{31.5}Sn_{10} droplets on metal films (Si, In, and Sn, respectively) with different roughnesses. The experimental results indicated that surface roughness had a crucial impact on wettability of liquid metal droplet.

Zheng et al. (2013) investigated the electrical reliability of the lines printed on the flexible substrate. EGaIn and coated paper were selected as the ink and the substrate, respectively. The length and the width of the printed line encapsulated by room temperature vulcanizing silicone rubber (RTV) was 18 cm and 1 mm, respectively. It can be seen from the results as shown in Figure 4A that the resistivity is almost invariant as the bending angle of the substrate is respectively at −180, −90, 0, 90, and 180◦. It indicates the good electrical stability of liquid metal circuit.

Wettability between liquid metal and substrates plays a key role in determining the printing feasibility. The substrates for liquid metal printing can be various materials with different surface roughnesses. Five representative substrates were selected by Wang and Liu (2015b) to investigate the wetting property of liquid metal. They were, respectively, silicon wafer, glass, PVC plastic film, PDMS, and paper substrates, and their corresponding root mean square (RMS) roughnesses were 1.05, 1.09, 3.81, 22.6, and 202 nm, respectively. The measured mean contact angles between Galinstan (68.5% Ga, 21.5% In, 10% Sn by weight, melting point is about 11◦C) and these five substrates were 119.2, 125.7, 111.4, 134.1, and 136.3◦, respectively, as shown in Figure 4B. It can be seen that the contact angle value corresponding to PVC plastic film substrate is the smallest among the five ones, which indicates the good wettability between Galinstan and PVC plastic film.

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FIGURE 5 | Images of GaIn24.5, Cu particles, and TransM2ixes (φ = 0.1) (A), and a piece of artistic work painted with a painting brush on plastic substrate using TransM2ixes (φ = 0.1) (B), and three TransM2ixes (φ = 0.1)-made Chinese calligraphy works written with a traditional Chinese brush on plastic, glass, and silicone substrates, respectively (C). Reproduced with permissions from Tang et al. (2017). Copyright 2017, American Chemical Society.

= 0.1) ink on plastic, glass and silicone substrates, respectively. It indicates the potential application of TransM2ixes ink in flexible electronics.

LIQUID METAL PRINTING METHODS

Liquid metal printing technology has its own uniqueness due to the high surface tension and the density of the ink. Zheng et al. (2014) proposed a concept of tapping mode electronic printing. The structure scheme of the printer is shown in Figure 6A. The ink storage tube is fixed at the printing driver, which is clamped on the slideway through a pulley. The printer head and the build platform can move along the X-direction and Y-direction, respectively. The printer head can be located at any position right above the build platform and its structure diagram is presented in Figure 6B. Once the printing starts, the printer head falls down to contact the substrate. Liquid metal ink disperses on the substrate with the rotating ball rolling due to the friction. At the end of printing, the printer head lifts up and leaves the substrate, for fear of destroying lines that have been printed. A flexible printed-circuit-on-board (PCB) and a printed copy of a Christmas greeting card, respectively, shown in Figures 6C,D were made in a low-cost manner through the tapping mode electronic printing technology. In 2015, such method has been developed by this lab (Yang et al., 2015) as a practical desktop personal liquid metal printer which now serves as a pervasive electronics manufacturing tool for the society. The printing resolution of the printer is <100 μm and the printing speed is preferred set in the range of 4–20 cm/s. Complex circuits or patterns with high quality can be rapidly printed out with the printer.

Zhang et al. (2013) demonstrated a non-contact printing method named as liquid metal atomized spraying technology, which could be utilized to draw circuit on arbitrary surfaces. The principle is shown diagrammatically in Figure 7A. The printing system is mainly composed of airbrush, mask, and substrate. Liquid metal ink in the container flows into the airbrush due to gravity. Then, it is atomized into fog microdroplets under the action of high atmospheric pressure at the nozzle. Microdroplets are deposited onto the substrate surface through mask pores. Liquid metal pattern will be formed as the mask is removed. A LED circuit shown in Figure 7B is printed through this way. In addition, patterns could also be printed on leaves, rubber, and so on (Figure 7C). Suppose that a screen mask is used, complex patterns can be fabricated in short time. Such printing technique is called liquid metal screen printing (Wang and Liu, 2015b). Figure 7D presents a picture of two dragons playing with a pearl pattern printed on black paper substrate through screen printing approach. Liquid metal spray printing is becoming ripe gradually and is used for fabricating skin electronics (Guo et al., 2014; Li et al., 2016; Gui et al., 2017).

