

# Fast Solidification of Pure Gallium at Room Temperature and its Micromechanical Properties

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With excellent electrical conductivity, fluidity, rheological property, and biocompatibility, gallium has been intensively studied in the fields of flexible electronics and devices, thermal management, and soft robotics. However, the large degree of supercooling of gallium presents a large limitation for phase transition-related applications such as the very low temperature required for solidification, the impurities, and side effects brought in by nucleating agents. In this study, solidification process of liquid gallium by using solid gallium as a nucleating agent is discovered to be fast and facile at room temperature compared with other agent materials including copper, iron, and nickel. Quantificationally, solidified gallium as a nucleating agent, can effectively reduce the supercooling degree from about 66.3 to 14.8 °C. The freezing velocity can reach to 200 mm<sup>3</sup> min<sup>-1</sup>. The possible mechanism is reducing the energy barrier via adding nucleation site, allowing rapid solidification at room temperature accompanying heat dissipation. Moreover, micromechanical properties are compared between raw solid Ga and the solidified Ga induced by Ga agent, which suggests a slight decrease in mechanical strength at room temperature with the nucleating agent. It will be beneficial to understand the phase change and also provide guidance for the application of gallium regarding its mechanical properties.

## 1. Introduction

Gallium (Ga), an intriguing transitional metal with a unique low melting point at 29.8 °C, has attracted tremendous attention in recent years owing to its unique properties such as excel-

lent fluidity at room temperature, electrical and thermal conductivity, deformability in response to various stimuli, etc. Thus it has been intensively investigated in the field of thermal management,<sup>[1,2]</sup> flexible electronics and devices,<sup>[3–7]</sup> additive manufacture,<sup>[8,9]</sup> medical therapies,<sup>[10–12]</sup> soft robotics,<sup>[13,14]</sup> etc. Among the applications, the solid-liquid phase transition of gallium can enable diverse and specific functions beyond the single liquid-state metal behaviors. For instance, the phase transition of gallium-based polymer can achieve reversible transitional insulator and conductor, which can be applied as temperature-controlled electrical switches and circuits.<sup>[15]</sup> Taking advantage of the mechanical strength of solid gallium, the mechanically transformative electronics, sensors, and implantable devices can be also realized by solid-phase phase transition.<sup>[10,16]</sup> Moreover, phase transition of the liquid gallium or its alloy composite can generate reversible and strong adhesion to different surfaces, which can be used as transformable grippers for various objects.<sup>[14,13,17]</sup> During the solid-liquid phase transition, the melting process is relatively quick as temperature rises above the melting point. However, the solidification of gallium usually requires a much lower temperature than the melting point as well much longer time due to the significant supercooling effect (the

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freezing point is far below melting point, 29.8 °C, the maximum of  $\Delta T = 76$  °C,<sup>[18]</sup> which means that they could not solidify even when cooled below their melting points over dozens of degrees Celsius. Such supercooling effect presents great limitations for these temperature-controlled gallium-based materials and devices for fast phase transition at moderate room temperature.<sup>[19]</sup> Some studies have been carried out to reduce supercooling by applying external forces such as impact<sup>[20]</sup> or electrical field,<sup>[21]</sup> and adding nucleating agents.<sup>[22,23]</sup> The methods using external forces are useful, but could not be applied easily in practical applications. For example, the method of adding an electric field may cause unnecessary reactions, which is detrimental to subsequent applications. On the other respect, Tang et al. observed the solidification of GaBi and found unique surface patterns during solidification.<sup>[24]</sup> Zhang et al. have attempted to use TeO<sub>2</sub>, CaO, and MgO as nucleating agents to reduce the supercooling.<sup>[22]</sup> Furthermore, Patrick J. Shamberger's group observed lattice-matched multiple cubic rock salt structure carbides and nitrides could decrease the undercooling.<sup>[19]</sup> It could be concluded that adding nucleating agents could effectively reduce the degree of supercooling of gallium. However, these methods will introduce a new substance in the solid gallium, which will affect its physiochemical properties. Previous explorations have mentioned that the solid gallium itself could be used as a nucleating agent to promote the solidification of liquid gallium.<sup>[8,25,26]</sup> However, the details such as the affecting factors, freezing rate, mechanism, etc. of the solidification process and the mechanical and chemical properties of the solidified gallium are still little known. As known that the solidification of materials is a key factor to know materials' properties, which could be used as phase-change materials and valuable in many research areas, such as energy storage,<sup>[2,27,28]</sup> biomedical engineering,<sup>[10,11]</sup> surface patterning,<sup>[24]</sup> even soft robotics,<sup>[13,14,29]</sup> material science.<sup>[30,31]</sup> Thus, in-depth understanding of the solidification process plays a crucial role in both application of materials and the development of new alloys or composites.

In the present study, it is discovered and confirmed that the solidification process of liquid gallium by using solid gallium as a nucleating agent is fast and facile at room temperature compared with other agent materials including copper, iron, and nickel. The possible mechanism is reducing the energy barrier via adding nucleation site, allowing rapid solidification at room temperature accompanying heat dissipation. And the affecting factors, including contact area of nucleating agent, solidification temperature with nucleating agent, thickness, and surface area of liquid gallium were explored to optimize the solidification conditions. Moreover, micromechanical properties were compared after adding solid Ga as nucleating agent at room temperature and without a nucleating agent. It will give insight into the phase change and also provide guidance for the application of liquid and solidified gallium regarding its mechanical properties.

## 2. Results and Discussion

### 2.1. Solidification with Nucleating Agent

In this study, the solidification of liquid gallium at room temperature was explored. First, to find a more effective solidified

