nature portfolio

Peer Review File

Pressure-constrained Sonication Activation of Flexible Printed Metal Circuit

Editorial Note: This manuscript has been previously reviewed at another journal. This document only contains reviewer comments and rebuttal letters for versions considered at Nature Communications.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

This paper proposed pressure-constrained sonication activation (PCSA) as a method by which flexible highly conductive electrodes based on metal particle ink can be made in a short period of time. Vibration of metal particles from the applied sonic wave helps interaction among the particles, reducing gaps in between and rearranging the particles, resulting in solid metal patterns. Although there are previous researches on pressure and/or sonication methods for high-quality metal film formation (hot-pressing and sonication for Ag nano particles: J. Phys. Chem. C 121, 28515 (2017); plasma treatment sintering of Cu ink: Adv. Mater. Tchnol. 8, 2300332 (2023); sonication of liquid metal composite: Science 378, 637 (2022)), authors well demonstrated their method for various metal particles and CNT, Graphene, PEDOT:PSS on various substrates. Authors emphasized that PCSA is good for flexible electrodes, but there are lack of information supporting mechanical properties of the fabricated electrodes. Top images of the electrodes show dense structure but cross section view (Fig. 1b) and Fig. 2i show that there are pores inside the electrodes. Therefore, bending cycle test and other flexibility test must be provided. The reviewer thinks that the paper can be published only after the bending cycle and flexibility supporting test including the following issues are fully addressed.

1. In paper, the purpose and mechanism of 1 wt% PVA introduced in the metal particle inks are well explained. Can other polymers play the same role? If conductive polymers are used, the conductivity of the electrodes can be further improved?

2. PCSA uses pressure and sonication, whose conditions will vary for properties of each material, such as hardness, melting point, etc. If authors can provide optimal conditions of pressure and sonication, provide trends in changing conditions, and explain why various conditions must be used, for each material, that would be very helpful for researchers. Authors just provided the change of conductivity before and after PCSA for each material.

3. Authors explain the principle of PCSA via heat softening and vibration bonding and well demonstrate the heat softening effect with an experiment for BiInSnZn with a low-melting-point (60 degree). The same explanation and demonstration work for high-melting-point materials? From the Supplementary, the temperature of Cu surface right after the PCSA process increases up to maximum 110 degree, but it is way lower than the copper-melting point of 1100 degree (Fig. 13). Conductivity and activation conditions of BiInSnZn were done for various temperature. The same data must be provided for Cu for better understanding by the researchers.

4. As mentioned before, mechanical performances and reliability of the fabricated electrodes must be provided.

5. In paper, PCSA can be used for bonding electronic devices on electrodes or contact pads. Can adhesion forces be measured and can resulting data can be provided in this case?

6. Since sonic wave is applied from one side of the electrodes in the thickness direction like other sintering methods of photonic, thermal sintering, the effectiveness of the method can be easily changed by the initial thickness of the particle patterns. Thicker particle patterns (like multiple printing of particle inks) can be also activated by the one-side PCSA method? Is there any limitation in pattern thickness for full activation by PCSA?

Pressure-constrained Sonication Activation of Flexible Printed Metal Circuit
NCOMMS-24-41008-T
Reply to Reviewers' Comments

By Lingxiao Cao[†], Zhonghao Wang[†], Daiwei Hu, Haoxuan Dong, Chunchun Qu, Yi Zheng, Chao Yang, Rui Zhang, ChunXiao Xing, Zhen Li, Zhe Xin, Du Chen, Zhenghe Song, Zhizhu He[*]

Response to Reviewer 1:

Summary comment: This paper proposed pressure-constrained sonication activation (PCSA) as a method by which flexible highly conductive electrodes based on metal particle ink can be made in a short period of time. Vibration of metal particles from the applied sonic wave helps interaction among the particles, reducing gaps in between and rearranging the particles, resulting in solid metal patterns. Although there are previous researches on pressure and/or sonication methods for high-quality metal film formation (hot-pressing and sonication for Ag nano particles: J. Phys. Chem. C 121, 28515 (2017); plasma treatment sintering of Cu ink: Adv. Mater. Tchnol. 8, 2300332 (2023); sonication of liquid metal composite: Science 378, 637 (2022)), authors well demonstrated their method for various metal particles and CNT, Graphene, PEDOT:PSS on various substrates. Authors emphasized that PCSA is good for flexible electrodes, but there are lack of information supporting mechanical properties of the fabricated electrodes. Top images of the electrodes show dense structure but cross section view (Fig. 1b) and Fig. 2i show that there are pores inside the electrodes. Therefore, bending cycle test and other flexibility test must be provided. The reviewer thinks that the paper can be published only after the bending cycle and flexibility supporting test including the following issues are fully addressed.

