Electronic Supplementary Information

Liquid Metal Composite with Carbon Nanotubes for Reliable Interconnection between Pt Electrodes

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This PDF file includes Supporting Figures S1-S15 and experimental details.

Experimental Section

Decoration of single-walled carbon nanotubes with Pt nanoparticles. As-synthesized single-walled carbon nanotubes (SWCNTs) (Carbon Solutions Inc.) were functionalized by nitric acid treatment in a 70% HNO_3 solution (Sigma Aldrich). The SWCNTs were refluxed in nitric acid at 120 °C for 5 hours, followed by filtration and rinsing with DI water. The remaining solids were dried overnight at 70 °C in an oven. IR spectra were obtained after this step (not included). After acid treatment, the SWCNTs with carboxylic groups were dispersed in water by tip sonication for 1 hour. The dispersed CNTs were then treated with 5 wt.% tetraammineplatinum(II) nitrate, Pt $(NH_3)_4(NO_3)_2$ (Sigma Aldrich), aqueous solution at 60 °C for 2 hours to form Pt nanoparticles on the sidewalls of SWCNTs by electrostatic attraction. The collected Pt-CNTs were reduced to Pt^0 metal in a hydrogen environment at 300 °C for 2 hours. The process is schematically illustrated in Figure S1. To verify that Pt nanoparticles were formed on the surface of SWCNTs, transmission electron microscopy (TEM) images were obtained (Figure S1).

Preparation of the CNT/eGaIn composite. eGaIn alloy is composed of 75.5% Ga and 24.5% In by weight (Sigma-Aldrich, 99.99% purity). There are two methods of producing CNT/eGaIn composites, as shown in Figure 1b. The key difference between the two methods is the centrifugation of the dispersed CNTs prior to adding them to eGaIn. For both methods, the initial steps were identical. The CNT/eGaIn composites were prepared by dispersing 3 mg of Pt@CNTs in N-Methyl-2-pyrrolidone (NMP) (Sigma-Aldrich) using bath sonication for 1 hour. Then, eGaIn was dispersed in the Pt@CNT/NMP solution using bath sonication. In a nitrogen-filled glove box, NMP was evaporated by continuously stirring with a magnetic stirrer. The distinguishing step in the second method occurred before mixing with eGaIn. We centrifuged the dispersed Pt@CNTs in the NMP solution using an ultracentrifuge to remove agglomerated CNT bundles. Then, the collected supernatant was mixed with eGaIn, and the NMP was evaporated in an oxygen-free environment.

Fabrication of eGaIn and CNT/eGaIn interconnects.

The fabrication of Pt metal contact pads. A positive photoresist (AZ5214E) was spin-coated at 4000 rpm for 30 s onto the SiO_2/Si substrate, resulting in a 1.4 μm-thick layer. The coated photoresist then underwent a soft bake at 105 °C for 90 s on a hot plate to improve adhesion and remove excess solvents. Next, the photoresist was exposed to UV light at an energy density of 100 mJ/cm^2 through a film mask. Development in an AZ 500 MIF developer (AZ Electronic Materials) for 1 min produced the desired photoresist patterns. Following the photolithography process, Pt film deposition was carried out using magnetron ion sputtering (Hitachi ion sputter E-1045). The sputtering was performed with a current of 20 mA for 60 s, resulting in a Pt layer 20-nm thick. Finally, the metal/photoresist layer (PR) underwent a lift-off procedure in acetone for 45 min, removing unwanted metal/PR layers from the substrate. As a result, Pt contact pads were formed on the substrate.

Patterning of liquid metal interconnects on the substrate. A negative photoresist (nLOF 2035) layer was spin-coated at 3500 rpm for 30 s onto the SiO_2/Si substrate containing Pt contact pads, followed by a soft bake at 105 °C for 90 s on a hot plate. The photoresist was then exposed to UV light at an energy density of 60 mJ/cm^2 through a film mask. Immediately after exposure, the substrate underwent a post-exposure bake at 100 °C for 120 s to ensure cross-linking of the exposed resist areas, rendering them insoluble in the developer. Development in AZ 500 MIF developer (AZ Electronic Materials) for 70 s produced the desired photoresist patterns with undercuts. To enhance bonding between eGaIn and the SiO_2/Si substrate, the exposed surfaces underwent oxygen plasma treatment (50 W, 30 sccm, 1 minute). The eGaIn pattern was then formed using a liquid metal stamping technique with a PDMS block. A non-structured PDMS block was wetted with eGaIn and gently pressed onto the open surfaces of the microstructure undercut, transferring the eGaIn. Finally, the photoresist layer was dissolved in acetone, resulting in the

formation of interconnects with a 4 μm height between two contact pads. The process is schematically illustrated in Figure S12.

