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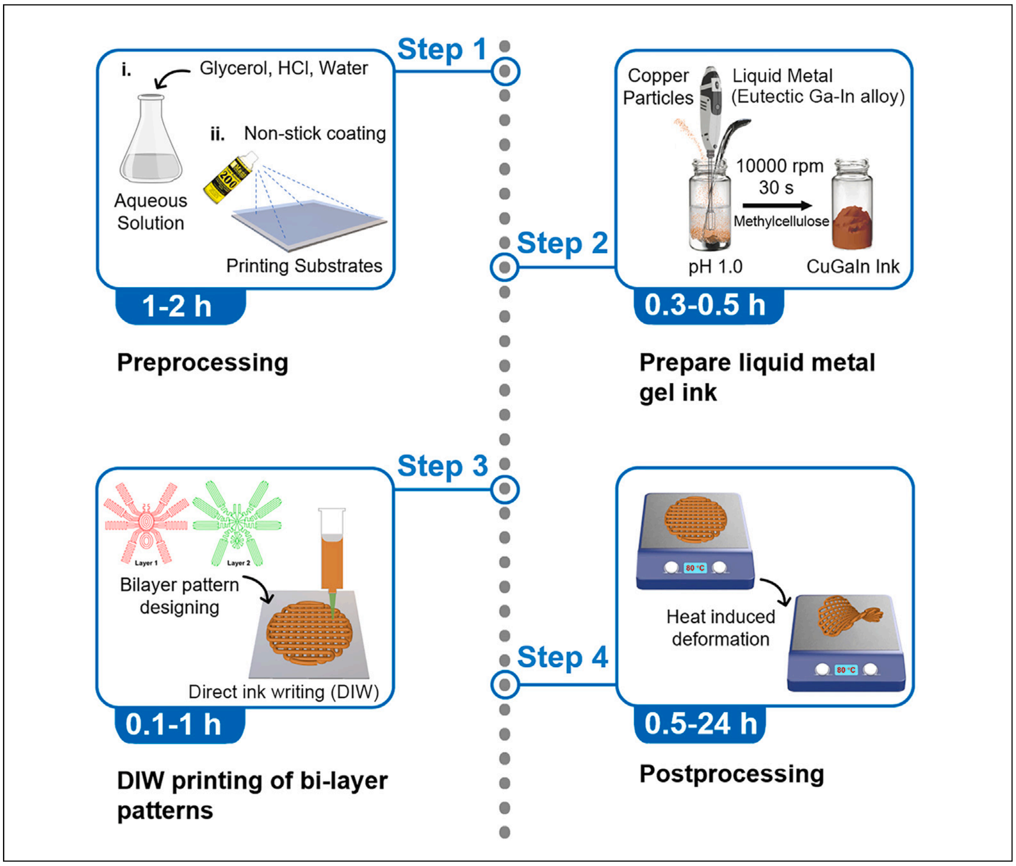
Protocol

Protocol for 3D and 4D printing of highly conductive metallic composite using liquid metal gels



3D or 4D printing of metal structures requires extreme conditions or a multistage process. Here, we present a protocol for the preparation of highly conductive metallic composites using liquid metal gels at ambient conditions. We describe the steps to prepare ternary gels composed of copper particles, liquid metal, and water. We then detail procedures for 3D or 4D printing gels into highly conductive structures after adding a small amount of rheological modifier (methyl cellulose) using direct ink writing techniques.

Publisher's note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.

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Highlights

Instructions for printing metallic composites at ambient conditions

Steps for 3D or 4D printing of highly conductive metallic structures

Detailed steps for preparing copper-liquid metal-water inorganic gels

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Protocol for 3D and 4D printing of highly conductive metallic composite using liquid metal gels

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SUMMARY

3D or 4D printing of metal structures requires extreme conditions or a multistage process. Here, we present a protocol for the preparation of highly conductive metallic composites using liquid metal gels at ambient conditions. We describe the steps to prepare ternary gels composed of copper particles, liquid metal, and water. We then detail procedures for 3D or 4D printing gels into highly conductive structures after adding a small amount of rheological modifier (methyl cellulose) using direct ink writing techniques.