Response: The reviewer's effort in evaluating our work, highly positive comments, and great help in improving the manuscript are sincerely appreciated. We have conducted new experiments to address your concerns. Specifically, the bending and twisting cycle tests have been included in the revised manuscript. We have also added the references (J. Phys. Chem. C 121, 28515 (2017), Adv. Mater. Tchnol. 8, 2300332 (2023), Science 378, 637 (2022)) in the introduction. Compared with the existing posttreatment methods, our PCSA method can enable the printed flexible circuits for more than dozens of metal inks (covering melting points from room temperature to 3422°C), even for nonmetal inks, which can be integrated with the roll-to-roll process for large-scale production.

Comment 1: In paper, the purpose and mechanism of 1 wt% PVA introduced in the metal particle inks are well explained. Can other polymers play the same role? If conductive polymers are used, the conductivity of the electrodes can be further improved?

Response: Thanks for this comment. The choice of polymer is primarily determined by the following two factors: 1) the polymer has a surfactant function, which facilitates uniform dispersion of the nanoparticles in the solution; 2) the polymer exhibits a low elastic modulus and is capable of adhering the particles to each other. For the water-based nano/micro-particle ink, the polymers of PVP and PU can also play the same role. However, the conductive polymers (such as PANI, Ppy and PTs) cannot enable uniform dispersion of the nanoparticles in the solution.

Comment 2: PCSA uses pressure and sonication, whose conditions will vary for properties of each material, such as hardness, melting point, etc. If authors can provide optimal conditions of pressure and sonication, provide trends in changing conditions, and explain why various conditions must be used, for each material, that would be very helpful for researchers. Authors just provided the change of conductivity before and after PCSA for each material.

Response: Thanks for this comment. The particle interaction during the PCSA process is strongly dependent on the operating parameters of constrained pressure (Ps), action time (ta), and sonication power density (Sp), which determine the electrical conduction of the printed pattern. In the revised manuscript, we have added the optimal conditions of pressure and sonication for different materials, as shown in Table R1 (also see Table 3 in Supplementary Materials).

Table R1. Optimal conditions of pressure and sonication for different materials

	Ga, In, Sn, Bi, Zn, Mg, Al, Ag (<1000°C)	Cu, Ni, Co, Fe, Ti, Pt, V (1000~2000°C)	Nb, Mo, Ta, Re, W (>2000°C)
P_s	0~0.4 MPa	0.3~0.5 MPa	~0.5 MPa
t_a	0.05~0.5 s	0.1~0.8 s	0.6~1 s
Sp	1~32 W/cm^2	8~32 W/cm^2	~32 W/cm^2

For the metal with a high melting temperature, its large hardness would weak plastic

deformation induced by heat softening during the PCSA process. Thus, the constrained pressure, action time, and sonication power density must be increased to improve the activated electrical conductivity.

As shown in **Fig.R1**(also see Fig. 16 in Supplementary Materials), the less hardness of metal particles could lead to higher activated electrical conductivities by the PCSA method with low constrained pressure. Increasing the constrained pressure for the high-temperature refractory metal could significantly improve the electrical conductivities while inducing heat damage to the flexible substrates. The higher melting temperature of metal particles results in higher hardness, which leads to heat softening-induced plastic deformation occurring at a higher temperature. However, the low-constrained pressure (<0.5MPa) is adopted here for flexible substrates to suppress the generation of high temperatures.

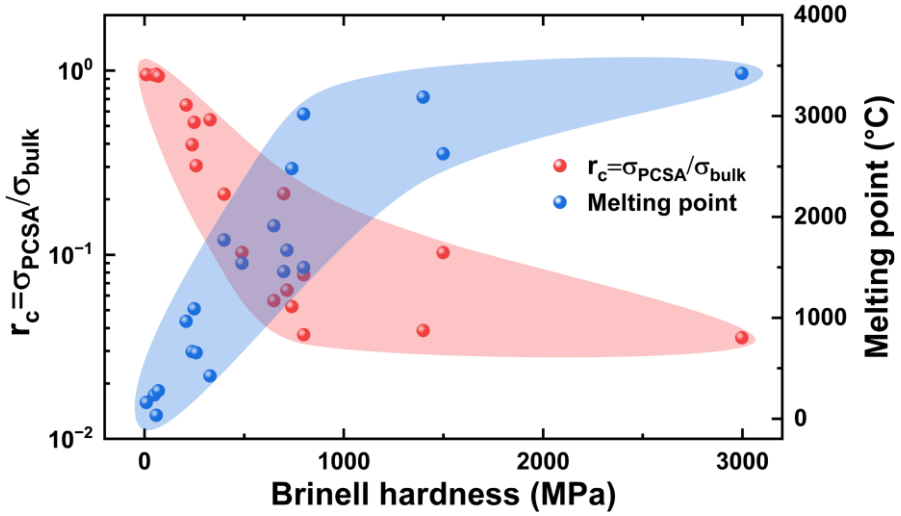

Fig.R1| Impacts of metal hardness on the activation performance of the PCSA processing.