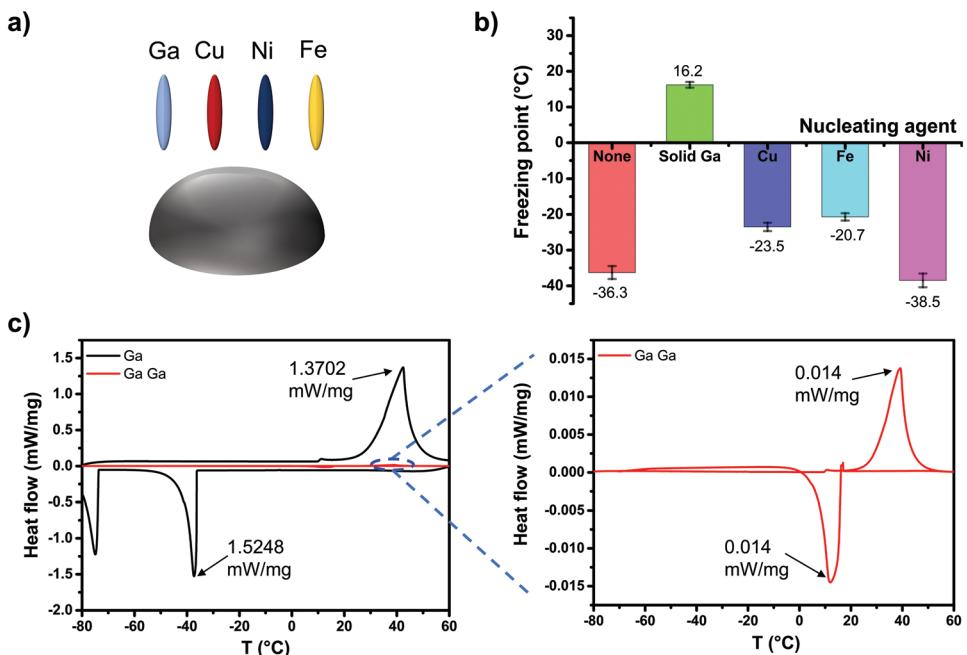
method, we detected the freezing point with Ga/Cu/Ni/Fe as nucleating agents added into liquid gallium. Then, the optimum solidification process conditions at room temperature were concluded, which will provide guidance for the rapid phase transition. Third, the microstructure after solidification was characterized to well understand the mechanism at room temperature with nucleating agent. Furthermore, the mechanical properties of solidified gallium with nucleating agent at room temperature and -20 °C without nucleating agent were analyzed, which is beneficial for providing guidance to the mechanical application of solidified gallium.

Freezing point change with different nucleating agents. To detect the freezing and melting point quantitatively, we used thin lines with a diameter of 300 μm of Ga/Cu/Ni/Fe as nucleating agents (Figure 1a and Figure S1, Supporting Information) during the DSC detecting process. As shown in Figure 1b, it could be seen obviously that solid Ga could improve the freezing point to 16.2 °C. Without nucleating agents, the freezing point is about -36.3 °C. That is to say, the supercooling degree is reduced from about 66.3 to 14.8 °C. The freezing point of gallium with Fe or Cu as nucleating agent is rising to some extent, -20.7 and -23.5 °C, respectively. It is consistent with the result of the previous work.<sup>[22]</sup> On the contrary, Ni could not reduce the supercooling degree. Compared to Cu/Fe/Ni, solid Ga as nucleating agent does show obvious effects. From the DSC curves, we could see that liquid gallium with solid Ga as nucleating agent will need to adsorb or release less energy to melt or freeze (about 0.014 mW mg<sup>-1</sup>) than that of gallium without nucleating agent (1.3702 and 1.5248 mW mg<sup>-1</sup>, respectively), shown in Figure 1c and Figure S2, Supporting Information. This result is consistent with the previous works,<sup>[8,14]</sup> which may be because the addition of nucleating agent provides a nucleation site for solidification and reduces the critical solidification energy barrier. Considering the structure between liquid gallium and nucleating agents, a similar structure with liquid gallium (a = 4.519 Å, b = 7.657 Å, c = 4.526 Å) will be beneficial to promote solidification.<sup>[19,22]</sup> Thus, it could be concluded that solidified Ga could be used as an effective nucleating agent for the solidification of liquid gallium at room temperature.

### 2.2. Solidified Process

As shown in Figure 2a, the solidification photograph could be seen at different times after adding a nucleating agent (Ga) at room temperature. The shaded part is solidified metal. Obviously, with the increase of solidification time, the solidified area increases gradually. As shown in Movie S1, Supporting Information, observed by metallographic microscope, the freezing rate is fast and could reach up to 200 mm<sup>3</sup> min<sup>-1</sup>. As shown in Table 1, we concluded the freezing rate with nucleating agents or extra forces. It could be seen that the solidification process using Ga as nucleating agent is ultrafast without extra forces. Even though the freezing rate is fast through adding extra energy ways, such as impact or electric field, the solidification process could not be carried out easily for mass production and is energy consumption.

To evaluate the heat change during phase transition in gallium, Infrared Thermography (IRT) meter was used. IRT

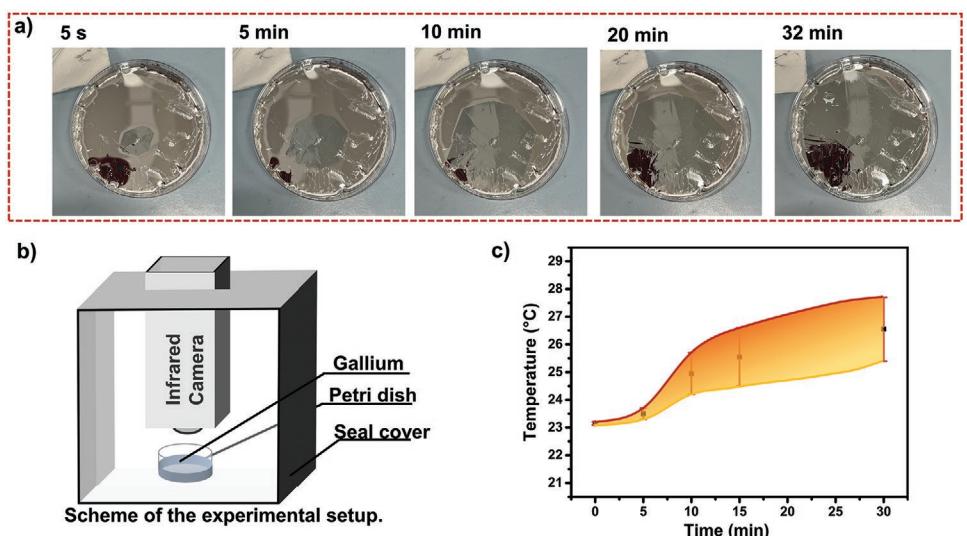


**Figure 1.** a) Schematic diagram of solidification process. b) Freezing point of liquid Ga without nucleating agent (red region) or with nucleating agent (solid Ga/Cu/Fe/Ni, respectively). c) DSC of pure Ga and solid Ga as nucleating agents.