For complete details on the use and execution of this protocol, please refer to Xing et al. (2023).[1]

BEFORE YOU BEGIN

This protocol describes the detailed steps for 3D or 4D printing of highly conductive parts using liquid metal gels according to the publication from Xing et al.[1] Before preparing the liquid metal gels, it is important to have a suitable aqueous solution ready since precise pH tuning of the solution becomes challenging after copper and liquid metals are mixed. Meanwhile, preparing a suitable printing substrate with low adhesion and good heat transfer properties is also a prerequisite step to ensure subsequent deformation response after printing.

Preparation of the aqueous solution

Timing: 0.5–1 h

1. Preparation of 8% glycerol solution with pH value of 1.0.
   a. Weigh 8.0 ± 0.1 *g* glycerol in a 100-mL glass beaker.
   b. Add 92.0 ± 0.1 *g* deionized water and stir until homogenized.
   c. Tune the solution pH to 1.0 ± 0.05 by adding concentrated hydrochloride acid (HCl, 37%) drop wisely while monitoring the pH using a pH probe.

Note: The aqueous solution can be stored at 4°C refrigerator with proper seal for no more than 30 days.

CRITICAL: HCl is irritating to eyes, skins, and the respiratory system. Handle it under a chemical fume hood, wear gloves, eye goggles and appropriate personal protective equipment.

Pre-treatment of printing substrates

Timing: 0.5–1 h

2. Cleaning the glass substrates.
   a. Rinse the glass substrate with distilled or tap water.
   b. Either air dry or wipe it clean with a clean non-woven cloth.

Note: Any flat substrate can be used as a carrier medium for the printed materials, but it is recommended to use glass substrates with a thickness of less than 5 mm to achieve proper thermal conductivity. This helps to avoid potential stress relaxation in the printed liquid metal gels due to heat insulation of the glass substrate, which can lead to a partial or complete loss of the 4D printing response to heat in the final step.

3. Low adhesion treatment of the print substrates.
   a. In a fume hood, spray Ease Release 200 onto the surface of the glass substrate. Hold the can 6–8 inches from the glass surface to ensure a light, even coating.
   b. Wait for it to dry by visual inspection.
   c. If needed, repeat step 3a-b for 3–4 times.

Note: For new substrates or substrates with film coatings, please apply Ease Release 200 at least 3 times to minimize the adhesion between the printed material and the substrate.

CRITICAL: Aerosol sprays can be irritating to eyes, skins, and the respiratory system. Handle it under a chemical fume hood, wear gloves, eye goggles and appropriate personal protective equipment. Avoid inhalation of excessive amount of solvent vapor.

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Copper powder (10–25 μm)	Sigma-Aldrich	CAS: 7440-50-8
Eutectic Ga-In alloy (EGaIn, 75.5 wt % Ga, 24.5 wt % In)	Indium Co.	LOT: LA382304J
Methyl cellulose (1500 cP)	Sigma-Aldrich	CAS: 9004-67-5
Glycerol	Sigma-Aldrich	CAS: 56-81-5
Hydrochloric acid (37%)	LabChem	CAS: 7647-01-0
Software and algorithms		
Mach3 software	Newfangled Solutions Software	N/A
Window notebook	Microsoft	N/A
Other		
3-axis stage	Minitech Machinery Co.	N/A
Pressure actuator	Nordson EFD	Ultimus V
Syringe barrels	Nordson EFD	Optimum
Dispense tips (tapered, 16–20G)	Nordson EFD	Optimum SmoothFlow
Rotary tool	Northern Tool and Equipment	NTE2103
pH probe	VWR	SP80PC
Glass vial	China	20 mL
Glass substrate	China	N/A
Hotplate	Fisher Scientific	Isotemp
Ease Release 200	Mann Release Technologies	Item No. ER200

MATERIALS AND EQUIPMENT

Note: All chemicals are stored at room temperature.

