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Molecular Copper Decomposition ink for Printable Electronics

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Nanostructured metal materials are the frontrunners of numerous electronic advancements. While realizing such potential, it is indispensable to address its oxidation and stability drawbacks, that are due to its high surface energies. Here, we report printable and air-stable molecular metal ink materials from metal-organic decomposition by using copper ions, including both copper formate and aqueous copper-amine complex. By complexing copper formate with amines, the decomposition temperature of printed molecular copper ink can be achieved at 100 °C, while maintaining its electric conductivity. The printed copper conductors exhibit a high electric conductivity of 35 MS/m (>50% of bulk copper's electric conductivity at room temperature) and an electromagnetic interference shielding effectiveness of 63 dB. The findings shown here of molecular decomposition ink is promising for applications in printable electronics.

Electronics have advanced rapidly, allowing for miniaturized sensors, antennas and circuits to be printable, compact, lightweight and flexible.[1-3] Recent years have seen an increasing emergence of interest in using printable materials, such as graphene,[4, 5] MXenes,[6, 7] metal nanostructures,[8-12] and conductive polymers.[13, 14] Of these materials, copper shows immense potential due to its abundance, low-cost, and inherently high conductivity.[8-12] Bulk copper has been extensively used in electronics, but copper itself suffers from oxidation which hinders its conductivity.[12] This is further exacerbated on the nanoscale due to higher surface energies, resulting in greater potential for oxidation.[11, 15, 16] The potential for oxidation overtime greatly limits the stability, reliability and printability of copper nanostructures. Another avenue for printable metal features would be to utilize molecular ink material instead.[3, 17-21] Unlike the nanostructures, molecular inks do not oxidize as they start as ions (such as Cu^{2+} instead of Cu^0).[16, 22] However, typical molecular inks suffer from having low concentrations and organic volatile solvents. In spite of these drawbacks, expanding the use of molecular inks can provide new avenues for printable electronics.[3, 16, 18-21]

In this study, we explore the printable and air-stable molecular copper ink materials from metal-organic decomposition (MOD) by using copper ions, including both copper formate (Cu-F MOD) and aqueous copper formate amine complex materials (Cu-A MOD). The decomposition temperature of Cu-F can be reduced by complexing with amines, allowing for lower temperature compatibility with paper and polyester based flexible electronics. The Cu-F MOD ink allows for significantly higher loading due to lower solvent content, while exhibiting high electric conductivity (35 MS/m) of printed features. Additionally, it shows high electromagnetic interference shielding (EMI-SH) efficiency of 63 dB. The Cu-A MOD ink, on the other hand, is focused on utilizing water as the solvent, to achieve high electric conductivities and EMI-SH capabilities.

Figure 1 shows the schematic diagram from the MOD ink preparation to the printed copper conductor. The preparation of Copper(II) Formate (Cu-F) can be made through a two-step reaction by first reacting copper sulfate with sodium carbonate to form copper carbonate, then reacting with formic acid to produce copper formate. The molecular MOD inks can be prepared in two different ways by using Cu-F to either yield Cu-FMOD or complexing with amines to form Cu-A MOD (The details are shown in the experimental section). The formation of Cu-F MOD particles increases the amount of Cu content loading in the ink, whilst resulting in a slurry paste. Complexing Cu-F with amines can alter its printability characteristics, such as improving solubility in different

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Electronic Supplementary Information (ESI) available: Experimental procedures and descriptions on the synthesis of Cu-F and Cu-A MOD ink and the electronic/thermal characteristics of printed Cu features.

