Supporting Information

Scalable Strategy to Directly Prepare 2D and 3D Liquid Metal Circuits Based on Laser-Induced Selective Metallization

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Figure S1. (a) PXRD pattern of antimony-tin oxide (ATO). (b) UV-vis-NIR spectroscopy of ATO in the region of 400-2000 nm (1064 nm is at the position of the red arrow). (c) XPS survey spectra of ATO. (d) SEM image of ATO.
Figure S2. (a) Computer vector of square patterns with different laser parameters; the laser frequency is fixed at 60 kHz, and the pulse width is fixed at 100 ns. (b) Photograph of SEPS/ATO composite after laser activation with different parameters. (c) Photograph of Figure S2(b) after 15 min electroless copper plating. (d) Photograph of Figure S2(c) after brushing liquid metal. (e) Photograph of the square copper pattern at (30%, 2000 mm/s) before Scotch tape test. (f) Photograph of the square copper pattern at (30%, 2000 mm/s) after Scotch tape test.

Figure S3. (a) Line copper circuit on the SEPS/ATO composite fabricated by laser-induced selective metallization. (b) Photograph of the sample (a) obtained by brushing liquid metal on the line copper circuit in the air. (c) The line liquid metal circuit prepared by brushing liquid metal on the copper line in 0.5 mol/L NaOH solution.
Confirmation of laser activation mechanism:

**Figure S4.** (a) SEM image of the SEPS/ATO composite after laser activation. (b) The magnified SEM image at the position of the red box in Figure S4(a). (c) SEM image of SEPS/ATO composite before laser activation. (d) The magnified SEM image at the position of the red box in Figure S4(b). (e) XPS survey spectra of the SEPS/ATO composite before laser activation. (f) XPS survey spectra of the SEPS/ATO composite after laser activation.

*Figure S4a* illustrates the SEM image of the laser-irradiation area on the SEPS/ATO composite after laser activation, and there form a number of irregular etching pits with different sizes. After electroless plating, these pits can act as the positions of rivets to improve the adhesion performance between the Cu layer and the SEPS substrate.¹ *Figure S4b* shows the
magnified SEM image of the red box in Figure S4a, revealing the complex pore structures caused by laser irradiation. Figure S4d is the magnified SEM image at the position of the red box in Figure S4b further. Obviously, after laser irradiation, many exposed ATO particles (denoted by red arrows) are observed. We also provide the surface SEM image of the SEPS/ATO composite before laser activation in Figure S4c. In contrast, its surface is very clean, and no ATO particles are observed. XPS tests were also conducted to analyze surface element compositions of the SEPS/ATO composite before and after laser activation, and the results are illustrated in Figure S4e and Figure S4f, respectively. Before laser activation (Figure S4e), only C and O elements are detected, indicating no ATO particles appearing on the surface. However, after laser activation, besides C and O elements, Sb and Sn elements are also observed, approving the existence of many exposed ATO particles on the surface of the SEPS/ATO composite. The XPS results are in accordance with those of SEM.

In order to analyze the chemical composition changes of SEPS and ATO in the SEPS/ATO composite after laser activation, Raman surface imaging and high-resolution XPS tests were carried out. Figure S5a is the Raman surface imaging on the surface of the SEPS/ATO composite after laser activation, and this image is rendered as the way of correlation degree. The length and width of the imaging are 90 μm and 90 μm with the scanning spacing of 3.0 μm, respectively. The corresponding micro-Raman spectra at blue (A), green (B), and yellow areas (C) are shown in Figure S5b. As a contrast, the micro-Raman spectrum of the SEPS/ATO composite before laser activation is also provided. In Raman spectroscopy, the ATO does not have any peaks in the region of 400-3500 cm\(^{-1}\), and therefore, in Figure S5b, the Raman spectrum only actually belongs to the SEPS matrix. From the results of the Raman surface imaging, we can observe some changes in SEPS chemical composition, but the distribution is not uniform. In Figure S5a, the micro-Raman spectra of blue (A) and green (B) areas are the same as that without laser activation; however, the micro-Raman spectrum of yellow area (C) appears a new broad peak within 1000-2000 cm\(^{-1}\), which is assigned to the amorphous carbon according to the literature,\(^2\) indicating the carbonization of some SEPS matrix after laser irradiation.

