Supporting Information

Copper inks formed using short carbon chain organic Cu-

precursors

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1. Experimental section

1.1 Materials

Copper hydroxide, copper acetate, hydroxyacetic acid, formic acid, cyclohexylamine, terpineol, ethanol and ethylene glycol were purchased from Beijing Chemical Factory of China and were used as received without further purification. Glass slides(20×20mm) were from Sail and cleaned with ethanol.

1.2 Synthesis

Organic copper decomposition conductive ink (Cu 20wt%), Ink₂₀ was prepared as follows: hydroxyacetic acid (7.6g) and copper hydroxide (3.9g) were first dissolved in 40 ml of water respectively, then mixed and continuous stirring for 1 h at room temperature. The product, copper glycolate, was collected by filtration, washed with water and dried. 4g of the obtained copper glycolate powder was dispersed in 6 ml of a medium containing terpineol and hydroxyacetic acid (1%), then ultrasound for an hour to form the ink. Terpineol was used as a ink solvent instead of ethylene glycol^[1] because it can solidify a wet film at lower temperature.

Organic copper ion ink, Ink_{9.6} was prepared as follows: copper acetate (2.4g) was first dissolved completely in 2.5ml of mixed solvent of ethanol and ethylene glycol under vigorous stirring, and then cyclohexylamine (2ml) was titrated into the above solution dropwise in 60s. After strongly stirring for 10min, formic acid (1.104ml) was added. The mixture was stirring for 60min to form the ink. The color of the solution turned from dark blue to clearly green.

1.3 Patterning and metallization

The copper inks were deposited on glass slides by a drop-coating and solidified at 60° C in oven for 2h, then, annealed in nitrogen at various temperatures for 60 min. The film thickness was controlled by dropping a given amount of copper inks on the glass slides within a fixed area. The sintered films were cleaned with alcohol and natural dried.

1.4 Characterization

The crystalline structure was measured by X-ray diffraction (XRD) using Cu K α and λ =0.15418nm. Fourier transform infrared spectra in the range of 400-4000 cm⁻¹ were recorded on an FTIR Tensor 27 spectrometer using KBr pellets. The thermal profile was measured under nitrogen atmosphere by differential scanning calorimetry (DSC, STA409C, Netzsch) with a heating rate of 10°Cmin⁻¹ from room temperature to 350°C; The chemical composition was

identified by surface energy disperse spectrometer. The morphology of the copper films was investigated by SEM (S-4300, Hitachi, Japan). The sheet electrical resistivity was measured using a four-point probe, and the thickness of the point measured sheet resistivity was measured by a surface profilometer (Dektak 150, Veeco, America) before the specific resistivity was calculated.

2. Organic copper decomposition ink, Ink₂₀

Fig.S1 shows the IR spectrum of the as-prepared copper glycolate, hydroxyacetic acid and copper hydroxide. The absorption peaks between 3,700 and 2,700 cm⁻¹ were undoubtedly the O–H stretch. The intense peak at 1,736 cm⁻¹ derived from CO²⁻ stretch of carboxyl group, which disappeared in the IR spectrum of copper glycolate and two new peaks at 1570 and 1408 cm⁻¹ appeared, meaning the hydroxyacetic acid was coordinated with copper ions.



Fig.S1. FT-IR spectra for copper hydroxide, hydroxyacetic acid and copper glycolate

The wave number difference (Δ) between the asymmetric CO²⁻ stretch peak and the symmetric CO²⁻ stretch peak in the carboxylate complex is used to estimate the type of interaction of the carboxylate moiety with Cu²⁺ ions. Unidentate complexes exhibit the largest Δ values (200–320cm⁻¹); and chelating (bidentate) complexes have the smallest Δ values (<110 cm⁻¹). The medium Δ values (140–190 cm⁻¹) for bridging complexes are greater than those of chelating complexes, and close to the ionic values^[2]. Therefore, we deduced that the carboxylate moiety and Cu²⁺ ions interacted in a bridge way (Δ value: 1736–1570 = 166 cm⁻¹).



Fig.S2. XRD patterns of the as prepared copper glycolate

Fig.S2 shows the XRD patterns of the as-prepared copper glycolate measured in 2θ from 5° to 90°. The main peaks appeared at 15.8°, 18.8°, 20.9°, 24.1°, 24.7°, 26.7°, 27.7° and 36.1°. No diffraction

peaks from copper hydroxide were detected, indicating that the following neutralization reaction was carried out completely.

$Cu(OH)_2 + 2OHCH_2COOH \xrightarrow{\Delta} Cu(OHCH_2COO)_2 + 2H_2O(l)$

Fig.S3(a, b) give the SEM image of the as-prepared copper glycolate, which clearly showed a flowerlike morphology of the sample with the average size of about $25\mu m$ in diameter. Further magnified image reveals that the flowerlike structure is assembled by well-defined flakes with difference sizes .



Fig.S3 SEM image (a) and corresponding magnified image (b) of the as-prepared copper glycolate

Fig.S4 is the EDS result of the as-prepared copper glycolate. Four elements (C, O, Cu and Au) were detected. Of them, C, O, Cu elements well accords with the original composition, and Au is from the coating for the electric measurement by SEM.



Fig.S4 The EDS result of the as-prepared copper glycolate

As Fig. S5 showed, the resistivity of the film decreased from $5.03 \times 10^{-5}\Omega \cdot \text{cm}$ to $2.01 \times 10^{-5}\Omega \cdot \text{cm}$ as the sintering temperature increased from 260°C to 320°C, which can be easy understood. At higher temperature, more copper glycolate decomposed, copper nanoparticles grew and better connected. However, the film surface annealed over 320°C looked a bit dark, probably due to a little amount oxidation of copper NPs at higher temperature.



Fig.S5. the resistivity of the deposited copper films sintered at various temperatures in nitrogen for 60 min



Fig.S6. Magnified SEM images and EDS spectra of Fig.4a, 4c and 4e

3. Organic copper ion ink, Ink_{9.6}



Fig.S7. XRD spectra of the copper film sintered at 220°C.



Fig.S8. SEM images and EDX spectra of the sintered copper films of $Ink_{9.6}$ with different solvent compositions: a, ethanol: ethylene glycol = 1:0; c, ethanol: ethylene glycol = 1:1; b and d were the magnified images of a and c; e is the cross-sectional image of the film; f taken from c)

The resistivity of sintered copper films was calculated using following equation:

 $\rho = Rab/l$

where ρ is resistance, a, b and l is the cross sectional width, thickness and length of the copper film, respectively.

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