Meter has been reported to be effectively applied for the qualitative detection of phase transitions in metal alloys.<sup>[32]</sup> The schematic diagram is exhibited in Figure 2b. A petri dish with liquid gallium was put into a sealed cover, and an infrared camera was placed above the sample. And the infrared photos could be seen in Figure S3, Supporting Information. Correspondingly, the temperature change was analyzed in Figure 2c. As the solidification progresses, the temperature is rising from about 23 to 26 °C, with the temperature range extended. That is to say, heat is released during solidification of liquid gallium. Moreover, it shows a trend of first fast and then slow,

which may be caused by the delay in heat dissipation during solidification.

In order to better understand the influence factors of solidification, several factors, such as contact area of nucleating agent, solidification temperature with nucleating agent, thickness, and surface area of liquid gallium were explored. On the one hand, the effect of nucleating agent was explored. First, solid gallium nucleating agents in different shapes (Figure S4, Supporting Information) were used to explore the effect of contact area on curing time. From Figure 3a, it could be seen that even with different contact areas under smooth surface, the curing time is



**Figure 2.** a) Photograph of solidification process. b) Schematic diagram of Infrared Thermography (IRT) experiment. c) Temperature change during solidification.

**Table 1.** Comparation of freezing rate with nucleating agent/extra forces.

Nucleating agent	Freezing temperature [°C]	ΔT [°C]	Freezing condition	Freezing rate at near RT	Ref.
-	-36.3	66.1	Cooling	-	This work
$\alpha\text{-TeO}_2$	-8.4	38.2	Cooling	-	[18]
CaO	-14.8	44.6	Cooling	-	[18]
MgO	-23.9	53.7	Cooling	-	[18]
Graphite			Cooling	-	[21]
Silicon			Cooling	-	[21]
- Impact	-10	39.8	Height 0.1–0.8 m	100 mg/29 ms	[13]
-Electric field	25	4.8	5 V	300 $\mu\text{L}/0.5 \text{ min}$	[17]
TiC	-29.7	59.5	Cooling	-	[16]
HfC	13.55	16.25	-	-	[16]
ZrN	15.8	14	-	-	[16]
TaC	1.8	28	-	-	[16]
Cu	-23.5	53.3	Cooling	-	This work
Fe	-20.7	50.5	Cooling	-	This work
Ni	-38.5	68.3	Cooling	-	This work
Ga	16.2	13.6	-	200 $\text{mm}^3 \text{ min}^{-1}$	This work

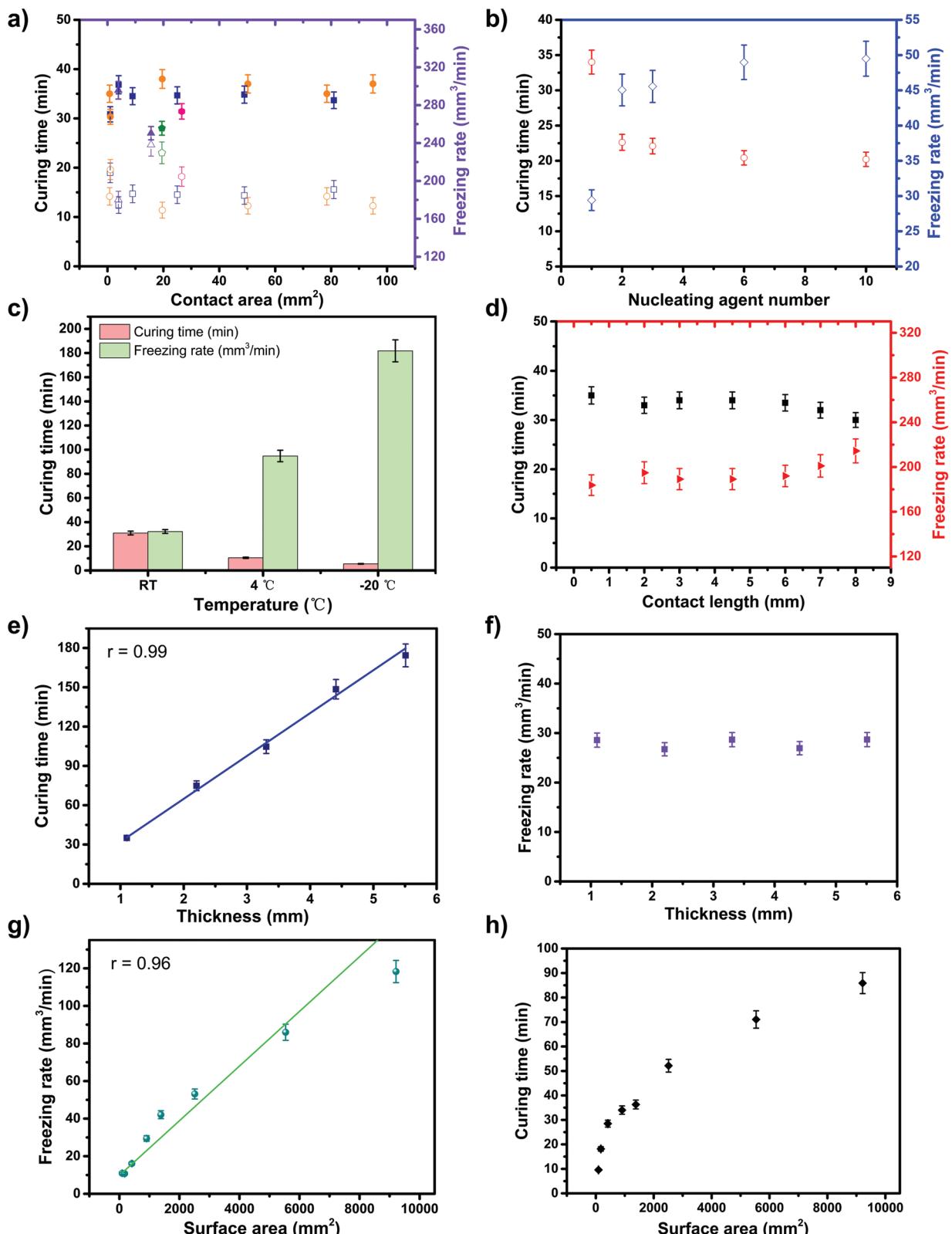
almost the same (around 35 min). It indicates that the contact area of nucleating agent with smooth surface has a negligible effect on solidification. Second, with the increasing nucleating agent number, the curing time is decreasing and freezing rate is rising in  $\text{mm}^3 \text{ min}^{-1}$  (Figure 3b). Moreover, the curing time tends to be stable until the nucleating agent number is more than 3, which maybe because the whole liquid metal needs the lowest energy to achieve liquid-solid conversion<sup>[21]</sup> so that the curing time will not increase when the amount of nucleating agent is more than 3. Thus, it does not need an extra nucleating agent to accelerate the solidification, which is beneficial to save resources in applications. Usually, the effect of temperature could not be neglected. We used solid Ga as a nucleating agent at room temperature, 4 and -20 °C to be the preliminary study. As illustrated in Figure 3c, with the lower temperature, it needs less curing time to solid, which is probably due to the rapid heat dissipation during solidification. Once touched by the nucleating agent, the freezing rate of liquid gallium could reach up to 180  $\text{mm}^3 \text{ min}^{-1}$  at -20 °C with nucleating agent, rather faster than that without nucleating agent (the curing time is 2 h of 1 mL liquid gallium). And from Figure S5 and Table S1, Supporting Information, it could be seen that the elements including Ga/O/C have little change, solidified at room temperature, 4 and -20 °C. Moreover, the contact length was explored. In Figure 3d, the curing time is shortened slightly as the increasing contact length. On the other aspect, the liquid metal needed solidification was researched. Figure 3e,f refers to the curing time and freezing rate at different thicknesses. Obviously, the curing time is linear growing with the thickness increasing, with a relative coefficient  $r = 0.99$  (Figure 3e). The freezing rate ( $\text{mm}^3 \text{ min}^{-1}$ ) has nearly no change (Figure 3f), which shows that the freezing rate is constant, and the solidification time increases with the increase of thickness under constant volume. While the freezing rate ( $\text{mm}^2 \text{ min}^{-1}$ ) is close to linear decreasing (Figure S6, Supporting Information). It

