Supplementary data

Metal Oxide Semiconductor 3D printing: Preparation of Copper (II) Oxide by Fused Deposition Modelling for Multi-functional Semiconducting Applications

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Materials and Methods

The irregular shape copper powder (Zigma Aldrich) with the average size of 45 μm and the purity of 99.99% was mixed with polylactic acide (MU03) with the weight ratio of 80:20. During the mixing, the polymer Cu blend composite was subjected to a high shear force from homogenizer at temperature of 220 ^{o}C. The filament was fabricated by the extrusion method with a controlled static pressure of 14 MN/m^2. The final filament diameter is 1.75 mm which can be used in any standard FDM 3D printing machine. The Cu-blend filament was printed by a FDM printing machine with the sample size of 20x4x4 mm and the procedure is shown in Figure 1A. The printed sample is designed to be internally filled. Afterward the Cu blend composite sample was sintered in the furnace at 400 ^{o}C for 2 hours and 900 ^{o}C for 1 hours under the atmospheric condition to obtain CuO with the same configuration as printed. Later on CuO sample was inspected by X-ray diffraction (XRD) and Scanning Electron Microscope with Energy-dispersive X-ray spectroscopy (SEM-EDX). Universal testing was used to measure mechanical properties such as compressive and flexural strength. Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA) under air flow with 10C/min rate were used to analyze weight loss of the sample and phase transformation. I-V measurement, Hall-effect (HMS-3000), photoluminescence and

UV-vis absorption was measured to observe the electrical and optical properties of CuO fabricated by FDM printer and heat treatment.

Filament characterization by EDX

After the extrusion process, the filament itself was still bendable and rolled up as shown in **Figure S1**A. The cross section of filament was observed by SEM image Figure S1B which implied a homogeneous distribution of (bright) Cu particles inside the (dark) polymer matrix. With a higher magnification in Figure S1C, Cu particles agglomeration is found. The agglomeration is a regular phenomenon in extrusion process, especially in a very high loading additive in this case. The distance between each agglomeration was around 50 μm. The surface of polymer was rough, and there could be more Cu particles which were still covered inside the polymer matrix. In Figure S1D, the combination of EDX signals between C, O, and Cu were shown, and the separated signal of C, O, and Cu were in Figure S1E, S1F, S2G respectively. The blue signal position of Cu in Figure S1G was coexisting with the dark area in C signal in Figure S1E. The Cu particles that was buried deeper than 1 μm were not detected in the image due to the depth limit of the interaction volume of x-ray signal. The signal of C appeared across the filament except at the position where Cu particles were placed. On the other hand, O signal appeared everywhere because PLA has O in the molecules and Cu surface was partially oxidized. The overall appearance of filament was in dark brown color. This filament can be feed into the FDM printer as shown in schematic Figure 1A.The printing injector temperature was set at 220 ^{o}C which was still high enough to melt and flow the Cu blend composite filament without clogging. The filament was extruded through the printing head which move around in x, y, and z directions. Though the sample for this work was printed with the dimension of 20x4x4 mm, the capacity of printer is much bigger as it can be printed in the size of 180x180x240 mm, and it can be bigger for a newer FDM printer model.

High loading composite printing

With the technique in this work, other high loading inorganic composite is possible. The example is shown in **Figure S2** where alumina composite, iron composite, cement composite, and copper composite are possible.

Mass change after oxidation

After the fabrication process, the mass of the sample should follow the Equation S1 which represented the mass action law.

$$W_f = f_m\left(\frac{M_f}{M_o}\right)W_o \qquad \text{(S1)}$$

Where W_f is mass of final sample after the total process. W_o is the original mass of printed sample. f_m is the mass fraction of metal particles in the composite material. M_f is the molar mass of metal oxide after the sintering and calcite process and M_o is the molar mass of metal particles inside the composite material.

The relation between pressure and resistance

The relation between pressure and resistance can be obtained by fitting the curve in Figure 3D with the following Equation S2.

$$P = -28.376 + 425.33\left(\frac{0.4}{1+e^{-\frac{R-111.5}{0.22}}} + \frac{0.6}{1+e^{-\frac{R-112}{1.2}}}\right) \qquad \text{(S2)}$$

Where P is pressure (Torr) and R is resistance (kΩ). With this equation, the pressure in the range of 20-360 Torr can be determined by the output resistance.

The relation between temperature and current

The relation between current and temperature was derived from the fitting curve in Figure 3E with the following Equation S3.

$$I = 10^4\left(e^{-\frac{T}{-19.15}}\right) + 0.1435 \qquad \text{(S3)}$$

Where I is current (mA) and T is temperature (^oC). With this equation, the temperature in the range of 25-150 ^oC

can be determined by output current.

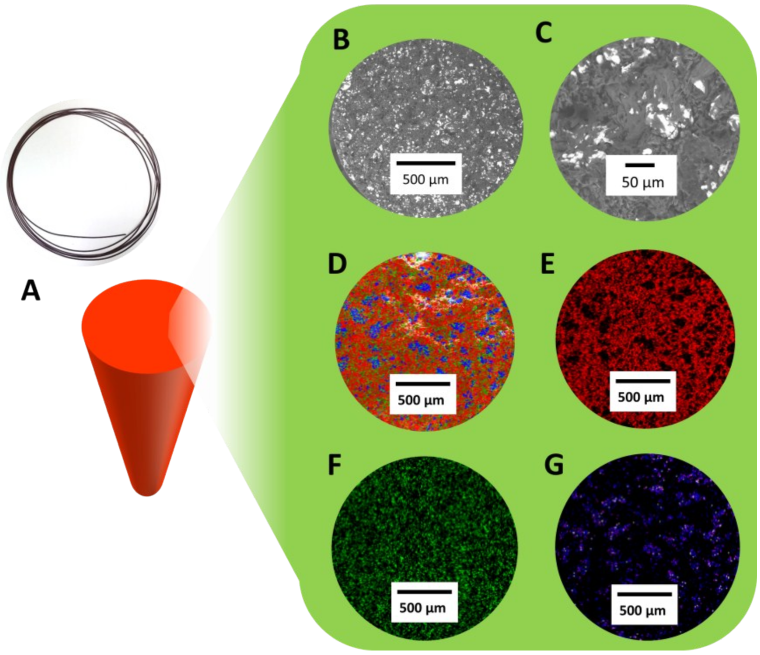

Figure S1. The structure of high Cu loading composite filament. A) The filament is flexible and can be bended around. This flexibility allows it to be feed into FDM printer. The filament has a circular cross section which is shown in schematic image. B) The total cross section of composite filament under SEM image. Cu particles distribute everywhere. C) The high magnification cross section image of composite filament. Cu particles agglomerate in some area. D) The EDX signal mapping from Carbon, Oxygen, and Copper in combination. E) EDX signal mapping from Carbon element. F) EDX signal mapping from Oxygen element. G) EDX signal mapping from Copper element.

Figure S2. FDM printing of high loading alumina composite, iron composite, cement composite, and copper composite.