Electrical measurement of eGaIn and CNT/eGaIn interconnects. A Keithley 2400 standard series source measure unit SMU was used for electrical measurement. The fabricated device was connected to the Keithley 2400 SMU using contact probes. The SMU applied a voltage sweep from -1 V to +1 V in 0.01 V increments, measuring the resulting current at each voltage point. We plotted the collected data to create the I-V curve, with current on the y-axis and voltage on the x-axis.

Supporting Figures

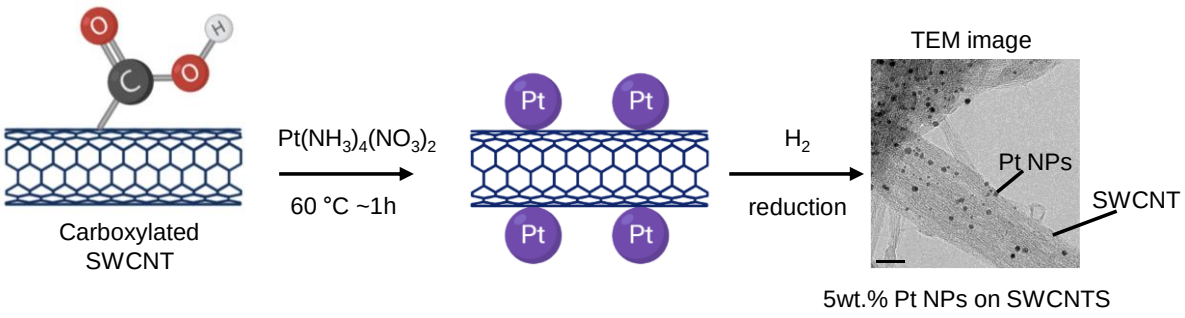

Figure S1. Schematic illustration of the decoration of platinum nanoparticles on functionalized single-walled carbon nanotubes, with a TEM image of the Pt-decorated CNTs (Pt@CNTs) shown on the right.

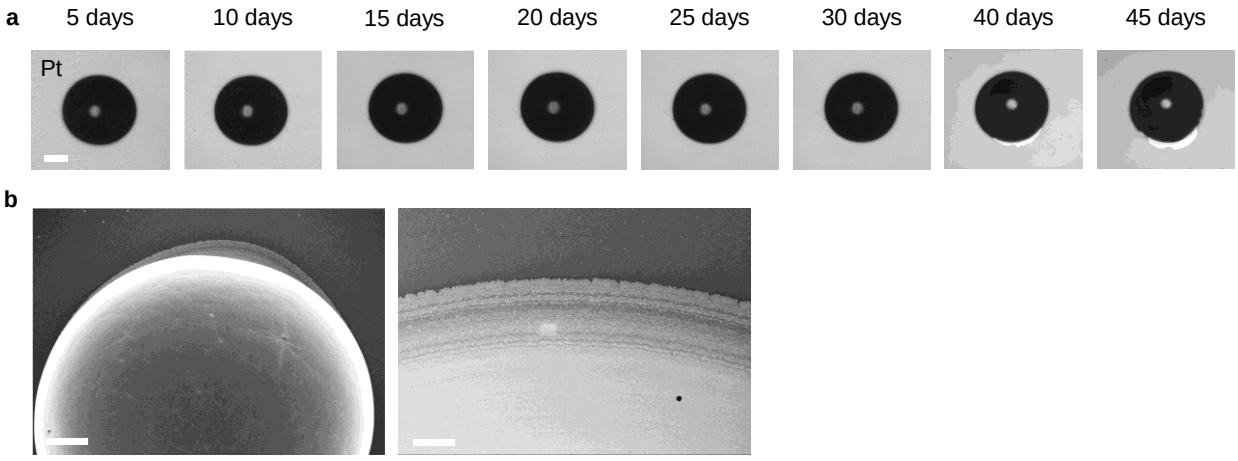

Figure S2. (a) Optical images of a 3 wt.% CNT/eGaIn composite droplet with minimized CNT bundles on a Pt film over 45 days. Scale bars: 200 µm in each optical image. (b) SEM images of the composite spreading on the Pt film. Scale bars: 50 µm (left) and 15 µm (right).