As shown in **Fig. R2** (also see Fig. 17 in Supplementary Materials), the simulations have demonstrated that the metal of W (Young's Modulus: 411 GPa, T_m=3422 ºC) needs a larger pressure to break its oxide compared to the softened metals of BiInSnZn (Young's Modulus: 12 GPa, T_m=60 ºC) and Cu (Young's Modulus: 110 GPa, T_m=1084.8 ºC). The different pressing forces of of 9.8 μN, 161 μN, and 967 μN are needed to fully break oxide layers for BiInSnZn, Cu, and W, which indicates that the smaller the Young's modulus of the metal, the oxide layer on the surface of the metal particles is to be destroyed under smaller pressure.

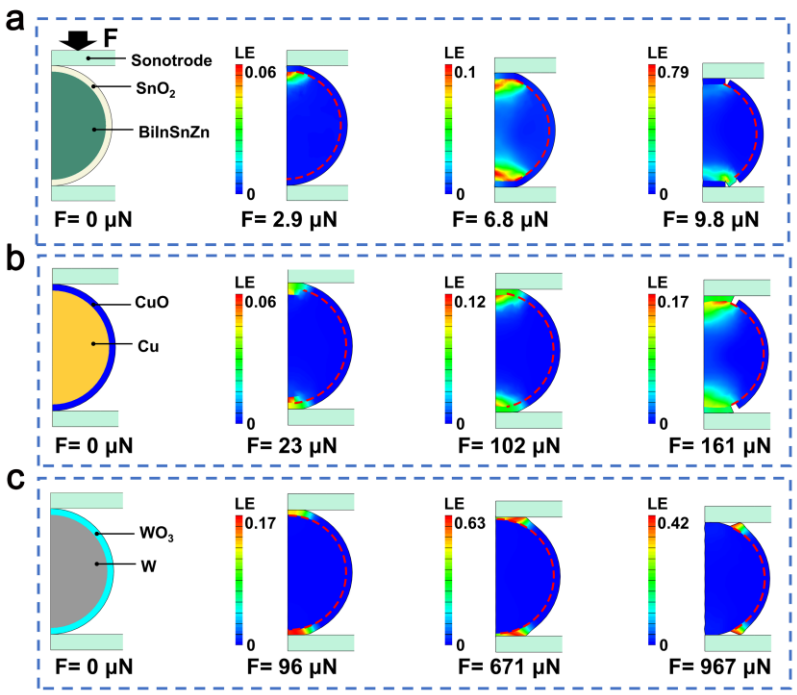

Fig. R2| Impacts of the mechanical properties on the particle deformation. a, BiInSnZn (Young's Modulus: 12 GPa, T_m=60 °C). **b**, Cu (Young's Modulus: 110 GPa, T_m=1084.8°C). **c**, W (Young's Modulus: 411 GPa, T_m=3422 °C).

Comment 3: Authors explain the principle of PCSA via heat softening and vibration bonding and well demonstrate the heat softening effect with an experiment for BiInSnZn with a low-melting-point (60 degree). The same explanation and demonstration work for high-melting-point materials? From the Supplementary, the temperature of Cu surface right after the PCSA process increases up to maximum 110 degree, but it is way lower than the copper-melting point of 1100 degree (Fig. 13). Conductivity and activation conditions of BiInSnZn were done for various temperature. The same data must be provided for Cu for better understanding by the researchers.

Response: Thanks for this comment. In the revised manuscript, we have added the conductivity and activation conditions of Cu, as shown in Fig.R3 (also see Fig. 15 in Supplementary Materials). The results indicate that increasing constrained pressure (Ps), action time (ta) and sonication power density (Sp) can enhance the electrical conductivity of the printed Cu-particle electrodes. It is challenging to directly record the friction-produced temperature at the particle interface during the PCSA process. As an alternative, we conducted the simulation to estimate interface temperature. As shown in Fig.R4 (also see Fig. 12 in Supplementary Materials), the friction-produced hot-spot temperature can reach 340°C for the Cu particles, which can induce the local dramatic

heat-softening effects to accelerate plastic deformation and trigger the atomic diffusion to bonding. Notably, the printed electrode's apparent surface temperature (maximum 110 ºC, as shown in Fig. 14 in Supplementary Materials) is measured to characterize sonication-induced frictional heating indirectly, which is significantly lower than the temperature at the particle interface.