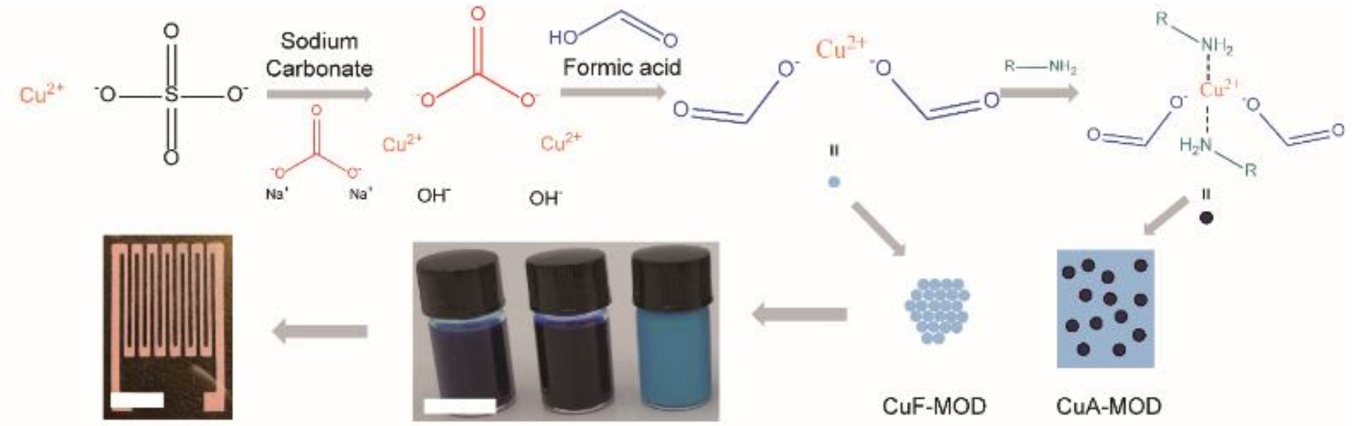

Figure 1. Schematic flow of the synthetic process towards copper formate and copper formate-amine complex (top) and printing of ink for printable electronics. The scale bar represents 15 mm.

solvents or decreasing the decomposition temperature of Cu-F. The two amines we investigate are tetramethylethylenediamine (TMEDA) and 2-amino-2-methyl-1-propanol (AMP). Importantly, the addition of TMEDA improves the Cu-A MOD complex's solubility in water.

Figures 2a shows the scanning electron microscopy (SEM) image for the printed Cu-F MOD features before (top) and after (bottom) sintering. The as-prepared Cu-F MOD materials are observed to be platelets, and once sintered the conductor formed a uniform and dense film (Further SEM images are shown in the Figure S1). The thermogravimetric curves (TGA) are shown in Figure 2b for the Cu-F MOD and Cu-A MOD complex. A significant decrease in weight around 200-220 °C for Cu-F correlates to the decomposition of Cu-F into the metallic Cu. On the other hand, Cu-A MOD complex shows a significant change in weight around 100-150°C, a decrease in decomposition temperature by 50 °C as compared to Cu-F MOD. The TGA of Cu-F with a single amine shows a significant change in weight at 150 and 175 °C for TMEDA and AMP, respectively, corresponding to the decomposition of Cu-A MOD with these amines (Figure S2). This decrease in decomposition temperature is attributed to the effect of amine complexation with the Cu ion.[17] To further confirm the formation of Cu-A MOD complex, Fourier transform infrared (FTIR) spectra for Cu-F and Cu-A MOD are shown in Figure 2c. The spectrum of Cu-F has a broad peak around 3000-3500 cm^{-1} which is indicative of O-H stretching bands, suggesting the presence of water. Cu-A, on the other hand, have defined and sharper peaks at this region which corresponds to both C-H (below 3000 cm^{-1}) and N-H stretching bands (3000 to 3300 cm^{-1}), the latter suggesting the presence of amines. Additionally, the C-H and N-H spectral features of Cu-F TMEDA and Cu-F AMP are also shown in Cu-A (Figure S3). The clear difference of bands in the FTIR between Cu-A and Cu-F further suggests Cu-F complexation.

In Figure 3a, electric conductivity of the printed samples made from Cu-F MOD are investigated as a function of solvent dimethylformamide (DMF) concentration (wt. %). At lower concentrations of DMF, it is observed that its electric conductivity can reach 35 MS/m (above 50% of bulk copper's conductivity). As the concentration of DMF increases, the conductivity decreases to 10 MS/m at 5 wt. %. This suggests that excess DMF in the ball-milling process will negatively affect the resulting Cu-F MOD once prepared for printing. Figure 3b demonstrates a sintering profile between 100 °C and 200 °C. An increase in conductivity is observed with increasing temperature from 7.4 MS/m to 35.8 MS/m. This suggests that 200 °C is the optimum temperature for Cu-F MOD. For Cu-A MOD ink, the amine ratio and sintering profiles play an important role in its electric conductivity. Figure 3c explores the amine molar ratios of TMEDA to AMP, where an amine ratio of 1:0 and 0:1 represents only TMEDA and AMP is used, respectively. It is observed that more TMEDA results in a complex which is water soluble, whereas more AMP decreases its solubility in water (Figure S4). Importantly, a molar ratio of 1:1 of TMEDA to AMP produces the printed copper feature with the optimum electric conductivity of 2 MS/m, while the other amine ratios show the decreased conductivities from 250 kS/m to 750 kS/m. Further printability studies of Cu-A MOD ink materials are carried out through investigating the addition of dodecanoic acid (DDA, Figure S5a-S5b), and hydroxypropyl methylcellulose (HPMC) concentration (Figure S5c). It is observed that the additive of DDA plays an important role in the percolation of the copper prints (The SEM images are shown in Figure S6). It should be noted that the role of DDA is a sintering agent, providing a control on the growth of the copper particle.[17] However, adding high content of DDA would decrease the conductivity due to the formation of small copper