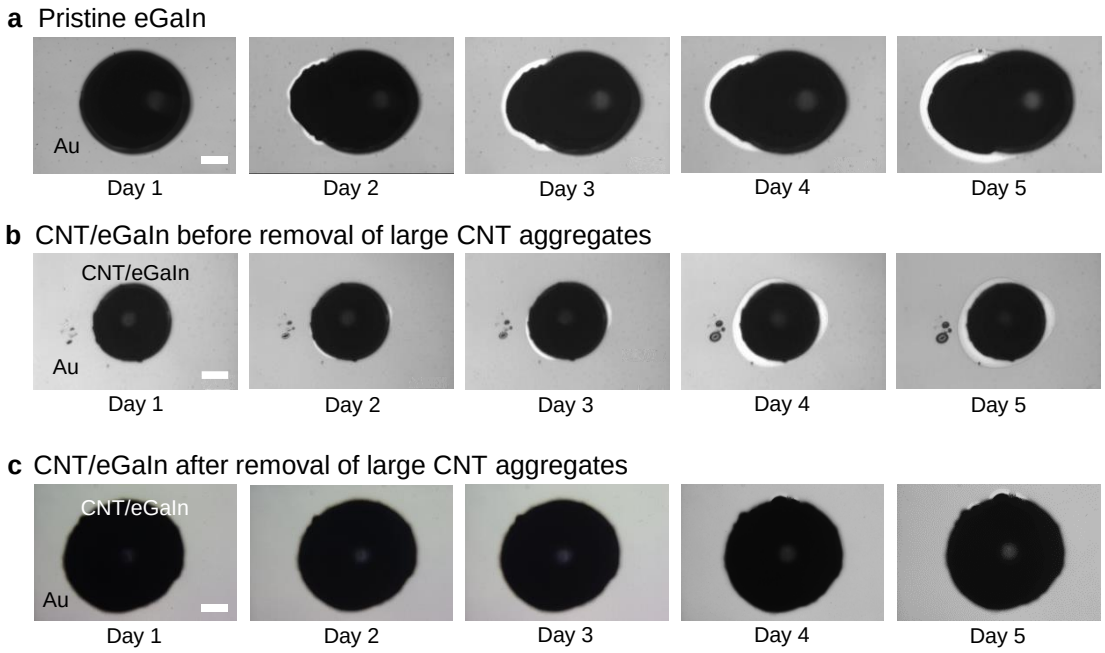

Figure S3. Suppressed spreading of CNT/eGaIn on a gold (Au) film. (a) Optical images showing the spreading of a pristine eGaIn droplet on the Au film over a 5-day period. (b-c) Optical images showing the spreading of a 3 wt.% CNT/eGaIn droplet (b) before and (c) after removal of large CNT aggregates by centrifugation, observed for 5 days. The Au film (70 nm thickness) was deposited on a SiO_2/Si substrate by thermal evaporation. All scale bars in each optical image are 200 µm long.

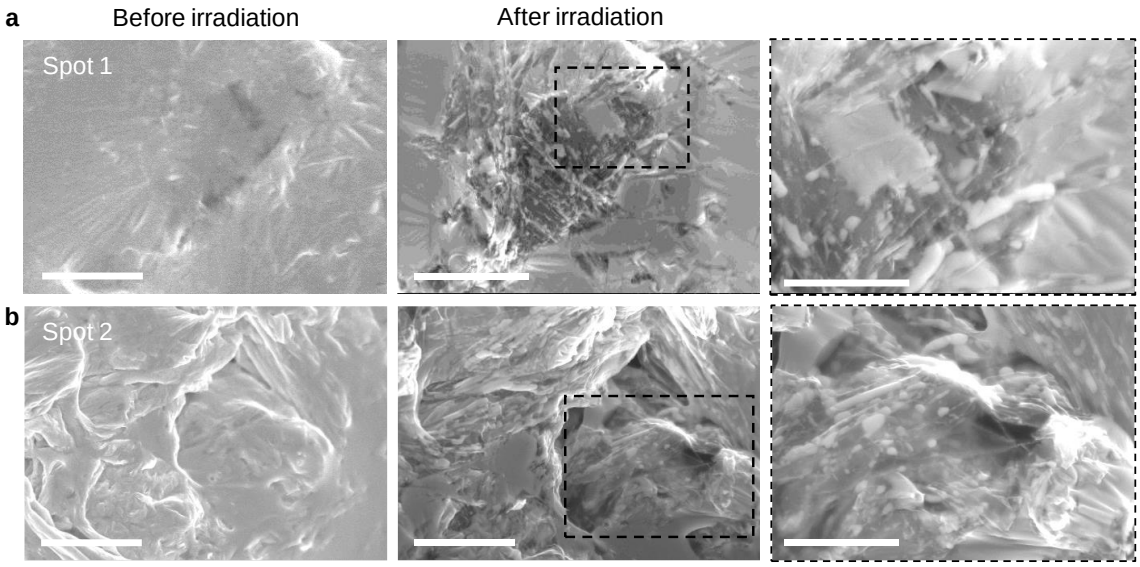

Figure S4. SEM images of the CNT/eGaIn composite film before and after electron beam irradiation at 10 keV for 15 min at different spots: 1 (a) and 2 (b). The scale bar in each SEM image is 5 μm in length, and the zoomed-in image within the dotted box is 2 μm in length.