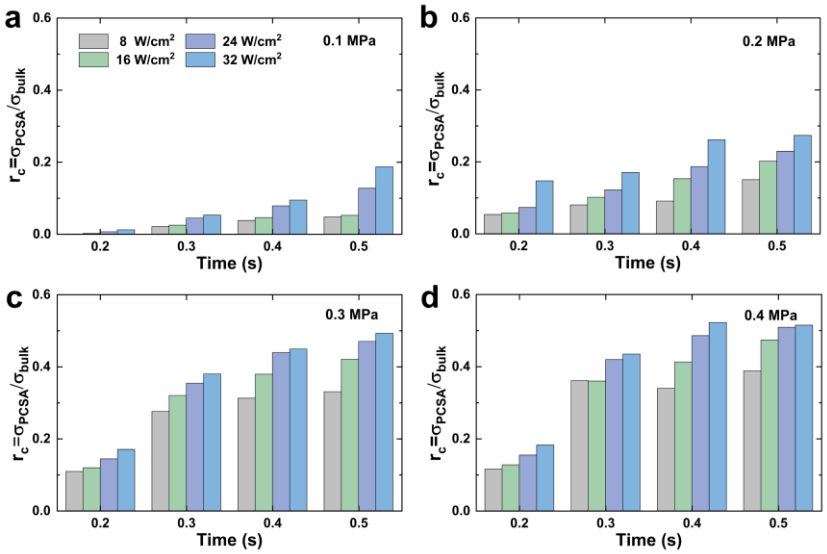

Fig.R3| The conductivity of the printed Cu-particle electrodes activated by PCSA under different operating parameters of constrained pressure, action time, and sonication power density.

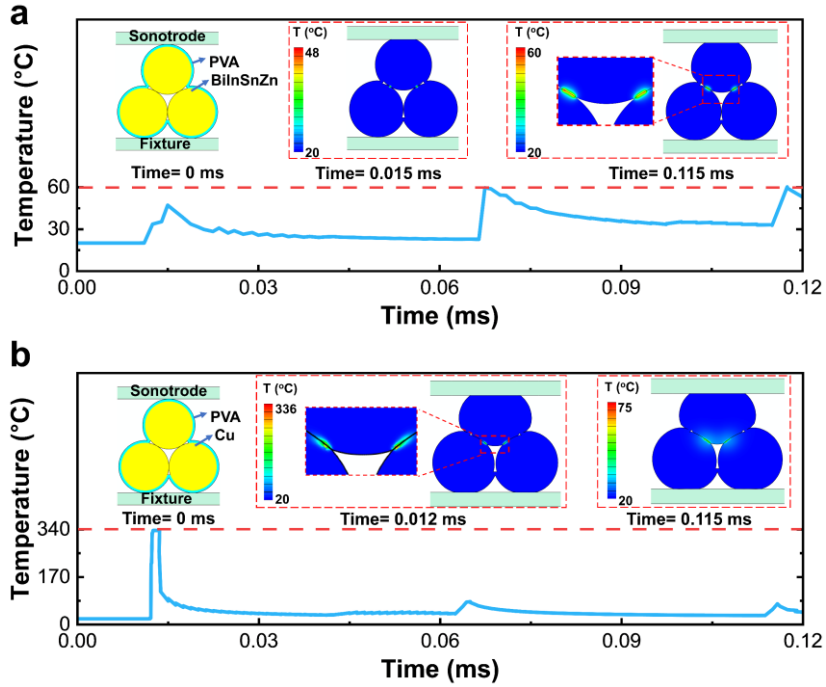

Fig.R4| Simulation results of peak temperature induced by particle interface friction. **a**, Peak temperature at the BiInSnZn particle interface with an amplitude of 0.05 μm vibration within three vibration cycles. **b**, Peak temperature at the Cu particle interface with an amplitude of 0.3 μm within three vibration cycles.

Comment 4: As mentioned before, mechanical performances and reliability of the fabricated electrodes must be provided.

Response: Thanks for this comment. In the revised manuscript, we have added the mechanical performances and reliability of the fabricated electrodes, as shown in Fig.R5 (also see Fig. 19 in Supplementary Materials). The results indicate that the electrical resistance of the printed electrode has less change under the conditions of the small bending radius of 2mm and large twisting angle of 180°. The printed electrode exhibits excellent mechanical flexibility, which is attributed to the strong bonding between the electrode and the flexible substrate.