shows that the freezing rate is related to the volume not to the thickness only. Thus, we should use the unit of  $\text{mm}^3 \text{ min}^{-1}$  for freezing rate. Furthermore, under certain thickness, with increasing the surface area of liquid metal, the freezing rate and curing time are almost linear increasing ( $r = 0.96$ ) as shown in Figure 3g,h. The volume increases with the surface area under a certain thickness, so that the curing time grows. That is to say, the solidification is related to the volume and thickness. Therefore, spreading liquid metal out into a thin layer to reduce the thickness and reduce volume could be profitable for rapid solidification.

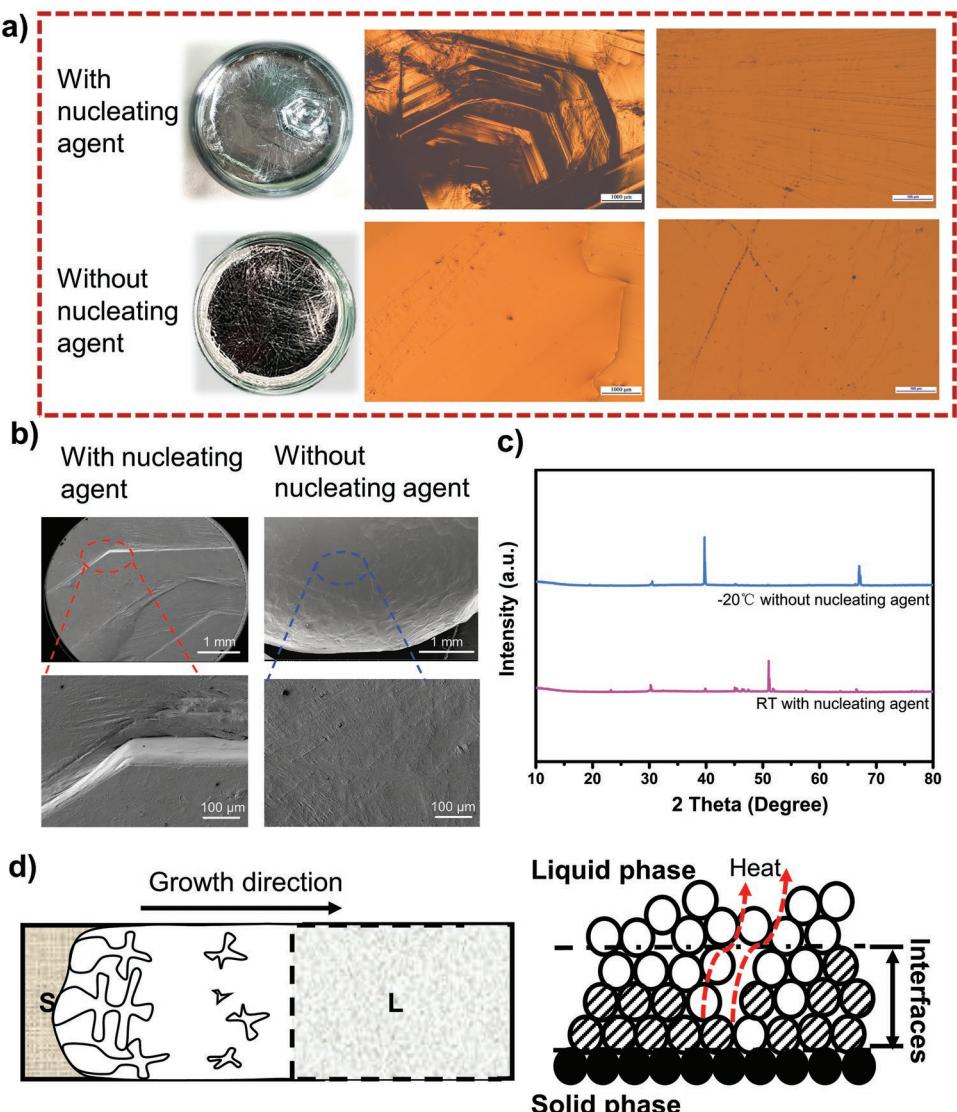
### 2.3. Microstructural Characterization

To explore the mechanism during solidification with or without nucleating agent, we observed the microstructure of the solid gallium. As exhibited in Figure 4a, the crystal was grown via the seeded growth method from the liquid at room temperature. Solidification begins at the place where nucleating agent is added. The contact place is circinate due to the high surface tension and the existence of a surface oxide layer. And it's easy to form layered structures at the beginning as shown at the right of Figure 4a, which is presumably related to heat dissipation is not timely in the rapid solidification. In contrast, without nucleating, the solidified surface of liquid gallium is flat. From the amplifying photographs of metallurgical microscopy, the surface of solid gallium could be observed striate texture, which could be used in nanopatterning, consistent with the previous report.<sup>[33]</sup>

As shown in Figure 4b, the morphology of solid gallium could be seen using a scanning electron microscope (SEM). After adding nucleating agent at room temperature, it is easier to form welding marks than that without nucleating agent at -20 °C. As is known that, the forming of metallic weld marks



**Figure 3.** Relationship of curing time and freezing rate ( $\text{mm}^3 \text{ min}^{-1}$ ) with different a) contact area, b) nucleating agent number, c) temperature, d) contact length, e-h) thickness, and surface area of liquid metal.