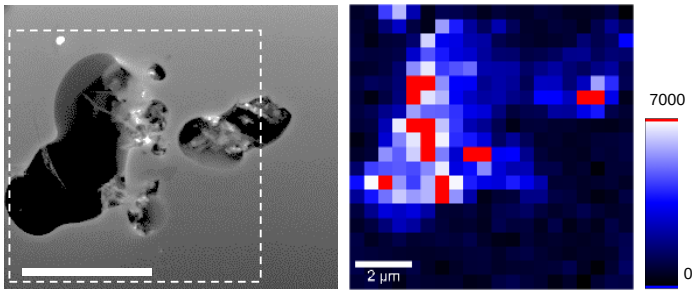

Figure S5. Confirmation of CNTs embedded in the liquid metal. Shown on the right is a Raman map of the G-band (1570-1620 cm^{-1}) for the dotted area in the SEM image (left), which corresponds to the dewetted area shown in Figure 2a. The result confirms the presence of carbon nanotubes in the liquid metal. The scale bar in the SEM image is 5 μm long, and the one in the Raman map is 2 μm long.

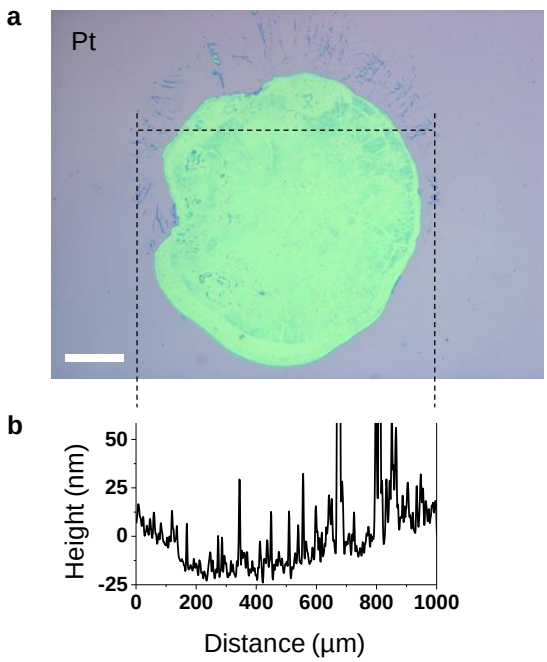

Figure S6. (a) Optical image of the contact area between an eGaIn droplet and a Pt film after droplet removal. The scale bar in the optical image is 200 μm long. (b) Height profile measurement along the black dotted horizontal line shown in the optical image, demonstrating the thickness changes in the contact area.