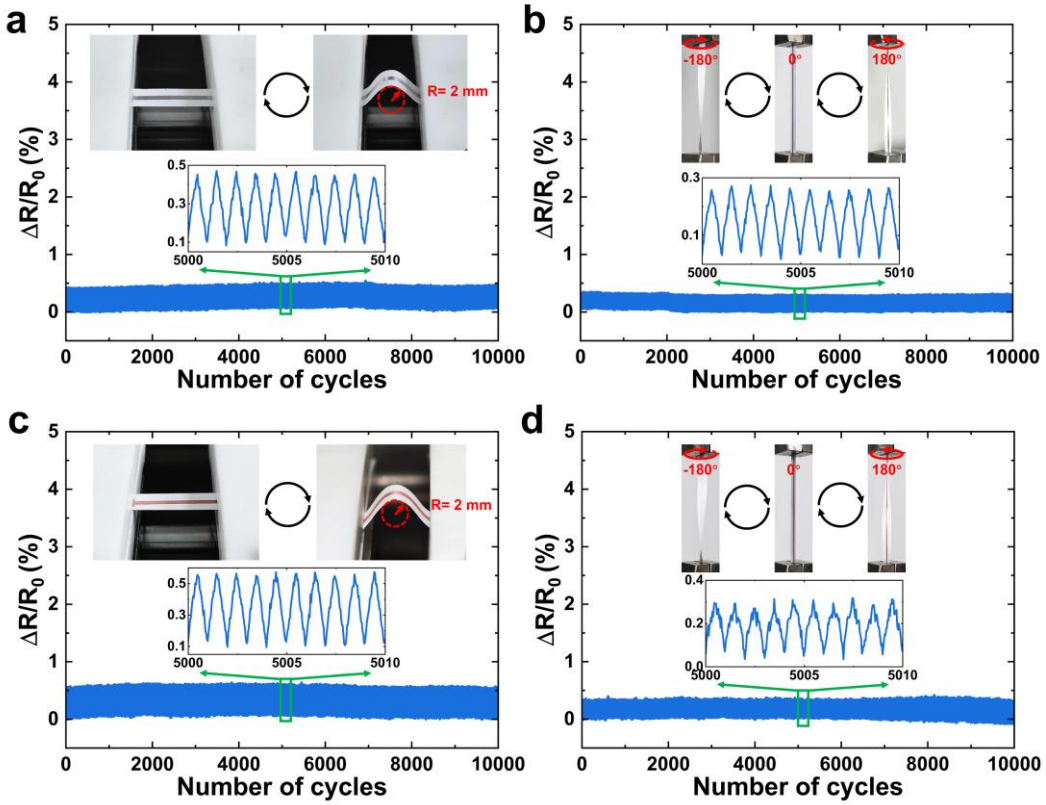

Fig.R5| Resistance change of the printed BiInSnZn electrode under the conditions of **a**, the bending (with a radius of 2mm), and **b**, the twisting. The same tests are conducted for the printed Cu electrodes, as shown in **c** and **d**.

As shown in Fig.R6 (also see Fig. 22 in Supplementary Materials), the printed BiInSnZn electrode can withstand repeated folding due to its flexibility and tight bonding with the porous paper substrate. It has a resistance rise of 1.6% for full-outward folding (77 μm in bending radius) and 28.5% for full-inward folding (close to zero in bending radius). The printed BiInSnZn electrode also has a good healing capacity

through heat softening because of its low melting point (**Supplementary Video 8**).