**Figure 4.** a) Photographs of solid gallium with or without nucleating agent using camera (left) and metallurgical microscopy (right, with different magnifications). b) SEM morphologies with or without nucleating agent. c) XRD spectrum of solid gallium at different conditions. d) Schematic diagram of solidification mechanism.

during the solidification process is related to the uneven heat dissipation.<sup>[34,35]</sup> Thus, it is speculated that the heat doesn't dissipate timely at room temperature. The heat dissipation is described in IRT detection (Figure 2c). Inspired by this phenomenon, we could add some welding marks to the patterned surface of solid gallium. Meanwhile, it is worth noting that the forming of weld marks will affect the mechanical properties of materials,<sup>[36]</sup> so the place adding nucleating agent should be away from the area to be applied, which should be considered in practical applications. And to avoid forming welding marks during solidification, reducing disturbance and the temperature difference between solid and liquid metals are useful ways. X-ray diffraction (XRD) measurements (Figure 4c) revealed the difference in crystal type between solid gallium with nucleating agent at room temperature and solid gallium without nucleating agent at low temperature. From the

comparison, it could be concluded that the peaks are all related to the structure of  $\alpha$ -Ga, even though the peak intensity is different due to the crystal orientation being different.<sup>[1,37]</sup> In detail, of the seven previously reported polymorphic modifications of gallium only the common orthorhombic form,  $\alpha$ -Ga [or Ga I], is thought to be stable at atmospheric pressure.<sup>[37]</sup>  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\varepsilon$ -Ga are all metastable.<sup>[38,39]</sup> The room temperature crystallized bulk  $\alpha$ -Ga had an orthorhombic crystal structure with space group  $Cmca$  ( $a = 4.519 \text{ \AA}$ ,  $b = 7.657 \text{ \AA}$ ,  $c = 4.526 \text{ \AA}$ ) and contained eight atoms in the conventional unit cell.<sup>[1]</sup> Furthermore,  $\alpha$ -Ga is divided into several different crystal types. The  $2\theta$  scan using Cu K $\alpha$  radiation showed strong peaks of (020), (040), and (060) preferred orientation from the (010) family.<sup>[1]</sup> Thus, solid gallium with different crystal orientation structures will affect the properties so that has a lot of potential in different applications.

From all of the above findings, it could be concluded that solid gallium itself is an effective nucleating agent at room temperature. It is known that solidification is related to Gibbs free energy.<sup>[19]</sup> Usually, solidification process occurs in two steps, including nucleation and growth. It should overcome the energy barrier to nucleation. According to the classical theory of nucleation, the critical energy for the heterogeneous nucleation of gallium can be calculated as follows:<sup>[20,22]</sup>

$$\Delta G_c = \frac{16\pi\gamma_{LC}^3 T_m^2}{3\rho_s^2 \Delta H^2 (T_m - T_s)^2} \left( \frac{2 - \cos\theta + \cos^2\theta}{4} \right) \quad (1)$$

where  $\gamma_{LC}$  (56 mJ m<sup>-2</sup>) is the interface energy between crystal and liquid gallium.  $\Delta H$  (80 161 J Kg<sup>-1</sup>) is the fusion enthalpy of gallium.  $\rho_s$  ( $5.9 \times 10^3$  Kg m<sup>-3</sup>) is the density of solid gallium.  $T_m$  (29.8 °C) is the melting point of gallium.  $T_s$  is the solidified point. Calculated  $\Delta G_c$  is related to the contact angle  $\theta$ . It could be concluded that the nucleating agent with a smaller angle requires less energy for nucleating and is more likely to solidify at a relatively smaller degree of supercooling. Thus, it is easier to solidify using solid gallium as a nucleating agent.

Therefore, about the mechanism of solidification (Figure 4d), it is speculated that, on the one hand, adding a nucleating agent especially more similar to the solidified metal itself, gallium, is more beneficial to solidification through reducing the Gibbs free energy, which is consistent to the result of the previous researches.<sup>[19,20,22]</sup> On the other hand, decreasing of temperature in ambient atmosphere will promote solidification, which could speed up heat dissipation. For the observation of grain of solidified gallium, it will be further explored in the follow-up research.

#### 2.4. Micromechanical Properties

As is known that the micromechanical properties are related to the solidification process.<sup>[40,41]</sup> Therefore, we detected the micromechanical properties of solid gallium at different conditions.

First, hardness is one of the key factors to know material mechanical properties. The samples are indented with a diamond pyramid of 136° and its microhardness value is calculated as follows,

$$\begin{aligned} HV &= \text{experimental force}/\text{indentation surface area} \\ &= F(\text{kgf})/A(\text{mm}^2) = 0.102F(\text{N})/A(\text{mm}^2) \quad (2) \\ &= 0.102 \times 2F \sin(136^\circ/2)/d^2 = 0.1891 \times F/d^2 \end{aligned}$$

where: HV-Vickers hardness, MPa;  $F$ —experimental force, N;  $d$ —The arithmetic mean value of the two diagonal lengths of indentation, mm.