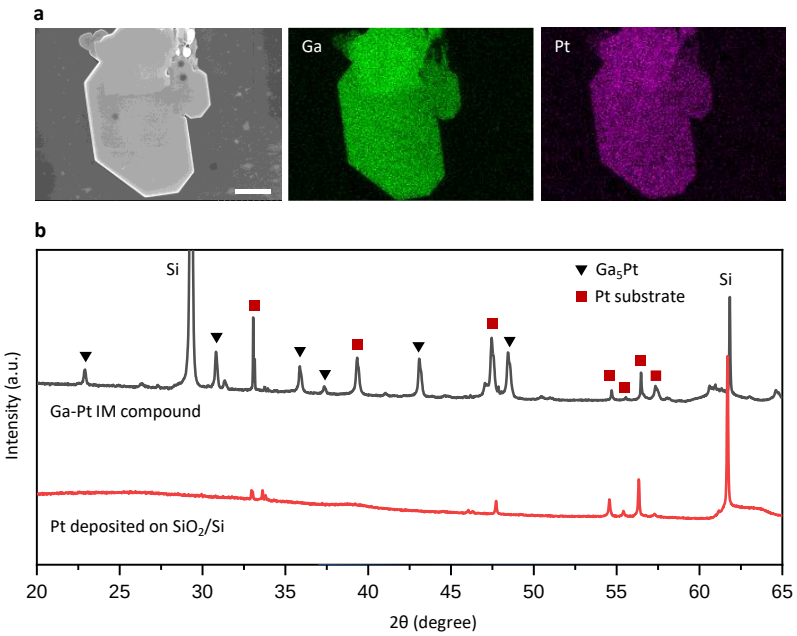

Figure S7. Characterization of intermetallic crystals (Ga_5Pt) formed during the spreading of eGaIn on a Pt substrate. (a) SEM image of an intermetallic crystal (Ga_5Pt) after the removal of excess gallium (left), with corresponding EDX elemental mapping of Ga (middle) and Pt (right). Scale bar: 3 μm. (b) XRD patterns of the intermetallic crystals (top) and the Pt-coated substrate (bottom).

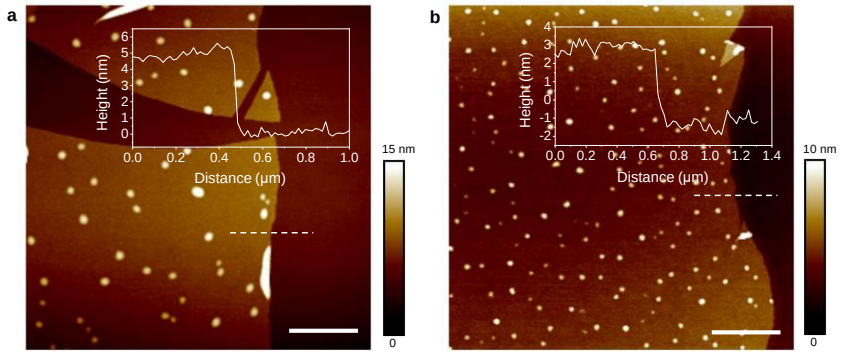

Figure S8. AFM characterization of the oxide layer thickness derived from eGaIn and CNT/eGaIn samples using the liquid metal balloon approach. (a) Height profile of the oxide layer derived from eGaIn (scale bar: 80 nm). (b) Height profile of the oxide layer derived from the CNT/eGaIn composite (scale bar: 1 µm).

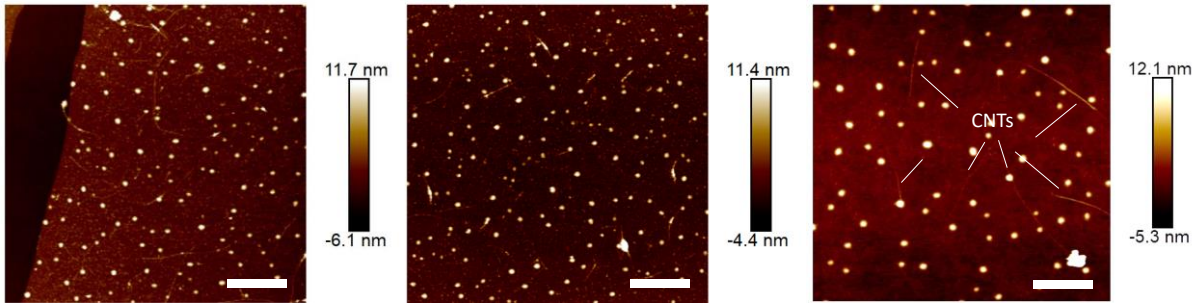

Figure S9. AFM image of gallium oxide derived from a CNT/eGaIn composite using the liquid metal balloon approach. The image reveals carbon nanotubes embedded within the gallium oxide surface, forming an internal barrier. Scale bars: 1 µm and 600 nm.