Alternatives: In this protocol, we use a pneumatic-controlled three-axis platform to achieve the 3D printing process. However, any 3D printing devices compatible with direct-ink-writing (DIW) technology can be used for this protocol, as long as they incorporate a pneumatic-controlled material feeding system (maximal system pressure is greater than 70 psi) and ensure that the material delivery pipelines do not contain structures with orifice smaller than 3 mm.

For the heat source, we use a temperature-controlled hotplate in this protocol, therefore a substrate that has a thermal conductivity greater than 0.6 W/(m·K), and a thickness preferably less than 3 mm is the preferred choice. This will ensure efficient heat transfer from the heat source to the printed material. However, any equipment capable of providing a constant heat source, such as an oven, can also be used as an alternative for this protocol.

Ease Release 200 can be replaced with other non-aqueous commercial nonstick coating materials, as long as they do not leave solvent residues on the substrate surface.

⚠ CRITICAL: DIW printing system with an auger pumping system is not suitable for this protocol, as the screw generates excessive shear forces within the chamber, leading to the over-extrusion of the liquid metal and consequently compromising the shear-induced alignment performance.

STEP-BY-STEP METHOD DETAILS

Preparation of liquid metal gel ink

⏲ Timing: 15–30 min

For successful 4D printing of highly conductive composite using copper (Cu)-liquid metal-water gels, it is crucial to ensure the uniform dispersion and contact between liquid metal and Cu particles, as well as to obtain the proper rheological properties of the gel ink. The following steps outline the process for creating a Cu-EGaIn-water gel ink suitable for 4D printing.

1. The aqueous solution is prepared according to the Part: preparation of the aqueous solution.
2. Preparation of Cu-EGaIn-water gel. Troubleshooting 1.
   a. Weigh 9.0 ± 0.1 *g* copper particles inside a 20 mL glass vial.
   b. Add 3.0 ± 0.1 *g* aqueous solution into the glass vial and pre-stir with copper particles thoroughly to avoid excessive splashing of copper powders when starting the high-speed stirring in step 2.
   c. In the glass vial from step 1b, add 3.0 ± 0.1 *g* EGaIn. Vigorously stir the mixture using a rotary tool equipped with a beater blade (Figure 1) at 10000–15000 rpm for 30 s.

Note: The weight of the liquid metal can be varied from 0.1 *g* to 5.0 *g*. This will not change the printability of the liquid metal gel ink; however, the deformation responsiveness and electrical conductivity may be changed. For more details, please refer to the reference Xing et al.[1]

3. Rheological tuning of Cu-EGaIn-water gel. Troubleshooting 2.
   a. Weigh 120 ± 2.5 mg methyl cellulose and add it to the glass vial from step 1c.
   b. Stirred the mixture using a rotary tool equipped with a beater blade at 10000–15000 rpm for 30 s.

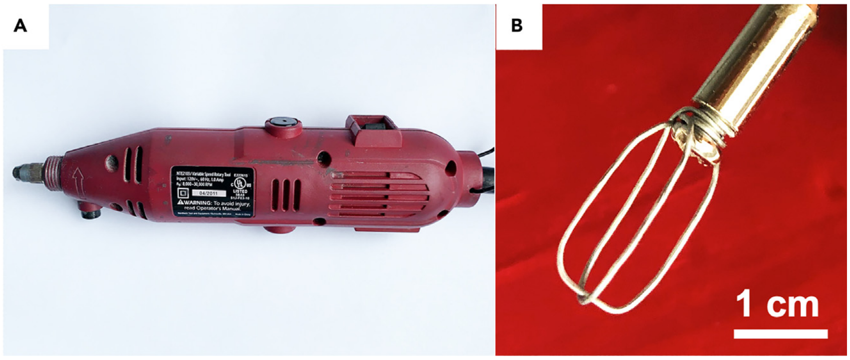

Figure 1. Photos of rotary tool used for creating liquid metal gels
(A) Universal rotary tool (8000–30000 rpm).
(B) Customized 316L stainless steel beater blade.

Note: If scaling up, please use appropriately larger capacity containers and beater blade.

⚠ CRITICAL: When operating the high-speed mixing equipment, wear eye goggles and other personal protective equipment to prevent materials from splashing onto your body.