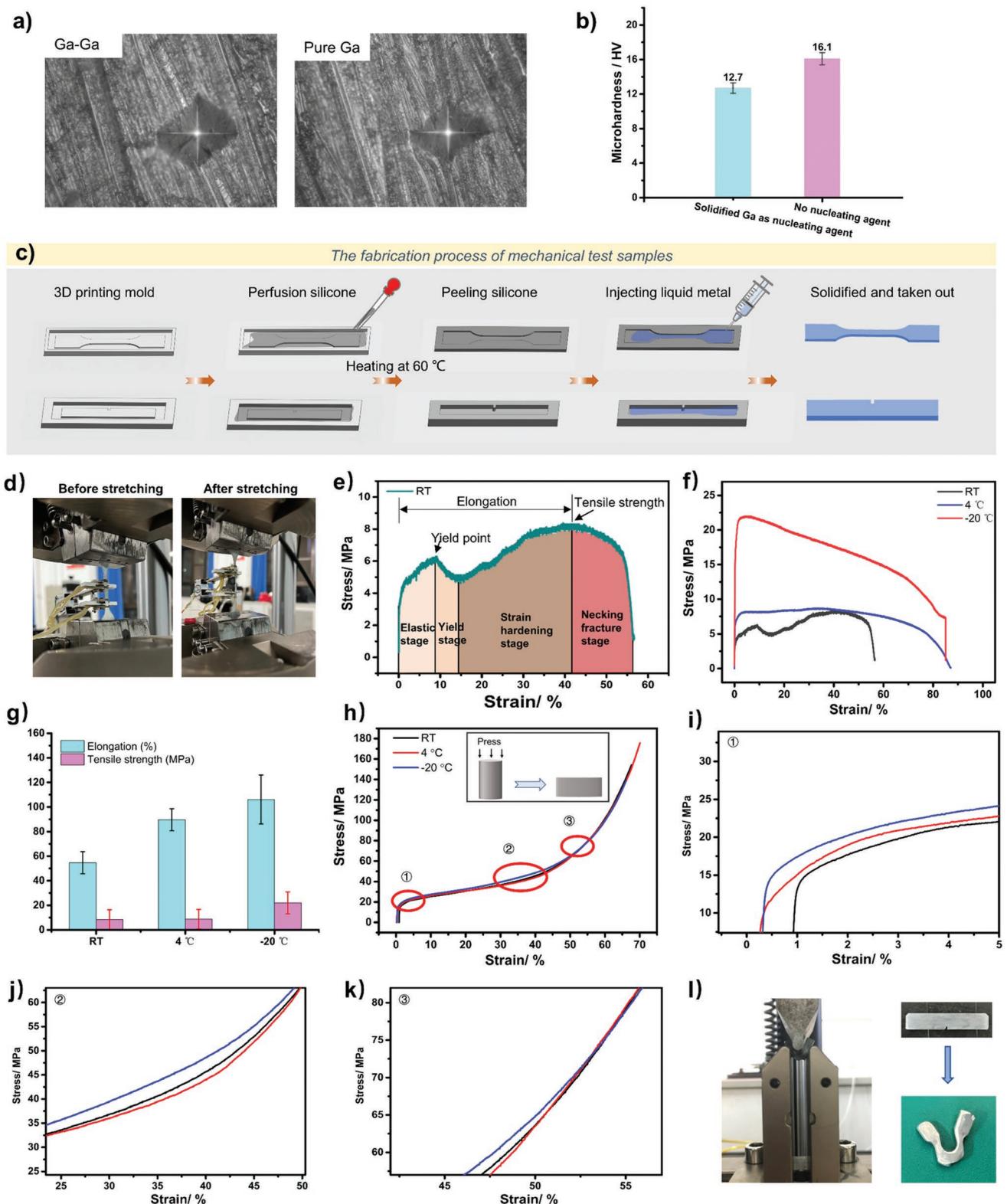
As shown in Figure 5a,b, it could be seen that the microhardness value of solidified at room temperature with nucleating agent (12.7) is lower than that of solidified at low temperature (-20 °C) without nucleating agent (16.1), which is consistent to the microstructure of solidified gallium. From this concept, the microhardness is slightly reduced, which is specifically good for application in flexible devices and causes minor damage to

human body tissues used in biomedical engineering. Moreover, it will not affect the detection if it is used as a wearable sensor as the solid gallium will be melted to liquid at body surface temperature.

The mechanical test samples were fabricated through five traditional steps, including 3D printing mold, perfusion silicone, peeling silicone, injecting liquid metal, solidifying, and taking out (Figure 5c). The size and photograph of samples could be seen in Figure S7, Supporting Information. The test before and after stretching could be seen in Figure 5d. And the stress-strain curve is shown in Figure 5e. Obviously, solidified gallium at room temperature shows four stages during stretching, including a significant necking fracture phenomenon, which indicates that it exhibits plastic characteristics. Compared with gallium solidified at -20 °C without nucleating agent, gallium solidified at room temperature or at 4 °C with nucleating agent owns lower elongation (55%, 80%) and tensile strength (8.38 MPa, 8.7 MPa). The elongation of gallium solidified at -20 °C without nucleating agent could reach up to 110%, and tensile strength could reach to 22 MPa (Figure 5f,g). That is to say, the elastic modulus and tensile strength decrease slightly after the addition of nucleating agent. To explore the reason for the difference, we characterized the fracture surface of solid gallium. As illustrated in Figure S8, Supporting Information, the stretch mark in SEM could be observed intuitively. The increasingly heavy stretch mark on gallium solidified at -20 °C without nucleating agent indicates that the atoms are tighter so that it is more difficult to be stretched. This result is consistent with the above tensile data. This difference in mechanical properties will provide guidance for the flexible application of solidified gallium. Furthermore, to know more about the mechanical properties, the compression experiments were executed. The schematic diagram is shown in Figure 5h. Based on the stress-strain curve, before yielding, the curves during compression and tensile basically coincide. After yielding, with the increase of pressure, the sample is pressed into a drum shape and finally pressed into wafer without fracture, so there is no strength limit for solid gallium compression, which could be concluded that solid gallium is a plastic material, which owns certain plastic deformation ability.<sup>[42]</sup> Figure 5i-k are enlarged figures in stress-strain curve. At yield point, it could be seen that gallium solidified at -20 °C without nucleating agent has lower strain under certain stress, which is consistent with the previous research on the other phase change materials.<sup>[43]</sup> It is presumed that this mainly may be because the microstructure is larger solidified at room temperature. Moreover, fracture toughness is measured using notched solidified samples. The result shows that the gallium could not be fractured within the range of the instrument, indicating its excellent toughness (Figure 5l). However, it shows big brightness when gets dropped, and the fracture surface is very neat (Figure S7d, Supporting Information), which could be further studied in future related applications.

#### 3. Conclusion

In summary, a facile and fast solidification method of liquid gallium at room temperature is provided and confirmed.



