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Pressure-assisted electrode fabrication using simply synthesized Cu_3Sn alloy nanoparticles

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Experimental Section

Synthesis: Copper(II) acetylacetonate ($Cu(acac)_2$, Aldrich, 0.1 g) and Tin(II) acetylacetonate ($Sn(acac)_2$, Aldrich, 0.028g) dissolved in 10 mL of Oleylamine (Aldrich, 70%) and 1mL Oleic acid (Aldrich, 90%) mixed solution was heated to 120 ^oC for 30minutes under vacuum conditions. The solution was then heated under nitrogen gas to a temperature of 310 ^oC with stirring. When the solution reached the temperature of 310 ^oC, the solution was left to react for 1 hour. The solution was then cooled to room temperature. Finally, the reacted solution was mixed with ethanol and hexane, and then the synthesized nanoparticles were conducted to centrifugation. The precipitates were washed with ethanol and hexane several times. The precipitated nanooparticles were dried in a vacuum oven (40 ^oC)

Preparation of Conductive Electrodes: The circle punched shielding layer (3M tape) of 5mm diameter attached on the PET substrates. The nanoparticle powder was loaded in the hole of shielding layer (powder mass : 0.03g) and covered the upper PET layer. Loading powder was applied to the setting pressure using a hydraulic pump press machine. The experiments were continued for 3 minutes at room temperature. The pressed sample was separated into an upper PET layer, a shielding layer on PET substrates and sample. We repeated the same process for fabricate a complex shape of conductive electrode. Then, the 3M tape, as an adhesive layer, attach the each sample such as round, line and complex shapes.

Resistivity measurements: Resistivity measurements of the sample were carried out in a four-point DC resistivity measurement setup. To make a four-point measurement base electrode tool, the patterned silver electrodes were evaporated on the PET or the glass substrate. The pattern had four electrodes with silver line thickness of 0.8 mm and a space distance of

0.6mm. The silver pattern was loaded using thermal evaporation. The pressed Cu_3Sn layer samples of diameter of 5mm were mounted onto a silver patterned PET substrate. And then 1kg weight was laid on the samples for uniform contact. A constant current of 10mA was applied using a Keithley 224 current source and voltage was measured for each experimental condition. In addition, the line patterned sample was measured to semiconductor parameter analyzer (Agilent 4155B) for the current-voltage characteristics.

Instrumentation and Measurements: HR-TEM images were captured using a JEOL JEM-3010 with an accelerating voltage of 100kV. The HAADF-STEM, EELS analysis and EDS mapping images were obtained using a JEOL JEM 2100F. To make a the cross-sectional TEM sample, we used a Focused Ion Beam (FIB) by NOVA 600 Nanolab(FEI). And then, the pressed sample was coated with a platinum-sputtering in order to protect the sample. The Pt coated cross-sectional TEM sample was loaded onto molybden TEM grid and conducted the TEM analysis. The XRD measurements were performed on the Bruker D8 DISCOVER diffractometer using a Cu Kα radiation source.