Printing 2D patterns with bilayer design

⏲ Timing: 10–60 min

The 4D printing of liquid metal gel ink is achieved through the anisotropic shrinkage of the printed filaments under shear. Therefore, the bilayer printing pattern design is used to realize programmable deformation. Details on the bilayer pattern design guideline can be found in the references Gladman et al.[2] The following steps outline a typical printing process for creating a rectangular bending lattice (Figure 4).

4. Design the bilayer structure.
5. Create a G-code file of the part to be printed based on the designed bilayer structure. The G-code used in Figure 4 is shown below:

```
>(Set parameters)
>#101=1.08 (Layer 2)
>#102=10.0 (Safe travel distance)
>#103=600 (Jog rate)
>#104=480 (Feed rate)
>(End set parameters)
>G1X0Y0F#104A100
>G1Z0.48
>G1X0Y10
>G1X2Y10
>G1X2Y0
>G1X4Y0
```

```
>G1X4Y10
>G1X6Y10
>G1X6Y0
>G1X8Y0
>G1X8Y10
>G1X10Y10
>G1X10Y0
>G1X12Y0
>G1X12Y10
>G1X14Y10
>G1X14Y0
>G1X16Y0
>G1X16Y10
>G1X18Y10
>G1X18Y0
>G1X20Y0
>G1X20Y10
>G1X22Y10
>G1X22Y0
>G1X24Y0
>G1X24Y10
>G1X24Y10
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>G1X28Y10
>G1X30Y10
>G1X30Y0
>G1X32Y0
>G1X32Y10
>G1X34Y10
>G1X34Y0
>G1X36Y0
>G1X36Y10
>G1X38Y10
>G1X38Y0
>G1X40Y0
>G1X40Y10
```

```
>G1Z#101A0
>G1X0Y10A100
>G1X0Y8
>G1X40Y8
>G1X40Y6
>G1X0Y6
>G1X0Y4
>G1X40Y4
>G1X40Y2
>G1X0Y2
>G1X0Y0
>G1X40Y0
>G1Z#102F#103A0
>G1X0Y0
>END
```

Note: The G-code can be obtained by manually typing in the notebook software or using G-code generating software (Simplified 3D) or scripts.

Note: The G-code format may vary between different devices due to hardware differences. To learn about the supported G-code formats, please contact the technical support responsible for your devices.

Note: In the G-code, try to utilize continuous printing paths to achieve a consistent micro-phase alignment within the liquid metal gels.

6. Import the G-code file of the part into the Mach3 software.
7. Load the liquid metal ink into a 3 mL syringe barrel (Figure 2A).
8. Place the piston (Figure 2B).
9. Assemble the adapter (Figure 2C).
10. Apply a mild pressure of 3–5 psi to push the ink to the ready-to-print state (Figure 2D).
11. Pause the air pressure, and replace the tip cap with the dispense tip (Figure 2E).
12. Adjusting the print pressure at the pressure actuator. For the ink recipe used in this protocol with an 18G tip, the dispensing pressure is set to 35 psi. (Figure 2F). Troubleshooting 3.

    Note: Adjust the print pressure to match the nozzle diameter and printing speed. Specific guidelines for DIW flow regulation can be found in the reference Saadi et al.[3]

13. Fix the substrate on the printer stage (Figure 3). The substrate used here is prepared according to the Part: pre-treatment of printing substrates.
14. Prepare the printer, shown in Figure 3, for printing the bilayer pattern.
    a. Balance the printing stage.
    b. Home all axes.
    c. Set zero point for all axes at proper position.
    d. Start printing. Troubleshooting 4.