**Figure 5.** Micromechanical properties of solid gallium. a) Hardness photograph and b) microhardness values with solid Ga as nucleating agent or without nucleating agent (Ga–Ga, Pure Ga, respectively). c) Fabrication process of mechanical test samples. d) Photos before and after stretching. e) Stress-strain curve of gallium solidified with nucleating agent at room temperature in stretching. f) Tensile stress-strain curve of gallium solidified at RT, 4 and -20 °C. g) Elongation and tensile strength of gallium solidified at RT, 4 and -20 °C. h) Compression stress-strain curve of gallium solidified at RT, 4 and -20 °C. i-k) Enlarged curves at different stress. l) Photos of fracture toughness test.

Compared to other nucleating agents (solid Cu/Fe/Ni), it is verified that solid Ga itself is an effective nucleating agent for the solidification of liquid gallium at room temperature, improving the freezing point from  $-36.3$  to  $16.2$  °C. That is to say, the supercooling degree is reduced from about  $66.3$  to  $14.8$  °C. The velocity could reach to  $200$  mm $^3$  min $^{-1}$ . And the affecting factors, including contact area of nucleating agent, solidification temperature with nucleating agent, thickness, and surface area of liquid gallium were explored. It is concluded that adding the amount of nucleating agent to no more than 3, and reducing the thickness could be profitable for rapid solidification. Furthermore, the possible mechanism is reducing the energy barrier via adding nucleation site, allowing rapid solidification at room temperature accompanying heat dissipation. Moreover, micromechanical properties were compared by adding solid Ga as nucleating agent at room temperature and without nucleating agent, which has a slight decrease at room temperature with nucleating agent. Inspired by the mechanism of solidification, more research related to liquid metal including simulation and the application of the phase-change LM, should be explored in the future. This work will be helpful to understand the solidification of liquid gallium at room temperature, and promote the application of solid gallium in 3D printing, phase-change flexible electrodes, nanopatterning, personalized consumption, and other fields.

## 4. Experimental Section

**Materials and Methods:** Liquid gallium with purity of 99.99% was purchased from Chalco Zunyi Alumina Company Limited. The raw material was added into a beaker and heated to 60 °C. A magnetic stirrer was used to stir the mixture uniformly after the metals had all melted. The liquid gallium was used in the subsequent experiments. Fe/Cu/Ni was purchased from Science Lab Store with a size of 300  $\mu$ m. Solidified Ga nucleating agent was prepared at room temperature. Deionized water (Milli-Q System, Millipore, USA) was used in all experiments.

**Characterization Methods:** Differential scanning calorimeter (DSC, Mettler DSC III) was used to measure the freezing and melting temperature points of pure gallium and gallium with a nucleating agent. The samples were scanned in the temperature range from  $-80$  to  $60$  °C, with a scanning rate of 10 °C min $^{-1}$ . The morphology and elemental analysis of prepared liquid metal samples were examined using a field-emission SEM (ZEISS Ultra 55) operated at an accelerating voltage of 10 kV and an Energy Dispersive Spectrometer (EDS). And to observe the morphology information on solidified gallium, SEM in backscatter mode (BSED) was used. Metallurgical microscopy (Nikon DS-Ri2) was used to characterize the microstructure of the samples after polishing and etching by a solution of 10 mL HF-10 mL HNO $_3$ -180 mL H $_2$ O. The structure and crystallinity of the solidified liquid metal were examined by XRD (-7000, Tokyo, Japan) with Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm, 40 KV, 200 mA). The samples were scanned over a  $2\theta$  range of  $10^\circ$ - $80^\circ$  with a step size of  $0.02^\circ$  and a count time of  $6^\circ$  per minute. IRT Meter (FOTRIC 224s) was applied to detect the temperature change during solidification after adding nucleating agent at room temperature. Non-contact 3D optical profilometer (KLA Tencor-MicroXAM-800, USA) was used to detect the surface roughness of nucleating agent.

**Micromechanical Detection:** Microhardness tester (FM-7000A, Japan) was carried out to detect the hardness of solidified Ga with loading 10 g for 20 s and with a loading speed of 50  $\mu$ m s $^{-1}$ . The cylinder samples with diameter (d) 8 mm and height (h) 13 mm (d: h =  $\approx$ 1-2) were prepared after solidification at  $-20$  °C and at room temperature. To compare the change of mechanical properties with and without nucleating agent, Instron universal testing machine (Instron 5565, 1 KN) was used during

the compression and stretching process. The stretching and fracturing samples were designed and prepared as GB/T 228.1-2010. The values of each parameter were the average values of the measurement results.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

## Keywords

gallium, liquid metal, micromechanical property, nucleating agent, solidification

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- [1] M. Yunusa, A. Lahou, M. Sitti, *Adv. Mater.* **2020**, *32*, 1907453.
- [2] H. Ge, J. Liu, *J. Heat Transfer* **2013**, *135*, 054503.
- [3] S.-H. Byun, J. Y. Sim, Z. Zhou, J. Lee, R. Qazi, M. C. Walicki, K. E. Parker, M. P. Haney, S. H. Choi, A. Shon, G. B. Gereau, J. Bilbily, S. Li, Y. Liu, W.-H. Yeo, J. G. McCall, J. Xiao, J.-W. Jeong, *Sci. Adv.* **2019**, *5*, 0418.
- [4] U. Daalkhaij, O. D. Yirmibesoglu, S. Walker, Y. Mengüç, *Adv. Mater. Technol.* **2018**, *3*, 1700351.
- [5] X. Wang, H. Wang, K. Sun, W. Li, X. Wang, X. Chen, L. Hu, Y. Fan, *Appl. Mater. Today* **2022**, *26*, 101265.
- [6] X. Zhang, Q. Wang, R. Zou, B. Song, C. Yan, Y. Shi, B. Su, *Engineering* **2022**, *15*, 196.
- [7] Z. Ma, Q. Wang, Z. Wu, D. Chen, C. Yan, Y. Shi, M. D. Dickey, B. Su, *Adv. Mater.* **2022**, *34*, 2203814.
- [8] X. Wang, X. Liu, P. Bi, Y. Zhang, L. Li, J. Guo, Y. Zhang, X. Niu, Y. Wang, L. Hu, Y. Fan, *ACS Appl. Mater. Interfaces* **2020**, *12*, 53966.
- [9] X. Wang, L. Li, X. Yang, H. Wang, J. Guo, Y. Wang, X. Chen, L. Hu, *Adv. Mater. Technol.* **2021**, *6*, 2100228.
- [10] X. Sun, B. Cui, B. Yuan, X. Wang, L. Fan, D. Yu, Z. He, L. Sheng, J. Liu, J. Lu, *Adv. Funct. Mater.* **2020**, *30*, 2003359.
- [11] L. Yi, C. Jin, L. Wang, J. Liu, *Biomaterials* **2014**, *35*, 9789.
- [12] Y. Lu, Q. Hu, Y. Lin, D. B. Pacardo, C. Wang, W. Sun, F. S. Ligler, M. D. Dickey, Z. Gu, *Nat. Commun.* **2015**, *6*, 10066.
- [13] Z. Ye, G. Z. Lum, S. Song, S. Rich, M. Sitti, *Adv. Mater.* **2016**, *28*, 5088.