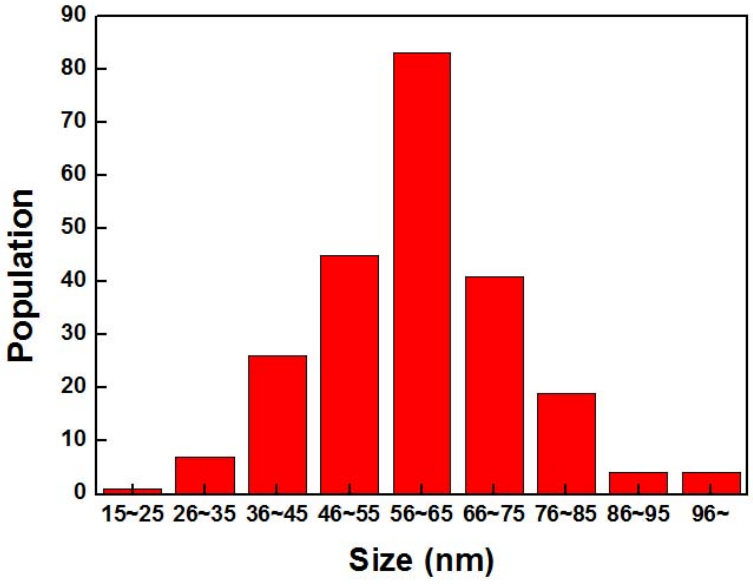

Fig. S1. Size distribution of synthesized Cu_3Sn alloy nanoparticles

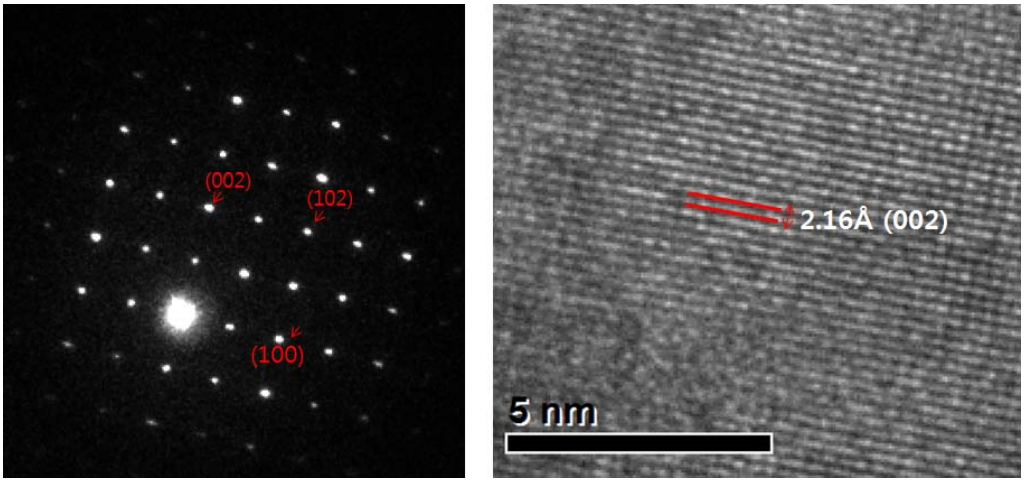

Fig. S2. Crystal characterization of the Cu_3Sn alloy nanoparticles. The left image shows the specific area electron diffraction (SAED) pattern of Cu_3Sn alloy nanoparticle. The right image shows the lattice parameter analysis. The lattice spacing is determined to be 0.21 nm, which corresponds to the (002) lattice spacing, in agreement with Cu_3Sn alloy nanoparticle crystal structures.

Table S1. Atomic ratio of individual Cu_3Sn alloy nanoparticles by TEM-EDS elemental analysis

Number	Atomic ratio (%)	
	Cu	Sn
1	75.33	24.66
2	76.67	23.33
3	77.13	22.87
4	75.73	24.26
5	73.6	26.4
6	72.2	27.8
7	72.9	27.1
8	77.88	22.20
Average	75.18	24.82

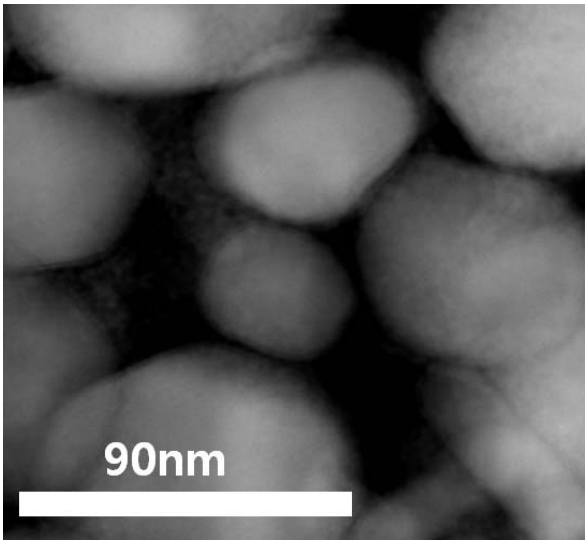

Fig. S3. TEM image for the EDS mapping analysis of **Fig. 1d** and **1e**, which shows the non-existence of the core-shell or bimetallic structures