Tabatabai et al. (2013) investigated a microcontact printing technique with which a liquid-phase circuit could be patterned on the substrate by using a microcontact printer. The print head is fabricated through casting PDMS, and the diameter of the hemispherical-shaped tip is 0.75 mm. Microcontact printing starts by dipping the print head into a liquid metal (EGaIn) pool and then retracting it (Figure 7E). Next, the print head wetted by liquid metal is pressed onto the substrate and thus a droplet is formed (Figures 7F,G). Repeat the process by controlling the
droplet spacing distance less than the droplet diameter, and the printed droplets can form a solid line (Figure 7H) or face on the substrate. Microcontact printing provides a method of patterning circuits on arbitrary planar geometries without the need for mold or mask fabrication.

Kramer et al. (2013) introduced a masked deposition of liquid metal (Ga$_{68.5}$In$_{21.5}$Sn$_{10}$) for fabricating liquid-embedded elastomer conductors. The schematic diagram is presented in Figure 8A. The process can be depicted as follows: glass slide, PDMS, tin foil, and PTFE photoresist are stacked in the bottom-to-top direction (1), and then tin foil is patterned with photolithography (2). Spin-coating a poly(acrylic acid) (PAA) release layer onto the elastomer surface without coating the super-hydrophobic photoresist (3), followed by sputtering indium on the surface (4). After rinsing the surface with acetone, the part on the tin foil surface is removed (5). Then, the surface is flooded with liquid metal (6), which reactively wets the tin foil (7). Excess liquid metal is removed with a thin-film scraper (8) and the remaining sputter mask is removed after rinsing the surface with water (9). Subsequently, the liquid features are cooled and encapsulated by coating with an elastomer (10). Such process incorporates liquid metal printing and photolithography, which could pattern a highly conductive liquid metal circuit within elastomer films without the need for molding, bonding, and syringe-filling (Kramer et al., 2013). The liquid-embedded elastomer shown in Figures 8B,C exhibits excellent bendability and stretchability.

Different from direct writing or printing of liquid metal, which is most commonly used, Wang et al. (2015) introduced an indirect printing method that is named as transfer printing. The printing process begins with fabricating a liquid metal circuit on the PVC film substrate, followed by covering liquid-phase
PDMS solution over the circuit. After curing of the PDMS, the whole structure is frozen to solidify the liquid metal (EGaIn). Considering the undercooling degree of Ga-based alloys, the cooling temperature should be lower than 0°C. As the PVC film is peeled off, the liquid metal circuit is embedded in the PDMS. Then, electronic components such as electronic chips, resistors, and capacitors are assembled on the circuit according to the circuit diagram. After encapsulating the transfer printed electronics with additional PDMS, a flexible liquid metal circuit is finally fabricated. Figure 9A shows the schematic diagram of the liquid metal transfer printing process. Figure 9B shows a printed complex liquid metal circuit encapsulated by PDMS with the thickness of 300 µm. The liquid metal circuit maintains an electrical connection as the PDMS substrate is stretched up to 130% of the original length, which indicates the good flexibility of the circuit. Figure 9C presents a printed wristband circuit in working state that exhibits its truly wearable characteristics.

Lu et al. (2017) demonstrated the liquid metal corrosion sculpture method for fabricating complex patterns on Al substrate. The schematic diagram of fabrication is shown in Figure 10A. A plastic mask with hollow pattern is placed on the Al substrate closely, and liquid metal (GaIn10) microdroplets generated by an airbrush are sprayed uniformly on the substrate. Al substrate will be in direct contact with liquid

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metal through the hollow space on the mask. Al-Ga metal solution will be formed at the interface between Al substrate and liquid metal. After a few minutes to several hours of removing the plastic mask and cleaning Al plates with alcohol, in order to obtain different corrosion depths, a sculptured pattern is thus formed on the substrate. Figures 10B–E present several patterns fabricated with such approach. Compared to traditional ceramic machining techniques, the liquid metal sculpture method has several advantages including high productivity, low cost, and good surface smoothness (Lu et al., 2017).