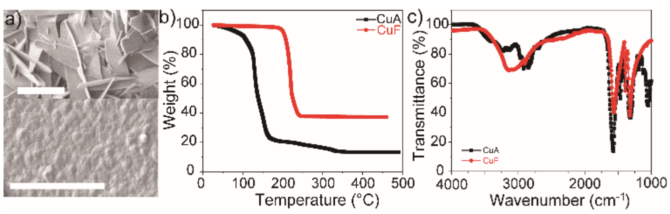

Figure 2. (a) The SEM image of prepared Cu-F particles (top) and sintered conductor (bottom). The scale bar is 5μm. A TGA curve (b) and FTIR spectra (c) are shown for Cu-F (red) and Cu-A (black) MOD ink.

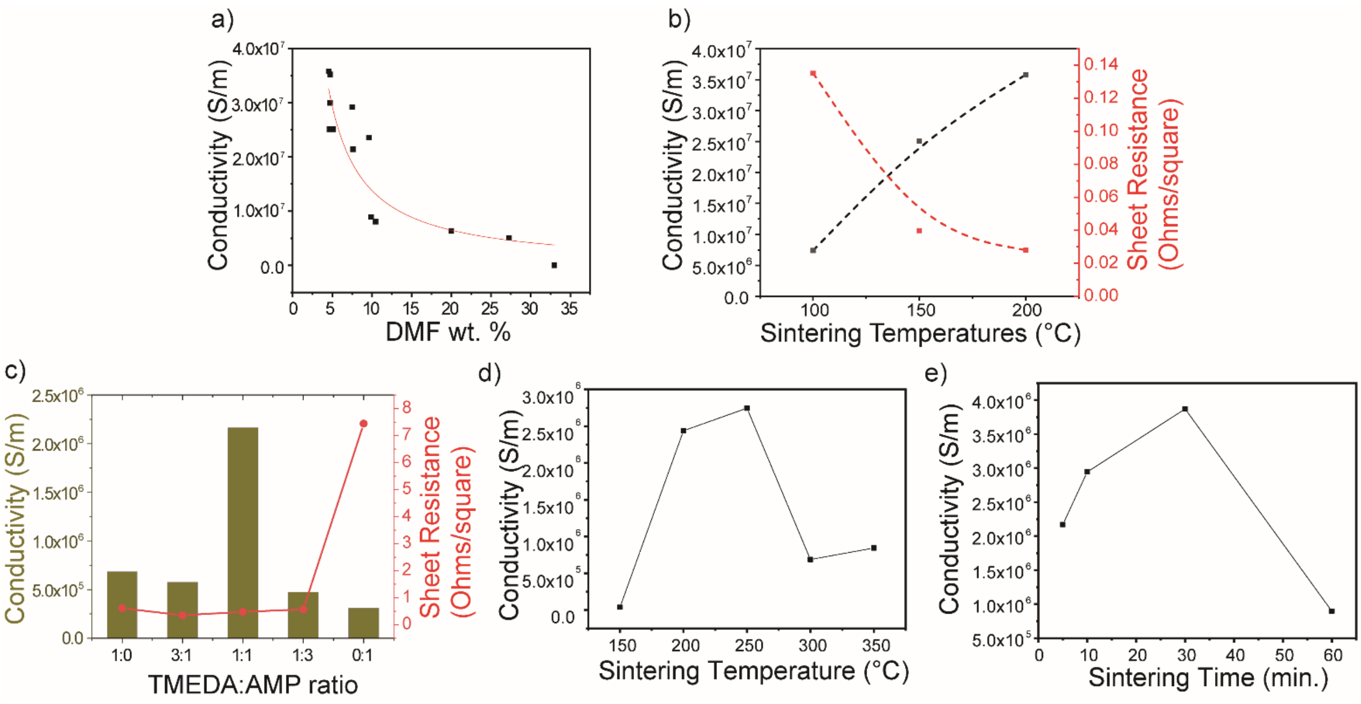

Figure 3. (a) A graph of the conductivity of sintered Cu-F MOD prints as a function of DMF wt %. (b) The conductivity values read at varying sintering temperatures for the optimal formulation of the Cu-F MOD ink. (c) The conductivity (green) and sheet resistance (red) values of sintered Cu-A MOD at varying amine ratios. The conductivity values of sintered Cu-A MOD at varying sintering temperatures (d) and times (e).