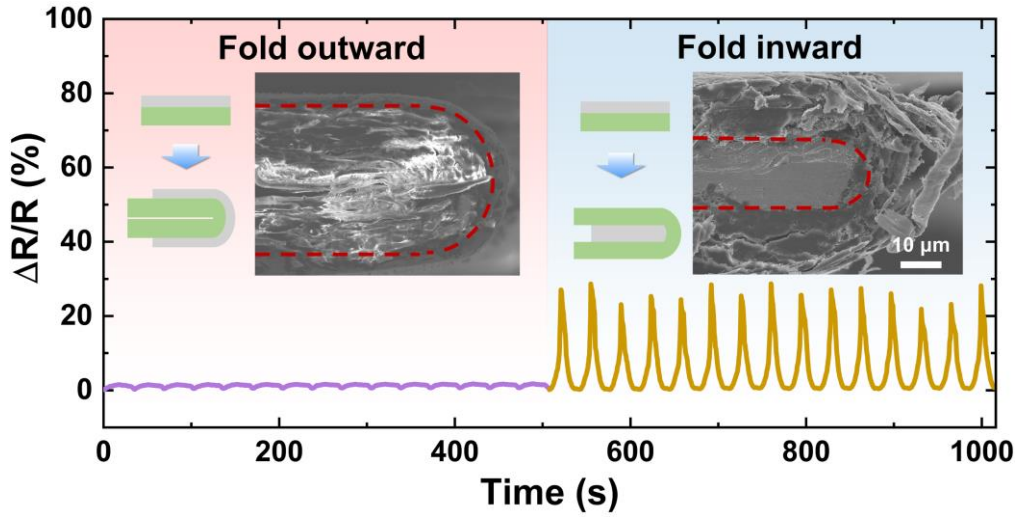

Fig.R6| Resistance change of the printed BiInSnZn line under full-outward and full-inward folding. For the full-outward folding, the SEM shows a bending radius of 77 μm.

More importantly, tension strength tests of two bonded homogeneous (or heterogenous) printed metal lines indicate that the joined area has high bonding strength beyond the substrate tensile strength (**Fig.R7**, also see **Fig.2i** and **2j** in the main text), where the crack did not occur at the joined site for all the tested cases.

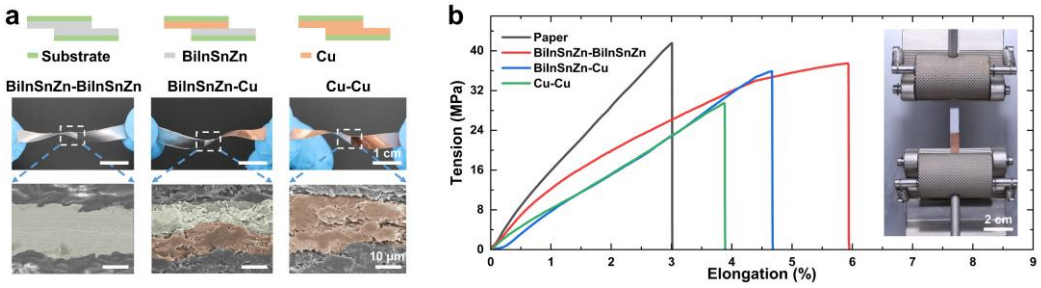

Fig.R7| **a**, Two stacked homogeneous (or heterogenous) printed metal lines (5 mm in width) on the paper substrates are bonded by the PCSA, including BiInSnZn-BiInSnZn, BiInSnZn-Cu, and Cu-Cu join. **b**, Tension strength tests of two bonded homogeneous (or heterogenous) printed metal lines. The crack did not occur at the joined area for all the tested cases.

Comment 5: In paper, PCSA can be used for bonding electronic devices on electrodes or contact pads. Can adhesion forces be measured and can resulting data can be provided in this case?

Response: Thanks for this comment. In the revised manuscript, we have added the adhesion force test, as shown in Fig.R8 (also see Fig. 22 in Supplementary Materials), which indicates that contact separation does not occur between the electrode and the

electronic device. The results demonstrate that the electronic devices bond with the printed electrodes tightly.

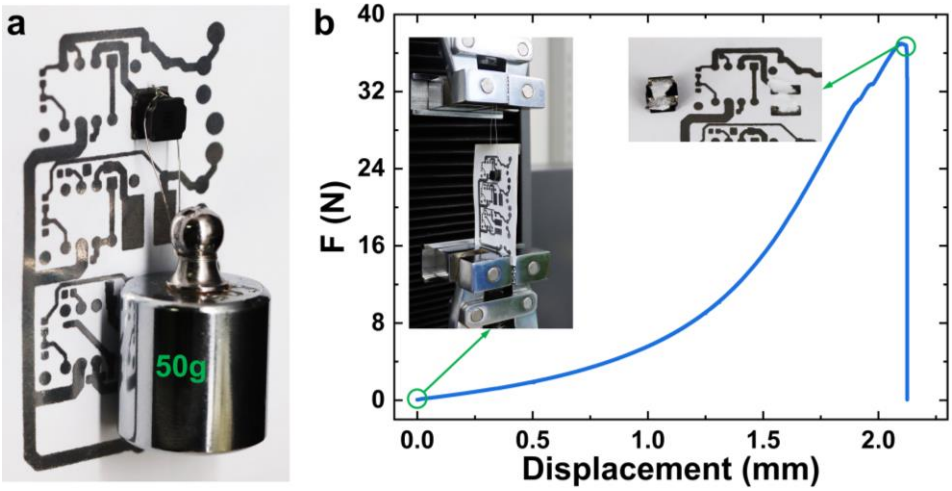

Fig.R8| a, Th electronic device strongly bonds with the printed BiInSnZn electrode activated by PCSA. **b**, Adhesion force testing of bonded electronic devices with printed electrodes. Contact separation does not occur between the electrode and the electronic device.