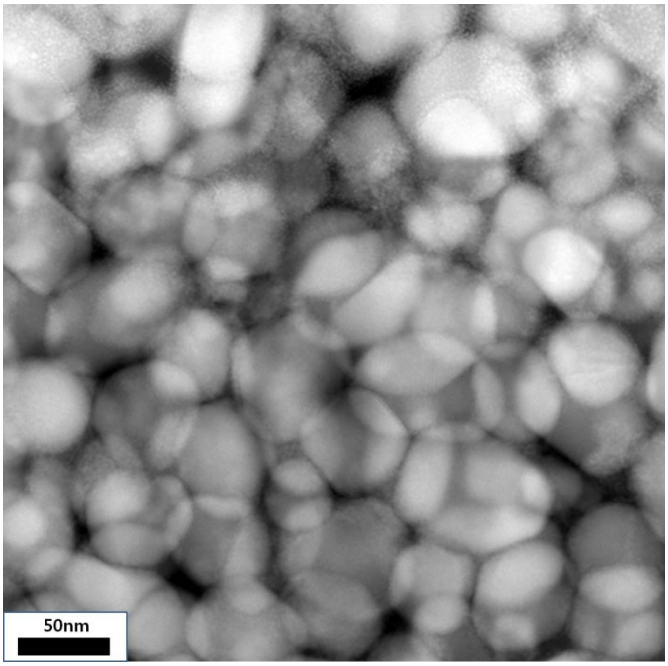

Fig. S4. White field cross-section TEM image of the pressed Cu_3Sn nanoparticle electrode at 131.3 MPa pressure condition

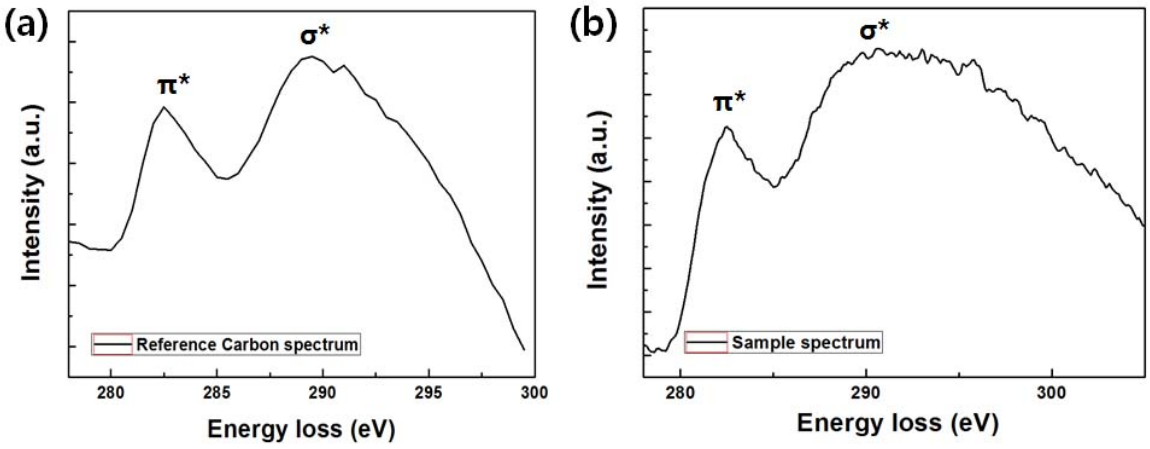

Fig. S5. A typical EELS spectrum (a) carbon reference, (b) carbon spectrum of the pressed Cu3Sn alloy nanoparticles, corresponding TEM-EELS elemental map (Fig. 3e)

Table S2. Resistivity of pressed Cu_3Sn nanoparticles layer fabricated at various pressures from 39.4 MPa to 170.7 MPa