particles. Additionally, the increase in HPMC concentration leads to the decreased electric conductivity of printed copper features. Therefore, the optimum sintering temperature and time for Cu-A MOD ink is shown in Figure 3d and 3e, respectively. For sintering temperature, it is observed that sintering at 150 °C produces a conductive copper feature (~30 kS/m). Increasing the sintering temperatures increases the electric conductivity to 3 MS/m at 250 °C. When evaluating the sintering time at 250 °C, an increase in electric conductivity is observed from 5 minutes (~2 MS/m) to 30 minutes (around 4 MS/m). This ink also successfully demonstrates the potential to be photonically sintered on varying substrates such as polyimide, polyester and paper (Figure S8).

Electromagnetic interference shielding of metallic materials is necessary to reflect or absorb the incident electromagnetic (EM) waves in electronic devices. They tend to be utilized in the bulk form. However, while effective, the bulk materials tend to be heavy, rigid, and are also energetically expensive to produce. Here, the copper molecular inks are printed and evaluated for its EMI-SH capabilities. A schematic image of the interaction between the printed Cu and the EM wave is described in Figure 4a. While the two mechanisms of EMI-SH are to reflect or to absorb the incident wave, due to high electric conductivities of copper conductors. As such, these printed materials have high EMI-SH efficiencies and have great potentials while decreasing the amount of material, resulting in a lighter and flexible film relative to bulk. Figure 4b shows the EMI-SH efficiency as a function of electric conductivity for both printed and sintered Cu-F and Cu-A MOD features. The EMI-SH coefficients for Cu-A MOD and Cu-F MOD show an optimum value of 50 dB and 63 dB, respectively. An increase in electric conductivity increases the EMI-SH efficiency of the printed copper features up to 3 MS/m before plateauing.

We report the copper-based MOD inks by using the copper ions as the material feedstock. The Cu-F MOD ink produces a dense and continuous film, yielding high electric conductivity of 35 MS/m (greater than 50% of bulk copper's conductivity) along with high EMI-SH efficiencies (63 dB). Once complex with an amine, a 50 °C decrease in decomposition temperature is observed, allowing for a lower temperature sintering. Comparatively, the aqueous Cu-A MOD complex exhibits an electric conductivity of 4 MS/m and EMI-SH effectiveness of 50

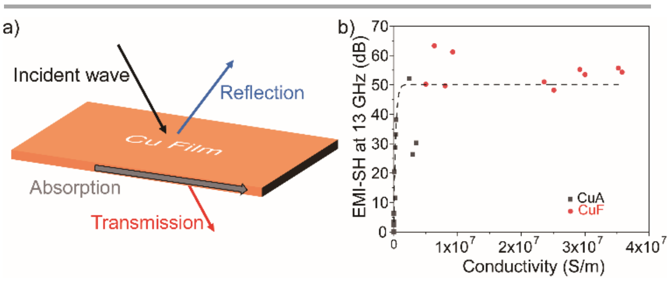

Figure 4. (a) A schematic of the EMI-SH process starting with the incident wave (black) and resulting in either a reflection (blue), transmission (red), or absorption (grey) of the wave. (b) The EMI-SH efficiencies as a function of conductivity for Cu-F (red) and Cu-A (black)-MOD complex prints. The fit is shown to describe the observed trend of EMI-SH with increasing conductivity.

dB. Utilizing copper-based MOD inks simplifies and shortens the processability of the materials for printable ready inks. In addition, exploring the potential for greener solvents or decreasing the temperature needed for sintering opens the potential towards printable inks that are more environmentally friendly.

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The manuscript was written through contributions of all authors. S. R designed and supervised the project. A. S and A. I worked on the synthesis of Cu molecular ink materials and the printable ink preparation. A.S, and A. I, did the sintering studies. A. S, A. I, and S. K did the characterization studies. J. Y supervised the project. Financial support was provided by the DEVCOM Army Research Laboratory supports S. R. under Award W911NF-20-2-0016

There are no conflicts to declare.

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