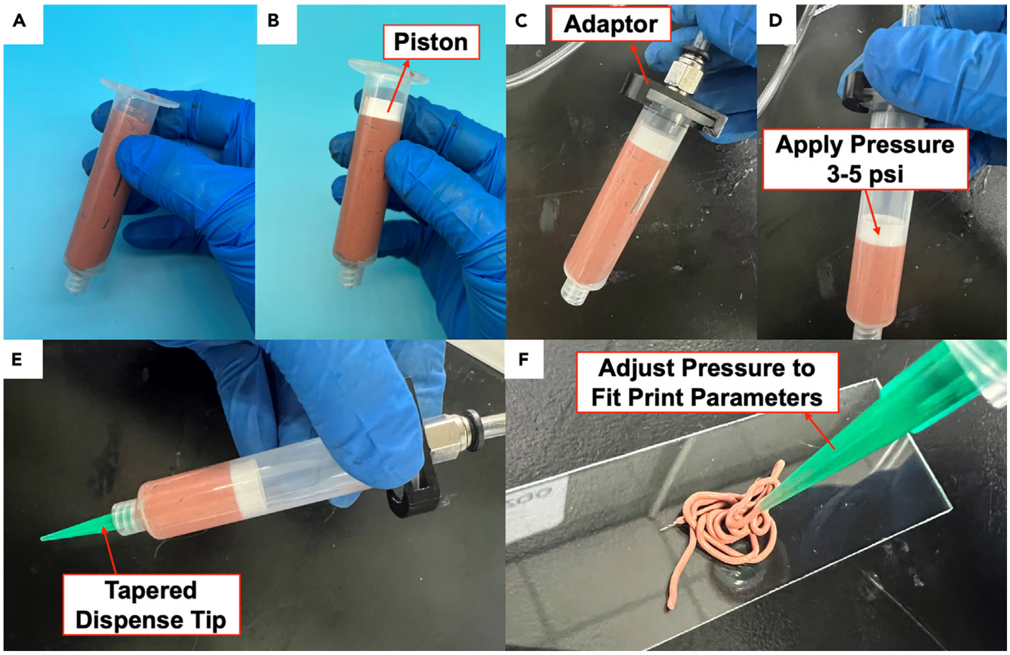

Figure 2. The preparation process of loading Cu-EGaIn-water gel ink before printing

Note: Step 14 may vary depending on the model of the printing devices. Please refer to the instruction manual of your devices.

Note: The printing parameters used in this protocol are listed in Table 1.

Note: The movement of print nozzle is controlled by a 3-axis CNC stage through Mach3 software. The ink dispensing system is controlled separately by a commercial dispenser defined in the G-code as A-axis. When A-axis is greater than 0, the pressure regulator in the dispenser changes to fully open, applying the pre-set pressure to the piston in the syringe barrel. More details can be found in the reference Neumann et al.[4]

Post-treatment of the printed pattern

Timing: 0.5–24 h

During printing, the Cu-EGaIn clusters align anisotropically within the liquid metal gel due to shear at the nozzle exit. As the water evaporates, it results in the anisotropic shrinkage of the filament (i.e., the diameter of the printed filaments shrinks more than the long-axis of the filament), which eventually causes shape deformation of the whole pattern. The following steps in post-treatment of the printed pattern enable it to achieve the designed spatial deformation.

15. Preheat the hotplate to 80°C.

Note: Different heating temperatures will result in varying degrees of bending in the sample. Choose the proper temperature according to your need. For guidance on temperature selection, please refer to the reference Xing et al.[1]

Note: If you do not desire deformation of the printed structure (i.e., for 3D printing), set the hotplate to 25°C.