Liu et al. (2018) introduced laser sintering method to print flexible electronics by selectively coalescing liquid metal nanoparticles. First of all, fabricate a 10-μm-thick nanoparticle film on the substrate through spray-printing liquid metal (EGaIn) nanoparticle inks. As a thin oxide skin could spontaneously form on the surface of Ga-based liquid metal exposed to air, these EGaIn nanoparticles are electrically insulated due to their oxide skins. Then, an ytterbium pulsed fiber laser is used to scan the nanoparticle film and the oxide skins are selectively ruptured and ablated. EGaIn nanoparticles are therefore coalesced to form a conductive line. Figure 11A presents the schematic diagram of laser sintering method, and Figure 11B shows a soft electronic circuit with intricate pattern fabricated directly onto an elastomer substrate which is adhered to a human wrist. It indicates the application potential of liquid metal laser sintering in wearable electronics. Figure 11C shows a printed gear pattern, and Figure 11D presents a comparison of the surface morphology between unsintered and sintered regions of the pattern. It can be seen that particles in the unsintered region remain spherical, while particles in the sintered region coalesce into a connected network. Laser sintering of liquid metal nanoparticles demonstrates a rapid approach for printing high-resolution flexible electronics.

In order to change the color appearance of the printed circuit, (Liang and Liu, 2018) proposed a colorful liquid metal circuit fabrication method, and the process flow diagram is presented in Figure 12A. First of all, a liquid metal (GaIn24.5) circuit on PVC or paper substrate is printed with direct desktop printing, spray printing, or screen printing method. Then, the circuit is solidified by placing it in a refrigerator for more than 2 h, followed by screen printing or direct writing (using a brush or a porous needle pen) the liquid pigments on the surface of the conductive wires at about 0°C. After the colorful liquid metal has dried naturally, it is packaged with PDMS solution. With this method, circuits or conductive patterns with various colors can be conveniently prepared (Figures 12B–D).

Guo et al. (2019b) proposed a semi-liquid metal and adhesion–selection enabled rolling and transfer (SMART) printing method. Ni-EGaIn is selected as liquid metal ink, which is in semi-liquid state. The preparation process of a flexible circuit begins with printing the predesigned pattern on a thermal
transfer paper with the PU glue by using a laser printer, followed by, printing Ni-EGaIn ink on the paper with the toner pattern by a roller. As the adhesion between Ni-EGaIn and toner is negligible in comparison to that between Ni-EGaIn and PU glue, the Ni-EGaIn ink is selectively printed on the PU glue part of the transfer paper. Subsequently, the liquid metal pattern is transfer printed by attaching the pattern side of the transfer paper to the surface of ecoflex substrate with a pressure of about 2.5 kPa. Finally, the liquid metal pattern on the ecoflex substrate is packaged by printing mixed ecoflex 00-30, which could cure in 15 min at room temperature. The whole process is indicated in Figure 13A, and a printed LED array flexible circuit on paper substrate is shown in Figure 13B. The preparation time of a circuit with SMART printing is typically within 30 min, which is less than other liquid metal printing methods such as direct writing, spray printing, and so on (Guo et al., 2019a). This method provides a super-fast way for fabricating soft electronics.

PROSPECT

Conclusively, printed electronics, which means instant manufacturing, has become a research focus in recent years. The potential applications cover from consumer electronics to energy, medical, and so on. Various kinds of liquid metal printing methods have emerged in succession and are in ascendancy. The substrates used for printing can be paper, plastic, metal surface, cloth, or even skin (Rogers, 2017; Wang et al., 2018). Among the factors affecting the printing effect, the ink is the most important one. As to the newly liquid metal printing ink, the way to increase ink types lies in developing more and more low melting point alloys or liquid metal-based conductive composites. (Wang and Liu, 2013) has put forward the concept of liquid metal material genome initiative, which is aimed to discover advanced functional alloys with low melting point with the help of physical and chemical methods. Liquid metal family can be expanded through reorganization of existing elemental metals or alloys. High-throughput calculation, preparation, and characterization techniques can be fully tried to screen out suitable liquid metal ink, which has desired properties including electrical conductivity, viscosity, wettability, oxidation property, and so on. Based on the various selectable inks, brand new kinds of printing techniques of liquid metal can also be further developed. In addition, it can be seen from the numerous literatures that electronic device printing (Andrews et al., 2018; Choi et al., 2019) is becoming one of the most important direction in flexible electronics. Liquid metal-based circuit printing including devices and conductive wires could provide a powerful strategy for the establishment of future smart homes (Wang and Liu, 2015a).

AUTHOR CONTRIBUTIONS

LW finished this review, including writing and formatting of the manuscript. JL revised the manuscript and made important supplementary.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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