Pressure [MPa]	39.4	65.6	91.9	131.3	170.7
Average [Ω•cm]	2.504×10^{-7}	2.257×10^{-7}	2.125×10^{-7}	1.986×10^{-7}	2.055×10^{-7}

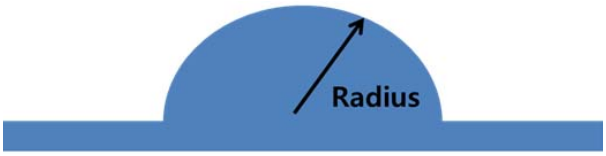

Fig. S6. Schematic showing of mechanical bending test condition

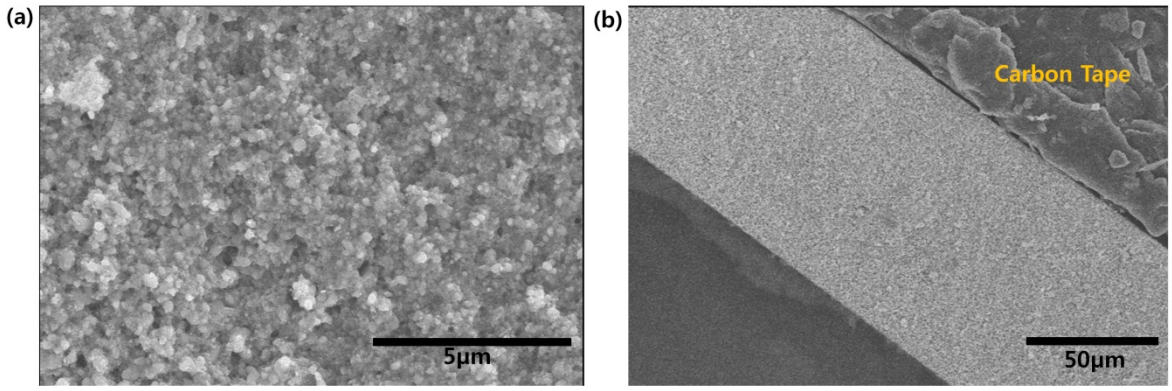

Fig. S7. (a) Plane view SEM and (b) cross section SEM images of the pressed Cu_3Sn nanoparticles. The thickness of the pressed Cu_3Sn nanoparticles electrode is ~ 89 μm in 65.6 MPa.

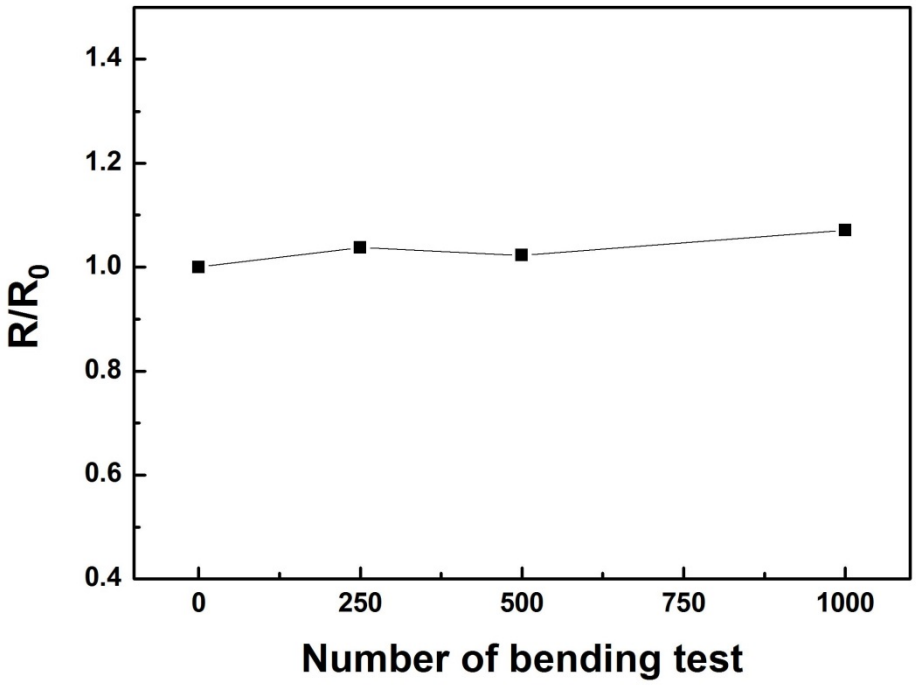

Fig. S8. Change of the resistivity during the bending test for the pressed Cu_3Sn alloy nanoparticles layer.