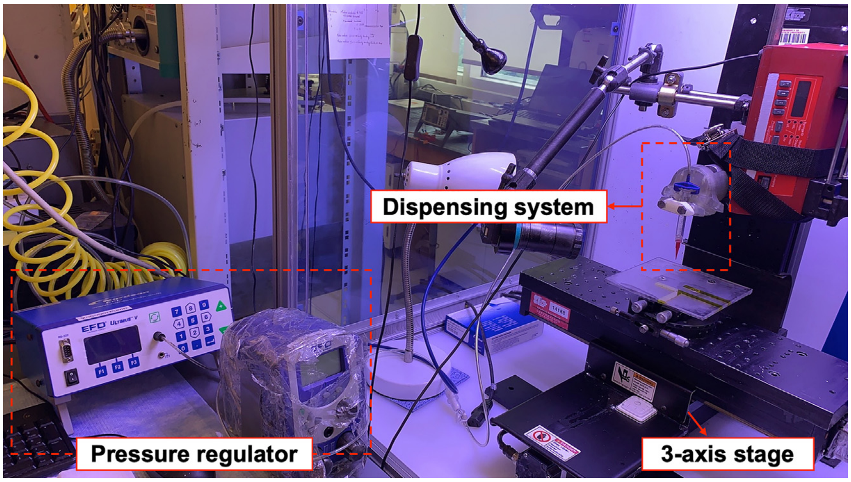

Figure 3. The DIW printing system used in this protocol

16. Transfer the printed pattern together with the glass substrate onto the hotplate (Figure 4).

    ⚠ CRITICAL: Ensure necessary hand and other body part protection when operating the hotplate to prevent burns.

17. Heat the printed sample until the deformation is complete. Troubleshooting 5.

    Note: Different temperatures result in varying rates of water evaporation within the metallic gel, leading to differences in the time it takes for the sample to fully dry and deform. Within a temperature range of 25°C–80°C, the complete deformation time for the sample ranges from 24 h to 0.5 hours. For the samples printed in this protocol, at 80°C, the evaporation time is 30 minutes.

EXPECTED OUTCOMES

Using this protocol, you will be able to achieve the preparation of Cu-liquid metal-water ternary gels. This liquid metal gel exhibits high electrical conductivity (greater than 10^5 S/m) after drying, making it highly promising for a wide range of applications, such as circuit printing and conductive coatings. Furthermore, by using this protocol to print and post-process this liquid metal gel through DIW technology, you will be able to achieve 3D or 4D printing of highly conductive materials with desired structures, depending on the specific post-processing temperature you use. Besides, in conjunction with the controllable heating techniques, the 4D printing material demonstrated in this protocol can achieve gradient deformation variations. This unique deformation process has been demonstrated to work by introducing heat insulating material on the hotplate. (See Xing et al.[1] for details).

LIMITATIONS

This protocol is applicable to copper-EGaIn-water ternary gels. For other mixed systems of liquid metals with copper and water, this protocol needs to be used only if the following conditions are satisfied: The liquid metal must contain gallium, with a mass content greater than 50%; the melting point of liquid metal should be below 40°C; the temperature of the liquid metal gel in steps 1–17 always remains above the melting point of the liquid metal.

Another limitation is that the use of an extremely acidic solution (pH 1.0 aqueous solution) is required to achieve the highly conductive property. This is because during stirring, it is necessary to ensure the dissolution of the oxide layer of liquid metal and copper, allowing gallium and copper to

Table 1. Printing parameters used in this protocol

Parameter	Value
Pressure	35 psi
Nozzle tip	18G
Layer height	0.6 mm
Nozzle stand-off distance	0.48 mm
Print speed	6 mm/s
Jog speed	10 mm/s

come into direct contact and partially alloy at the interface. This process is essential for effectively establishing electronic pathways within the printed material and achieving high electrical conductivity.

The third limitation is that the deformation of the printed structure is not reversible. This is because the primary source of deformation arises from the anisotropic shrinkage resulting from the evaporation of water within the liquid metal gel.

TROUBLESHOOTING

Problem 1

The Cu-liquid metal-water mixture does not form a gel after high-speed stirring.

Potential solution

Check ambient and sample temperature to make sure that they are above the melting point of liquid metal.

Check the particle size of copper under scanning electron microscope (SEM) if it is within the range of 10–25 μm. To ensure size matching of liquid metal and copper, we recommend using copper particles with size range between 5−50 μm.

Inspect the shape of copper particles under SEM to ensure they do not exhibit strong anisotropic morphologies, such as rods or flakes.

Check if the color of the copper particles is shiny reddish-brown. If the color of the copper particles darkens or turns into a dark reddish-brown, it indicates the presence of a significant amount of oxide on the surface, which can hinder the contact between copper and liquid metal.