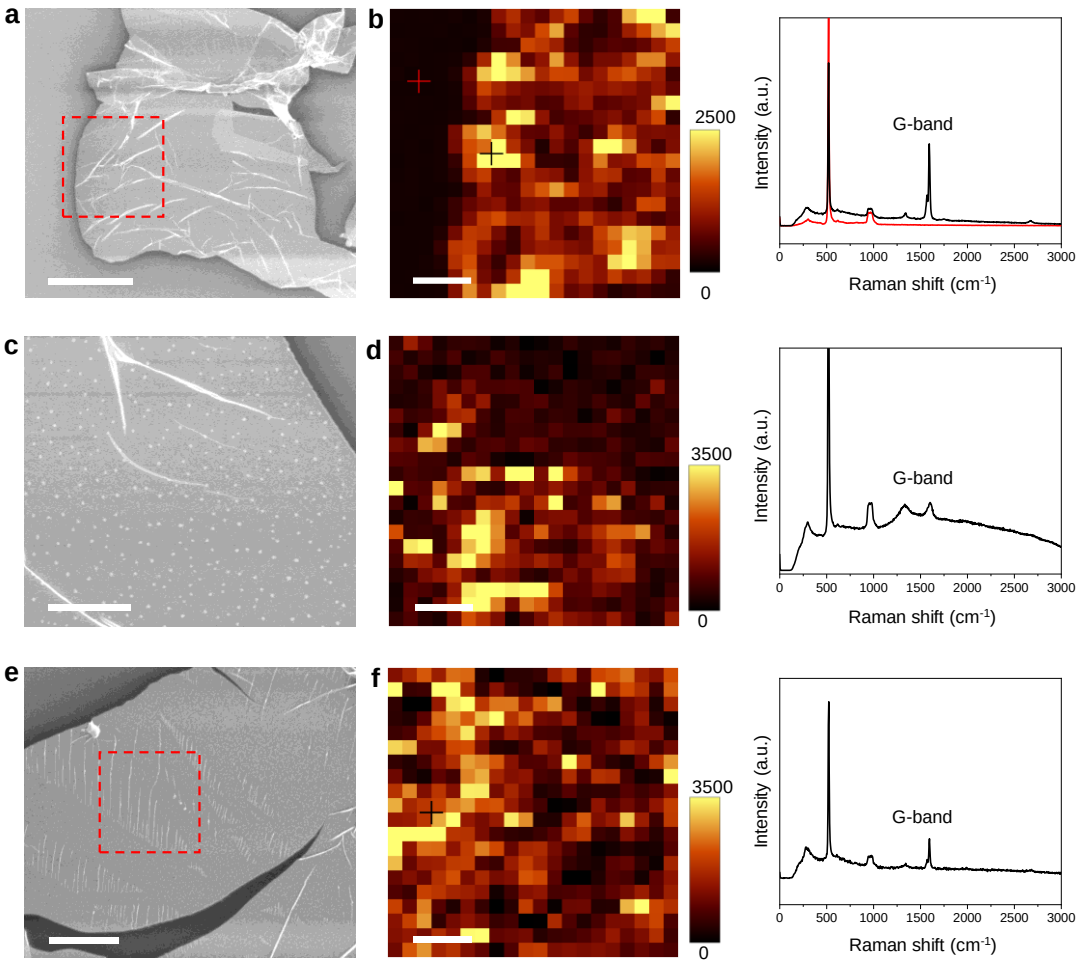

Figure S10. Characterization of the oxide layer derived from the CNT/eGaIn composite using the liquid metal balloon approach at three spots. (a, c, e) SEM images and (b, d, f) corresponding Raman maps and spectra of the CNT G-band (1585–1600 cm^{-1}) for spots #1, #2, and #3, respectively. Scale bars: (a, b) 10 μm and 2 μm; (c, d) 2 μm; (e, f) 5 μm and 2 μm.

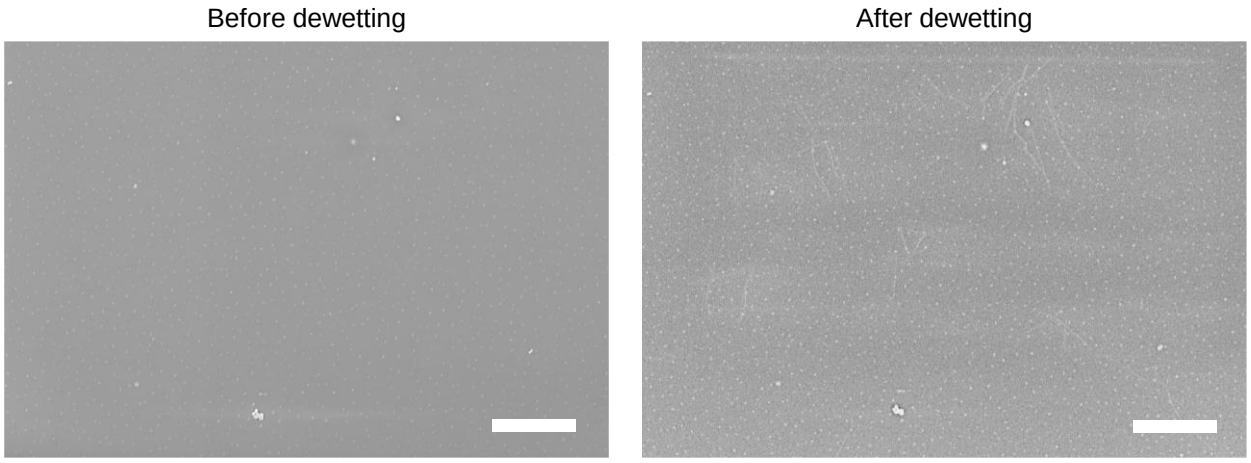

Figure S11. SEM images of the oxide layer derived from the CNT/eGaIn composite using the liquid metal balloon approach, shown before and after electron beam irradiation at 15 keV for 1 h. Scale bars: 2.5 μm.