- [14] H. Wang, S. Chen, H. Li, X. Chen, J. Cheng, Y. Shao, C. Zhang, J. Zhang, L. Fan, H. Chang, R. Guo, X. Wang, N. Li, L. Hu, Y. Wei, J. Liu, *Adv. Funct. Mater.* **2021**, *31*, 2100274.
- [15] H. Wang, Y. Yao, Z. He, W. Rao, L. Hu, S. Chen, J. Lin, J. Gao, P. Zhang, X. Sun, X. Wang, Y. Cui, Q. Wang, S. Dong, G. Chen, J. Liu, *Adv. Mater.* **2019**, *31*, 1901337.
- [16] S.-H. Byun, J. Y. Sim, Z. Zhou, J. Lee, R. Qazi, M. C. Walicki, K. E. Parker, M. P. Haney, S. H. Choi, A. Shon, G. B. Gereau, J. Bilbily, S. Li, Y. Liu, W.-H. Yeo, J. G. McCall, J. Xiao, J.-W. Jeong, *Sci. Adv.* **2019**, *5*, eaay0418.
- [17] Y. Hao, J. Gao, Y. Lv, J. Liu, *Adv. Funct. Mater.* **2022**, *32*, 2201942.
- [18] D. Turnbull, *J. Appl. Phys.* **1950**, *21*, 1022.
- [19] S. Chakravarty, D. J. Sharar, P. J. Shamberger, *J. Appl. Phys.* **2021**, *130*, 125107.
- [20] C. Zhang, L. Li, Z. Li, H. Chang, J. Liu, *Int. J. Heat Mass Transfer* **2022**, *183*, 122142.
- [21] Y. Xin, T. Gao, J. Xu, J. Zhang, D. Wu, *ACS Appl. Mater. Interfaces* **2021**, *13*, 50392.
- [22] C. Zhang, L. Li, X. Yang, J. Shi, L. Gui, J. Liu, *Int. J. Heat Mass Transfer* **2020**, *148*, 119055.
- [23] S. A. Kozlov, N. A. Potolokov, A. V. Gusev, V. A. Fedorov, *Inorg. Mater.* **2003**, *39*, 1267.
- [24] J. Tang, S. Lambie, N. Meftahi, A. J. Christofferson, J. Yang, M. B. Ghasemian, J. Han, F.-M. Allioux, M. A. Rahim, M. Mayyas, T. Daeneke, C. F. McConville, K. G. Steenbergen, R. B. Kaner, S. P. Russo, N. Gaston, K. Kalantar-Zadeh, *Nat. Nanotechnol.* **2021**, *16*, 431.
- [25] Z. W. Yu, Y. C. Chen, F. F. Yun, X. L. Wang, *Adv. Eng. Mater.* **2017**, *19*, 1700190.
- [26] K. Pan, Y. Li, Q. Zhao, S. Zhang, *JOM* **2018**, *71*, 737.
- [27] W. Fu, X. Yan, Y. Gurumukhi, V. S. Garimella, W. P. King, N. Miljkovic, *Nat. Energy* **2022**, *7*, 270.
- [28] J. Luo, D. Zou, Y. Wang, S. Wang, L. Huang, *Chem. Eng. J.* **2022**, *430*, 132741.
- [29] F. Long, Y. Cheng, Y. Ren, J. Wang, Z. Li, A. Sun, G. Xu, *Adv. Eng. Mater.* **2021**, *24*, 2100863.
- [30] T. Kawasaki, H. Tanaka, *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 14036.
- [31] G. Bai, D. Gao, Z. Liu, X. Zhou, J. Wang, *Nature* **2019**, *576*, 437.
- [32] C. Mailhé, A. Godin, A. Veillère, M. Duquesne, *Appl. Sci.* **2021**, *11*, 8885.
- [33] J. Tang, S. Lambie, N. Meftahi, A. J. Christofferson, J. Yang, J. Han, M. A. Rahim, M. Mayyas, M. B. Ghasemian, F.-M. Allioux, Z. Cao, T. Daeneke, C. F. McConville, K. G. Steenbergen, R. B. Kaner, S. P. Russo, N. Gaston, K. Kalantar-Zadeh, *Anti-Cancer Drugs: Nat., Synth. Cell* **2022**, *1*, 158.
- [34] G. Wang, G. Zhao, X. Wang, *Mater. Des.* **2013**, *44*, 509.
- [35] G. Wang, G. Zhao, X. Wang, *Int. J. Adv. Manuf. Technol.* **2013**, *68*, 1293.
- [36] X. K. Wang, Y. Mei, X. C. Wang, L. Q. Yang, *Adv. Mater. Res.* **2013**, *706–708*, 1606.
- [37] R. D. Heyding, W. Keeney, S. L. Segel, *J. Phys. Chem. Solids* **1973**, *34*, 133.
- [38] J. Fu, C. Zhang, T. Liu, J. Liu, *Front. Energy* **2019**, *14*, 81.
- [39] H. Niu, L. Bonati, P. M. Piaggi, M. Parrinello, *Nat. Commun.* **2020**, *11*, 2654.
- [40] M. Mahmoudi Ghaznavi, A. Ekrami, A. H. Kokabi, *Sci. Technol. Weld. Joining* **2013**, *16*, 174.
- [41] E. Guo, S. S. Singh, C. Mayer, X. Meng, Y. Xu, L. Luo, M. Wang, N. Chawla, *J. Alloys Compd.* **2017**, *704*, 89.
- [42] V. Lahtela, S. Silwal, T. Karki, *Polymers* **2020**, *12*, 2517.
- [43] Y.-W. Kim, *J. Mater. Sci. Technol.* **2008**, *24*, 838.