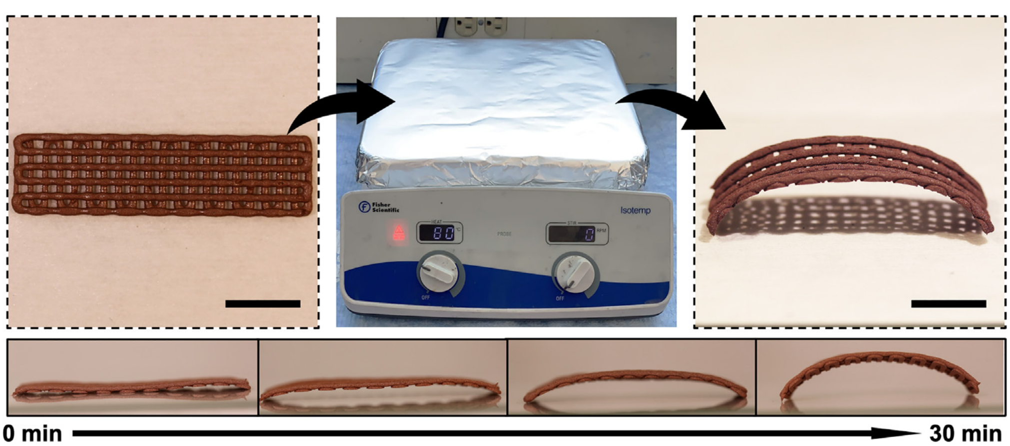

Figure 4. Post-treatment of the printed bilayer structure to induce shape deformation
Scale bar is 10 mm.

Make sure the proportions of all the ingredients fall within the gelation range of copper-EGaIn-water ternary phase diagram. (Xing et al.[1]).

Make sure the rotary tool works at least at 10000 rpm.

Make sure the beater blade is mounted correctly.

Extend the stirring time appropriately, but do not exceed 15 s.

Problem 2

The methyl cellulose powder splashes out of the bottle upon starting the stirring.

Potential solution

Redo steps 2–3. Add the MC powder in 2–3 portions, and after each addition, stir for 2–3 s. After the final addition, stir for 15 s.

Problem 3

The liquid metal gel cannot be extruded through an 18G tip at pressure of 35 psi, or it cannot self-support after extrusion.

Potential solution

The above situation usually indicates very poor printability of the gel ink. If the Cu-liquid metal-water mixture does not exhibit a gel-like state at step 2, please refer to the solution outlined in troubleshooting 1. Otherwise, this situation arises due to differences in the viscosity of the methyl cellulose solution. First, check if the labeled viscosity of the methyl cellulose you are using is within 1500 cP. If it is, you can try the following steps. Start by adjusting the pressure within $\pm$10 psi to see if you can extrude the gel normally. If not, try adjusting the amount of MC within $\pm$10% of the current dosage.

Problem 4

The printed liquid metal gel filament does not adhere to the substrate.

Potential solution

There might be two reasons causing the printed filament not to adhere to the substrate. The first one is the improper setup of the stand-off distance. Run your G-code once without applying pressure and check if the distance between the nozzle tip and the substrate during the first layer printing is much greater than the pre-set stand-off distance. Also, inspect the substrate surface you are using for any residual solvent from prior treatment steps or if you are using a non-stick coating formula with slow solvent evaporation.

Problem 5

The printed pattern does not deform as expected or at all.

Potential solution

There are several reasons that can lead to the printed structure not exhibiting the pre-designed deformation, which can be categorized into the following scenarios:

If the printed structure does not deform at all, this usually indicates that the shrinkage stress generated during solvent evaporation is unable to overcome the material's own gravity. The reason could be the shear forces provided at the nozzle are unable to effectively align the Cu-EGaIn clusters within the liquid metal gel. To solve this issue, consider the following solutions. 1) Examine the average particle size of the liquid metal particles under a microscope. If the average particle size exceeds 100 μm, it indicates that the shear forces provided by your stirring equipment in steps 2–3 are insufficient. Consider using higher rotational speeds or beater blade with greater shear forces. 2)