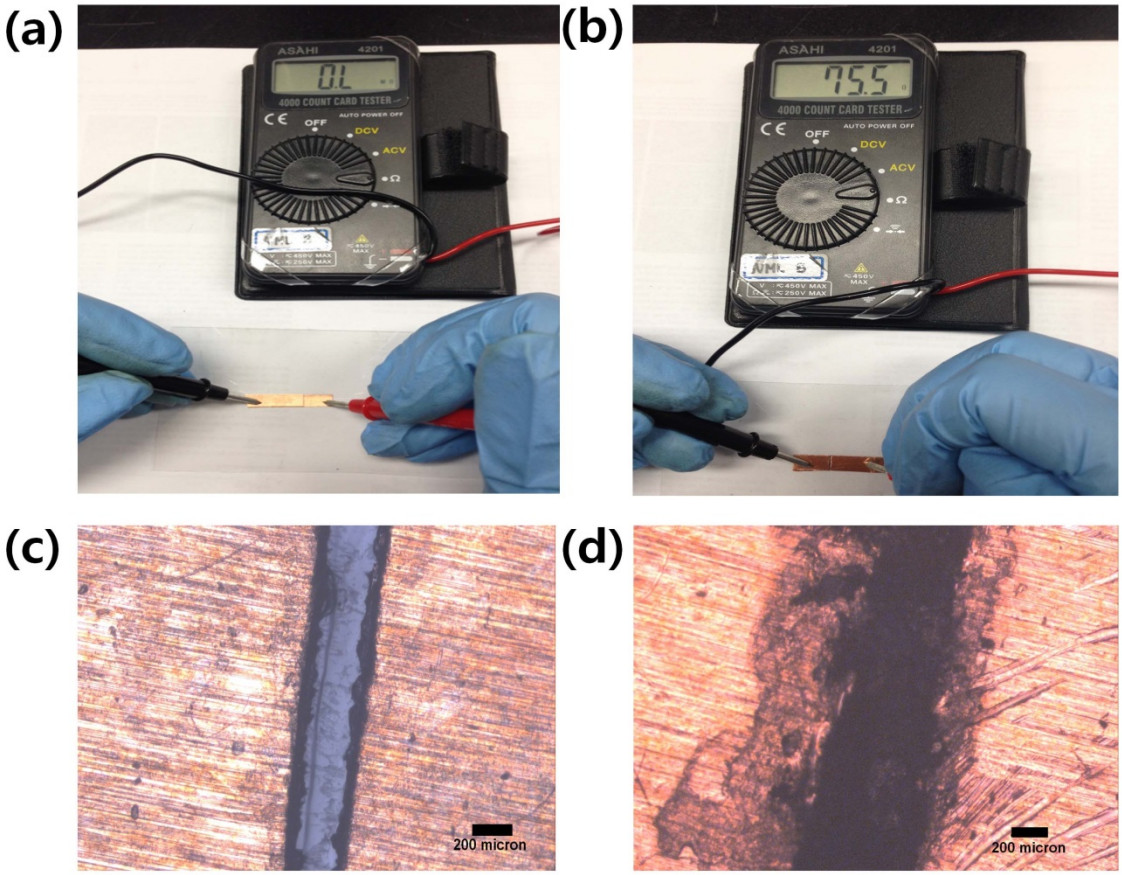

Fig. S9. (a) Optical images of the disconnected copper electrode wire and (b) well connected electrode wire (c) Optical microscopy images of disconnected electrode wire and (d) well connected electrode wire by pressed Cu_3Sn nanoparticles layer

Table S3. Resistivity variation of the pressed Cu_3Sn nanoparticle electrode under ambient air conditions for 4 weeks

