Supplementary Information

Highly Durable Cu-Based Electrodes from a Printable Nanoparticle Mixture Ink: Flash-Light-Sintered, Kinetically-Controlled Microstructure

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Experimental details

Synthesis of Cu, Ni, Ag, Cu/$Cu_{10}Sn_3$ core/shell nanoparticles

Cu, Ni, Ag and Cu/$Cu_{10}Sn_3$ core/shell NPs were synthesized by a wet-chemical synthesis method, as reported in our previous papers.[7,15,17,19] All chemicals were used as-received without further purification. Cu acetate ($Cu(CO_2CH_3)_2$, 98%), Ni(II) acetylacetonate ($Ni(C_5H_7O_2)_2$, 95%), tin(II) 2-ethylhexanoate {$Sn[CH_3(CH_2)_3CH(C_2H_5)CO_2]_2$, 95%}, octylamine ($C_8H_{17}NH_2$, 99%), oleylamine (C18H35NH2, 99%), oleic acid ($C_{18}H_{34}O_2$, 90%), phenylhydrazine ($C_6H_5NHNH_2$, 97%), and toluene ($C_6H_5CH_3$, anhydrous, 99.8%) were purchased from Aldrich. Ag nitrate ($AgNO_3$, 99.9%) was purchased from Kojima Chemicals.

For the synthesis of Cu NPs, 10.4 g of Cu acetate and 25.1 g of oleic acid were added into a three-neck round-bottomed flask containing 73.6 mL of octylamine. The flask was fitted with a reflux condenser and a mechanical stirrer. The solution was purged with nitrogen for 60 min and then heated to 150 ^oC. Then, phenylhydrazine was added dropwise, and the reaction was continued for 30 min. After completion of the synthesis reaction, the synthesized Cu nanoparticles were separated by centrifugation and washed with toluene.

For the synthesis of Ni nanoparticles, 5.0 g of Ni(II) acetylacetonate and 4.2 g of oleic acid were added into a four-neck round-bottomed flask containing 61.9 mL of oleylamine. The flask was fitted with a reflux condenser and a mechanical stirrer. The solution was purged with nitrogen for 60 min and then heated to 240 ^oC. Then, phenylhydrazine was added dropwise, and the reaction was continued for 60 min. After completion of the synthesis reaction, the synthesized Ni nanoparticles were separated by centrifugation and washed with toluene.

For the synthesis of Ag NPs, 9.5 g of Ag nitrate and 25.4 ml of oleic acid were added into a three-neck round-bottomed flask containing 93.2 ml of octylamine. The prepared reacting solution was heated to 80 ^{o}C and stirred with a magnetic stirrer under refluxing conditions. When the temperature approached 80 ^{o}C, 87.4 g of phenylhydrazine was injected at an injection rate of 5 ml/min. The reaction was continued for 60 min, and then the mixture was cooled to room temperature. The synthesized Ag nanoparticles were washed with toluene by centrifugation.

For the synthesis of $Cu/Cu_{10}Sn_3$ core/shell nanoparticles, 2.72 g of copper acetate, 2.13 g of tin 2-ethylhexanoate, and 4.23 g of oleic acid were added to a three-neck round-bottom flask containing 71.84 mL of oleylamine. The flask was fitted with a reflux condenser and a mechanical stirrer. The solution was purged with nitrogen for 60 min and then heated to 220 °C. Then, phenylhydrazine was added dropwise, and reaction was continued for 60 min. After completion of the synthesis reaction, the synthesized $Cu/Cu_{10}Sn_3$ core/shell nanoparticles were separated by centrifugation and washed with toluene.

All synthesized nanoparticles were kept in air without additional surface-passivation procedures. For the preparation of spray-printable inks, nanoparticles were dispersed in toluene with a solids loading of 0.7 wt%. The metal nanoparticle inks for spin-coating were prepared with a solids loading of 20 wt%.