Comment 6: Since sonic wave is applied from one side of the electrodes in the thickness direction like other sintering methods of photonic, thermal sintering, the effectiveness of the method can be easily changed by the initial thickness of the particle patterns. Thicker particle patterns (like multiple printing of particle inks) can be also activated by the one-side PCSA method? Is there any limitation in pattern thickness for full activation by PCSA?

Response: Thanks for this comment. The penetration depth of sonic waves is significantly better than that of heat and light in the materials. The ultrasonic energy is mainly dissipated at the material interface, especially the multiple interfaces between particles. As shown in **Fig.R9** (also see Fig. 21 in Supplementary Materials), we have demonstrated that the PCSA can enable multilayer circuit interconnection. The flexible substrates printed with the designed double-sided circuits are layer-by-layer aligned by the marker points (**Figs. R9a-i**), where the interlamination electric paths are connected by through-holes filled with metal particle ink. The multilayer circuits and the interlamination electric paths are simultaneously activated by the PCSA method for the substrate layer number less than five (**Figs. R9a-iii**), which can achieve good electric performance (**Figs. R9b**). The layer-by-layer PCSA processing should be conducted to

achieve better activation performance when the substrate layer number is beyond five. The PCSA can activate the printed circuits with different thicknesses, such as 5 μm and 100 μm shown in **Figs. R9c** and **9d**.

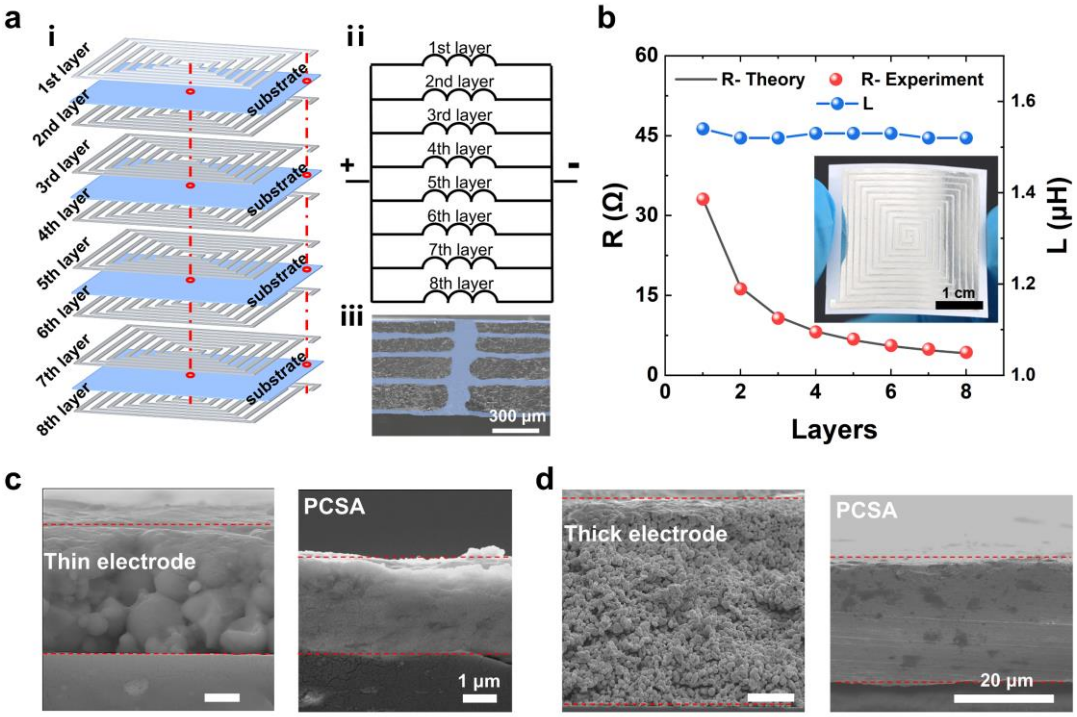

Fig. R9| PCSA method for interconnection of multilayer circuits. **a**, Interconnection illustration of multilayer inductance coil and its microstructure from SEM. **b,** Inductance and resistance of the multilayer coil. **c,** SEMs of the printed thin electrode before/after the PCSA processing. **d**, SEMs of the printed thick electrode before/after the PCSA processing.