Time [week]	1	2	3	4
Average [Ω•cm]	1.986×10^{-7}	2.042×10^{-7}	2.103×10^{-7}	2.013×10^{-7}

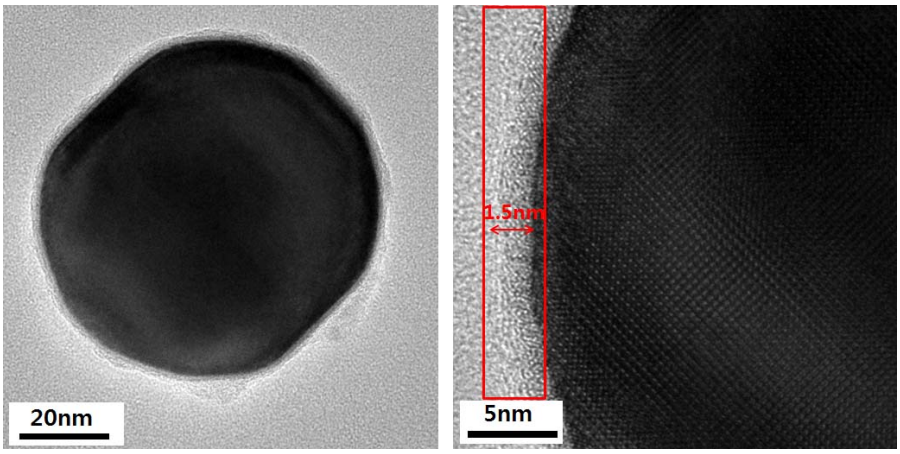

Fig. S10. HR-TEM image of Cu_3Sn alloy nanoparticles and the red line indicate the oxide layer and the oxide layer thickness is measured to 1.5nm

(a) Just Synthesized

Element	Wt%	Atomic %
O	2.80	11.91
Cu	65.37	69.88
Sn	31.83	18.22
Total:	100.00	100.00

(b) After 4week

Element	Wt%	Atomic %
O	2.82	12.27
Cu	60.30	66.09
Sn	36.88	21.64
Total:	100.00	100.00

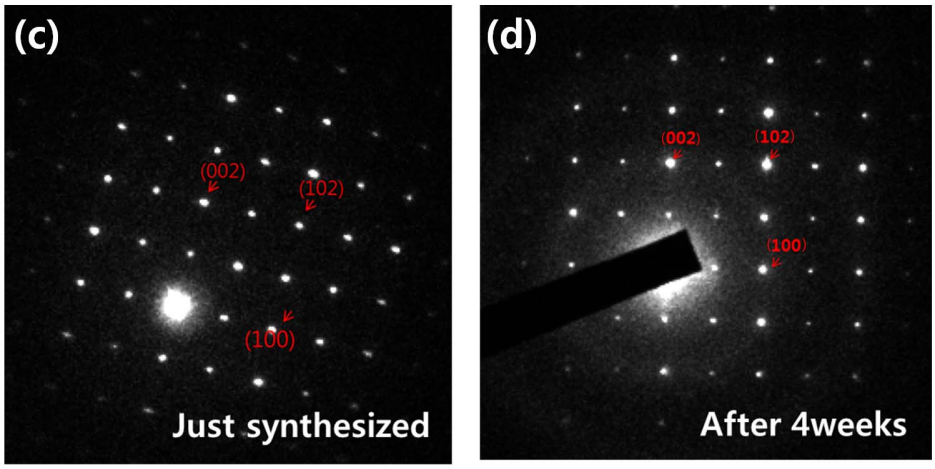

Fig. S11. EDS analysis of (a) just synthesized Cu_3Sn alloy nanoparticles and (b) stored in ambient air condition (RH 50%, 25 ^oC) for 4 weeks The SAED pattern analysis of the Cu_3Sn alloy nanoparticles compared with the stored time in (c) just synthesized nanoparticles and (d) stored in ambient air condition (RH 50%, 25 ^oC) for 4 weeks