Printing metal nanoparticle inks and flash-light-sintering process

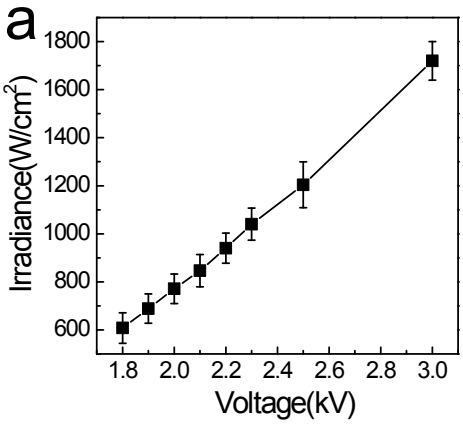
Air-brush printing was carried out using the metal nanoparticle inks with a solids loading of 0.7 wt% on PI (thickness(t) = 75 μm, Kapton film 300HN, Teijin DuPont Films) substrates heated at 100 ^{o}C. An automated spray machine was equipped with a moving

stage/nozzle. For bi-layered electrode structures, the Ag nanoparticle inks with a solids loading of 20 wt% were spin-coated at a rotation speed of 3,000 rpm on O_2-plasma-treated plastic substrates. Flash-light sintering was accomplished using a Xenon flash lamp system (Sinteron 2010, Xenon Corp.) in which an A-type lamp was equipped with a broadband spectrum of 370 to 800 nm. The flash lamp was 0.75 inch in width and 12 inch in length, and the size of the moving stage was 900 cm^2. The air cooled xenon linear flash lamp, located 2 inches away from the substrate stage, delivered optical energy of from 0.26 to 3.49 J/cm^2 as a function of the electrical voltage and duration time for generating the electrical pulse energies. The optical energies of flash lamp irradiation were measured by a radiometer (ITL1700, International Light Technologies) with a detector (SED033, 200-1100 nm, International Light Technologies).

Characterization

The sizes and shapes of the nanoparticles and the microstructures of the conductive layers were examined by high-resolution transmission electron microscopy (HRTEM, Talos F200S, FEI) and scanning electron microscopy (SEM, JSM-6700, JEOL). The crystal structures of the nanoparticles and conductive layers were analyzed by X-ray diffractometry (XRD, D/MAX-2200V, Rigaku). The resistivities of the conductive layers were analyzed by a four-point probe (FPP-HS8, Dasol Eng.). The 85/85 tests were carried out by measuring the electrical properties of the samples stored in a chamber where a harsh environment, of 85 ^oC in temperature and 85 % in humidity, are maintained.

a



b

Time (10^{-3} sec)

Voltage(kV) \ Time	0.5	1.0	1.5	2.0
1.8	0.26	0.61	0.97	1.30
1.9	0.30	0.69	1.10	1.46
2.0	0.34	0.77	1.22	1.63
2.1	0.38	0.84	1.33	1.79
2.2	0.43	0.94	1.48	1.96
2.3	0.48	1.04	1.63	2.16
2.5	0.54	1.21	1.90	2.52
3.0	0.81	1.74	2.67	3.49

(unit: J/cm²)

Figure S1. (a) Intensity variation of the xenon lamp used in this study as a function of voltage, and the variation in optical dose according to the voltage and duration time.

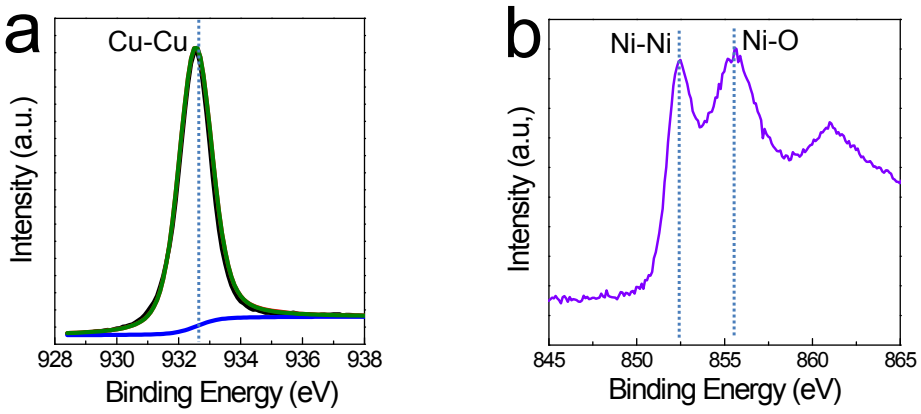


Figure S2. (a) Cu $2p_{3/2}$ and (b) Ni $2p_{3/2}$ XPS spectra of Cu and Ni nanoparticles synthesized in this study.