High-resolution XPS tests were performed to explore the chemical valance state of Sn and Sb elements in the SEPS/ATO composite after laser activation, shown in Figures S5c-S5f.
High-resolution XPS tests of neat ATO without any laser irradiation were also recorded (Figures S5c-S5e). The XPS spectra were fitted by the XPSPEAK4.1 software. The characteristic peaks of Sn 3d$_{3/2}$ and Sn 3d$_{5/2}$ of neat ATO without laser irradiation appear at 495.4 eV and 486.9 eV, respectively, which are assigned to the Sn$^{4+}$ in ATO according to the previous work (Figure S5c). However, for the ATO in the SEPS/ATO composite after laser activation (Figure S5d), besides the two peaks at 495.4 eV and 486.9 eV, two small new peaks are detected at 494.1 eV and 485.6 eV, which are ascribed to the Sn$^{2+}$ in ATO, indicating that a part of Sn$^{4+}$ is reduced to Sn$^{2+}$ after laser irradiation. From the peak areas of Sn$^{4+}$ 3d$_{3/2}$ (495.4 eV) and Sn$^{2+}$ 3d$_{3/2}$ (494.1 eV) in Figure S5d, the calculations show about 10.7% Sn$^{4+}$ is reduced to Sn$^{2+}$. Certainly, the amorphous carbon generated from the carbonization of SEPS acts as the reducing agent of this reduction reaction. Similarly, in Figures S5e-S5f, high-resolution XPS spectra of the Sb element were also recorded. The characteristic peaks of Sb element in XPS are located at 540.7 eV and 539.9 eV, which are attributed to Sb$^{5+}$ 3d$_{3/2}$ (540.7 eV) and Sb$^{3+}$ 3d$_{3/2}$ (539.9 eV), respectively. For the ATO in the SEPS/ATO composite, although no new chemical valance states of the Sb element are found after laser activation, the proportion of Sb$^{5+}$ and Sb$^{3+}$ is changed greatly. Before laser activation, the percentage of Sb$^{5+}$ is 58.3% calculated by the peak areas of Sb$^{5+}$ 3d$_{3/2}$ (540.7 eV) and Sb$^{3+}$ 3d$_{3/2}$ (539.9 eV) in Figure S5e. After laser activation, the percentage of Sb$^{5+}$ turns to 45.9% in Figure S5f, indicating that about 12.4% Sb$^{5+}$ is reduced to Sb$^{3+}$. In brief, after laser activation, a part of Sn$^{4+}$ and Sb$^{5+}$ is reduced to Sn$^{2+}$ and Sb$^{3+}$, which is caused by the amorphous carbon generated from the carbonization of SEPS.
Figure S5. (a) Image of Raman surface imaging on the surface of the SEPS/ATO composite after laser activation. (b) Corresponding micro-Raman spectra at different positions in Figure S5(a). (c) High-resolution XPS of Sn element in ATO without laser irradiation. (d) High-resolution XPS of Sn element on the surface of the SEPS/ATO composite after laser activation. (e) High-resolution XPS of Sb element in ATO without laser irradiation. (f) High-resolution XPS of Sb element on the surface of the SEPS/ATO composite after laser activation.
**Figure S6.** Surface topographic image of the SEPS/ATO composite after laser activation, recorded by laser scanning confocal microscopy.

**Figure S7.** (a) Water contact angle on the surface of SEPS/ATO before laser activation. (b) The water contact angle on the surface of SEPS/ATO after laser activation.
**Figure S8.** (a) XPS survey spectrum of the square Cu pattern in Figure 2(d). (b) XPS survey spectrum of the square liquid metal pattern in Figure 2(g).

**Figure S9.** XRD of the copper layer on the SEPS/ATO composite.
Figure S10. (a) Surface SEM image of neat Galinstan and the corresponding EDX mapping of (b) Ga, (c) In, and (d) Sn elements.

Figure S11. Resistances of the copper circuit in the states of (a) “slight stretch,” (b) “bend inward,” (c) “bend outward,” and (d) “twist.” Resistances of the liquid metal circuit in the states of (e) “slight stretch,” (f) “bend inward,” (g) “bend outward,” and (h) “twist.”
Figure S12. Resistances of the liquid metal circuit at different lengths from 0 to 100% strain during 50-times cycling tests.

Figure S13. Resistance of the liquid metal circuit after 500-times cycling tests from 0% to 100% strain in a horizontal way, and the error limits of resistance are ±0.02 Ω.
Figure S14. Photographs of the liquid metal circuits based on laser-induced selective metallization in 1.0 mol/L HCl solution in the states of (a) “bending,” (b) “twisting,” and (c) “stretching.” Photographs of the liquid metal circuits based on laser-induced selective metallization in 1.0 mol/L NaOH solution in the states of (d) “bending,” (e) “twisting,” and (f) “stretching.”

Figure S15. Resistances of the pressure sensor at different pressures.
Figure S16. (a) Computerized vectors of the butterfly pattern. (b) The butterfly pattern on the SEPS/ATO composite after laser activation. (c) The copper pattern of the butterfly on the SEPS/ATO composite after 15 min electroless copper plating from Figure S16(b). (d) Computerized vectors of the circuits. (e) The circuits on the SEPS/ATO composite after laser activation. (f) The copper circuits on the SEPS/ATO composite after 15 min electroless copper plating from Figure S16(e). (g) Computerized vectors of the heater pattern. (h) The heater pattern on the SEPS/ATO composite after laser activation. (i) The copper heater pattern on the SEPS/ATO composite after 15 min electroless copper plating from Figure S16(h).

Table S1 The resistances under different storage time and distortion states

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<tr>
<th>Distortion states</th>
<th>0 day</th>
<th>30 days</th>
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<tr>
<td>Slight stretch</td>
<td>0.61±0.01 Ω</td>
<td>0.61±0.01 Ω</td>
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<tr>
<td>Bend inward</td>
<td>0.56±0.01 Ω</td>
<td>0.57±0.01 Ω</td>
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<tr>
<td>Bend outward</td>
<td>0.95±0.02 Ω</td>
<td>0.97±0.02 Ω</td>
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<tr>
<td>Twist</td>
<td>0.83±0.02 Ω</td>
<td>0.86±0.02 Ω</td>
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<tr>
<td>Stretch (100% strain)</td>
<td>1.93±0.02 Ω</td>
<td>1.96±0.02 Ω</td>
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References