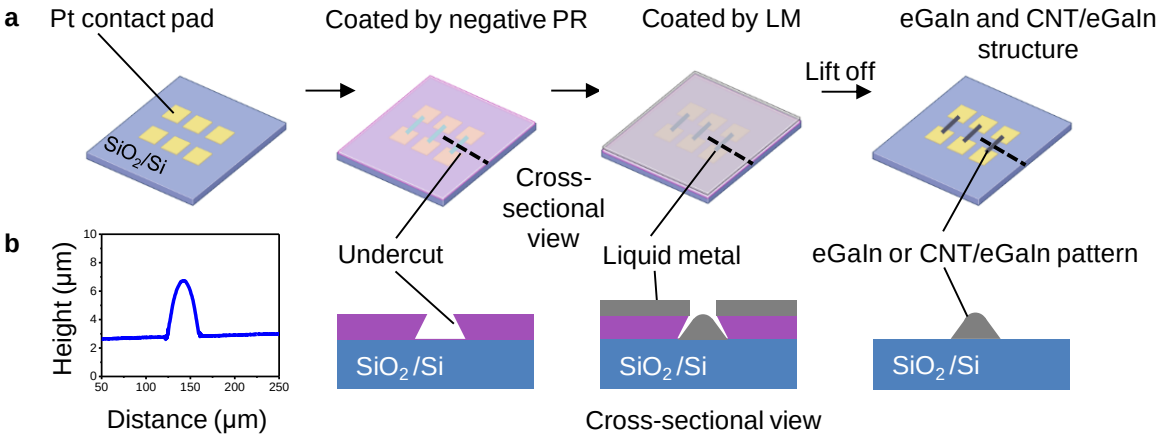

Figure S12. (a) Schematic illustration of the fabrication process for eGaIn and CNT/eGaIn interconnects on a rigid substrate. (b) Height profile of the eGaIn pattern measured by confocal laser microscopy using a 310 nm laser. The height profile shows that the pattern height is 4 μm.

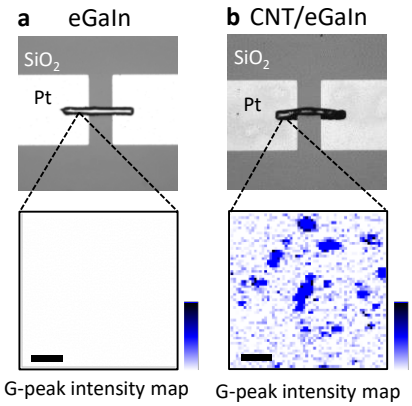

Figure S13. Raman intensity maps for G-band of CNTs from (a) eGaIn interconnect and (b) CNT/eGaIn interconnect shown in Figure 4. The scale bars in the Raman map are 6 μm long.