Thanks to the excellent penetration of ultrasound, we even demonstrate that the PCSA method could also be used to activate the printed electrodes embedded into the 3D structure. As shown in Fig. R10 (also seeFig.1C in the main text), the preparation of the temperature-RFID (radio frequency identification) tag onto the curved surface is a proof-of-principle demonstration. The RFID antenna is printed on the styrene-butadiene-styrene (SBS) film and gripped by the 3D-printed acrylonitrile-butadiene-styrene (ABS) structure. The PCSA performed through an arc-shaped sonotrode not only triggers the electrical conductivity of the printed antenna circuit and welds the ABS support structures tightly. The accuracy of the measured temperature of the embedded RFID tag is checked by comparing it with that of the thermocouple, which also demonstrates the feasibility of the PCSA for the curved circuit preparation.

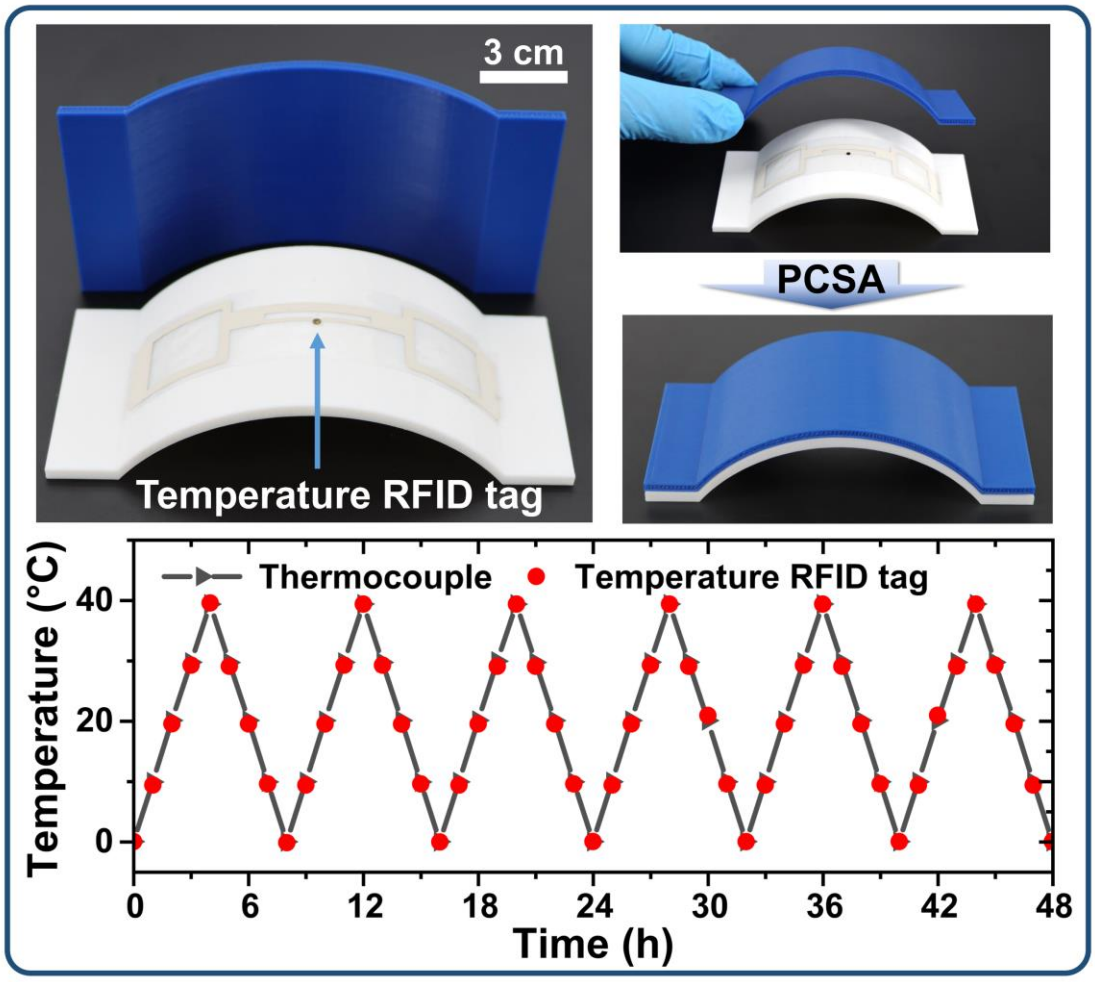

Fig.R10| Photographs of the Ag-based printed temperature-RFID antenna on the curved surface embedded into a 3D structure and the measured temperature accuracy demonstrated by the thermocouple.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

Now the paper looks much better than the previous one. Authors did the diligent work to address all the issues that the reviewer raised. Therefore, the paper is good for publication.