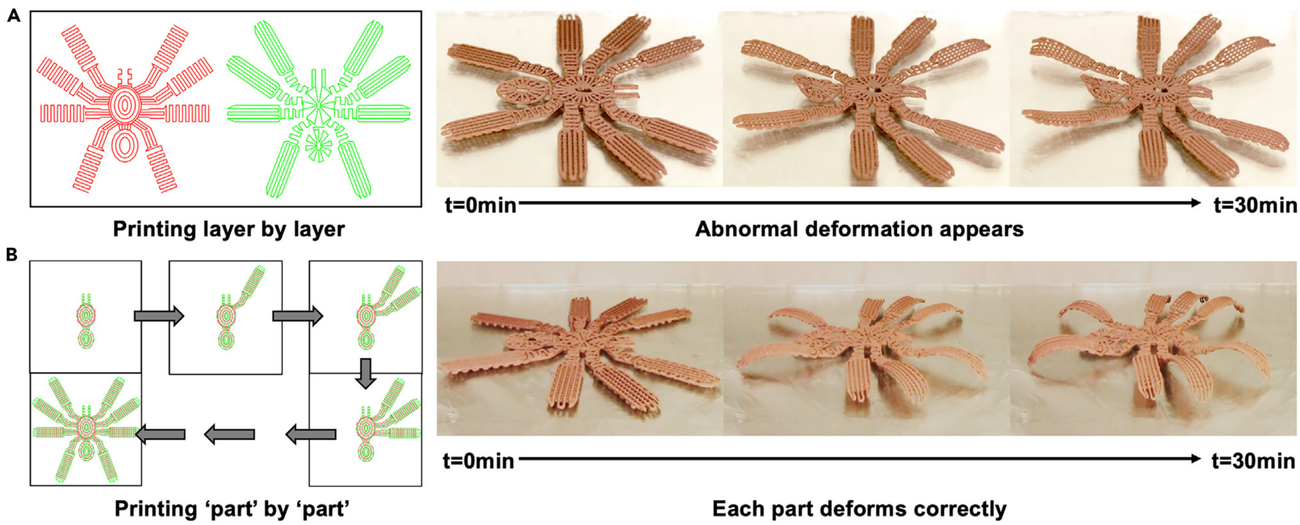

Figure 5. Achieve the desired (programmed) deformation of the printed structure by optimizing the printing sequence
(A) print layer by layer.
(B) print 'part' to 'part'.

Measure the apparent viscosity of the liquid metal gel ink. If the apparent viscosity is less than 10^3 Pa s, consider the solution in troubleshooting 3.

If the printed structure deforms but not as much as expected or towards the wrong direction, this usually indicates that the poor alignment of the Cu-EGaIn clusters. To solve this issue, consider the following solutions. 1) Reduce the amount of the aqueous solution within a 10% range of the original used quantity. Increase the printing pressure and the print speed accordingly. 2) Reduce the overall printing time, especially the time between printing the first layer and the second layer. For larger models such as the one in Figure 5, consider breaking them down into separate units and printing the first and second layers for these units separately, rather than completing the first layer for all units before moving on to the second layer. 3) Move the printed structure immediately to the hotplate.

MC-class solutions are robust, time-dependent materials. A lower evaporation rate may facilitate stress relaxation, gradually reducing shrinkage strain to a critical level where deformation is no longer feasible. Therefore, for the uniform deformation of large-scale structures, typically requiring printing times greater than 10 min, we recommend printing each part individually.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Michael D. Dickey (mddickey@ncsu.edu).

Technical contact

Technical questions on executing this protocol should be directed to and will be answered by the technical contact, Ruizhe Xing (rzxing@nwpu.edu.cn).

Materials availability

This study did not generate new unique materials.

Data and code availability

Raw datasets and G-codes are available from the lead contact upon request. Processed datasets are provided in Xing et al.,[1] 2022.

ACKNOWLEDGMENTS

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AUTHOR CONTRIBUTIONS

R.X. and M.D.D. conceptualized and designed the experimental workflow. R.H. and W.Q. optimized the protocol. R.X. performed all the experiments and generated the figures. R.X., J.K., and M.D.D. discussed the protocol and wrote the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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