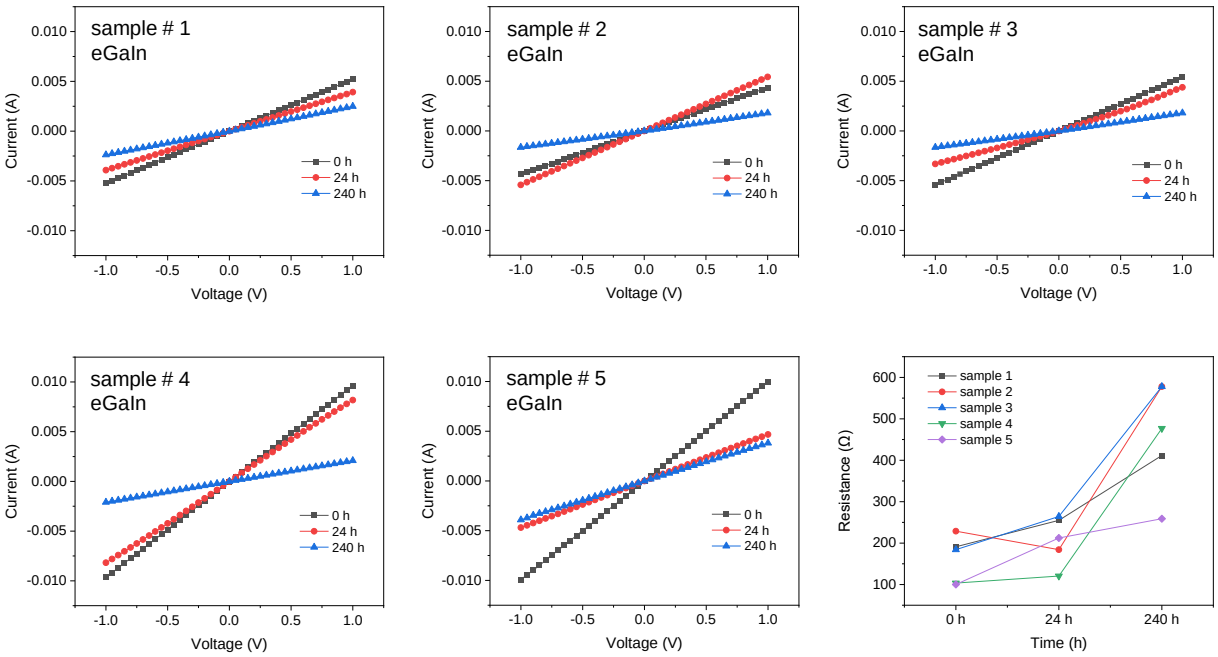

Figure S14. I-V curves of Pt electrodes connected by an eGaIn interconnect, measured over a 10-day period for five different samples. For all samples, the resistance increased significantly over the period.

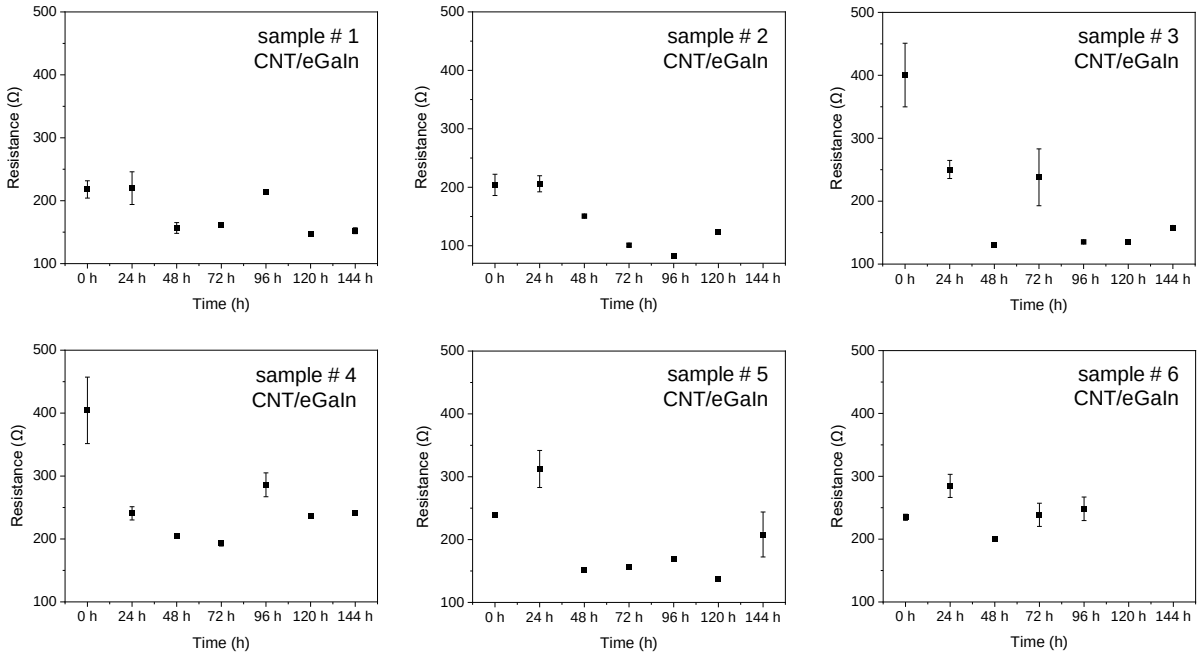

Figure S15. Resistance of six different CNT/eGaIn interconnects across Pt electrodes monitored for up to six days, with some measurements completed within 4–5 days. The resistance was calculated from the slopes of the I-V curves, with error bars representing one standard deviation from multiple measurements. In contrast to the resistance increase observed in the eGaIn interconnect (Figure S14), the CNT/eGaIn interconnect exhibited a resistance decrease from 200–400 Ω to 100–250 Ω, demonstrating the formation of stable electrical contact between Pt and CNT/eGaIn.