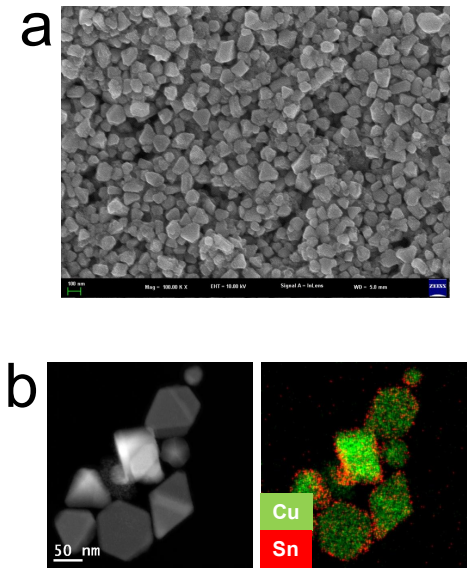


Figure S3. (a) SEM image and (b) HRTEM image and compositional mapping image of $Cu/Cu_{10}Sn_3$ core/shell nanoparticles synthesized in this study.

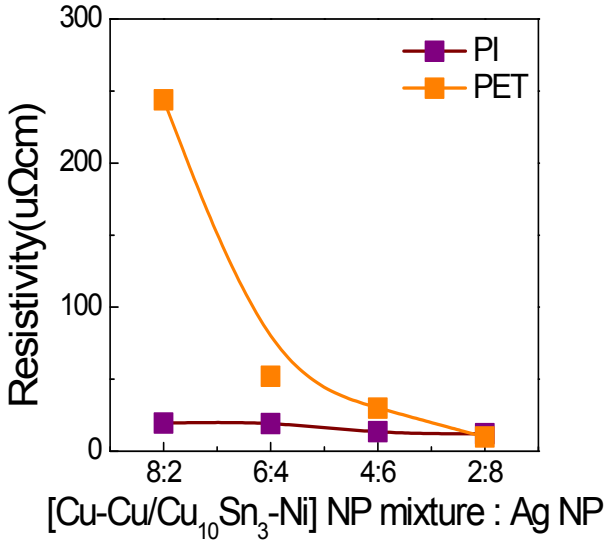


Figure S4. (a) Variations in resistivity for electrodes prepared from Ag-Cu-Cu/$Cu_{10}Sn_3$-Ni nanoparticle mixture inks on PI and PET substrates. Flash-light-sintering was carried out at 2.3 kV for 1.5 msec (1.63 J/cm^2) and 2.0 kV for 1.5 msec (1.22 J/cm^2) for PI and PET substrates, respectively.

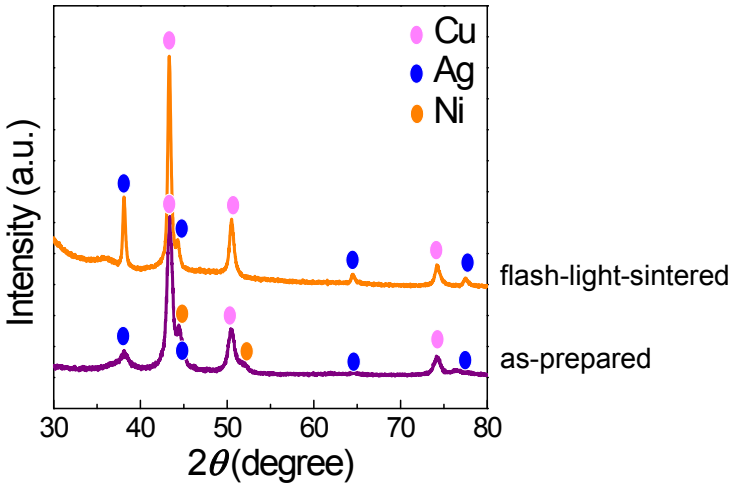


Figure S5. XRD spectra for as-prepared and flash-light-sintered bi-layer electrodes on PET substrate. Flash-light-sintering was carried out at 2.0 kV for 2.0 msec (1.63 J/cm^2).