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A Self-Reducible and Alcohol-Soluble Copper-Based Metal–Organic Decomposition Ink for Printed Electronics

Dong-Hun Shin,[†] Seunghee Woo,[‡] Hyesuk Yem,[§] Minjeong Cha,[†] Sanghun Cho,[†] Mingyu Kang,[‖] Sooncheol Jeong,[§] Yoonhyun Kim,[§] Kyungtae Kang,[‖] and Yuanzhe Piao*[,†,⊥]

[†]Program in Nano Science and Technology, Graduate School of Convergence Science and Technology, Seoul National University, Suwon 443-270, Republic of Korea

[‡]Department of Chemistry, Seoul National University, Seoul 151-747, Republic of Korea

[§]R&D Center, Chang Sung Co. Ltd., 11-9 Namdong Industrial Area, Namdong-gu, Incheon 405-100, Republic of Korea

[‖]Korea Institute of Industrial Technology, Ansan, Gyeonggi 426-173, Republic of Korea

[⊥]Advanced Institutes of Convergence Technology, Suwon 443-270, Republic of Korea

S *Supporting Information*

ABSTRACT: We report a novel method for the synthesis of a self-reducible (thermally reducible without a reducing atmosphere) and alcohol-soluble copper-based metal–organic decomposition (MOD) ink for printed electronics. Alcohol-solvent-based conductive inks are necessary for commercial printing processes such as reverse offset printing. We selected copper(II) formate as a precursor and alkanolamine (2-amino-2-methyl-1-propanol) as a ligand to make an alcohol-solvent-based conductive ink and to assist in the reduction reaction of copper(II) formate. In addition, a co-complexing agent (octylamine) and a sintering helper (hexanoic acid) were introduced to improve the metallic copper film. The specific resistivity of copper-based MOD ink (Cuf-AMP-OH ink) after heat treatment at 350 °C is 9.46 μΩ·cm, which is 5.5 times higher than the specific resistivity of bulk copper. A simple stamping transfer was conducted to demonstrate the potential of our ink for commercial printing processes.

KEYWORDS: *conductive ink, metal–organic decomposition ink, alkanolamine, copper formate*

1. INTRODUCTION

Simplicity is an important attribute of printed electronics techniques, and for this reason, such techniques are regarded as promising candidates to replace other methods commonly adopted in the fabrication of conductive lines or electrodes in electronic devices.[1,2] The conventional photolithography method takes multiple steps to obtain conductive patterns on substrates, including deposition, masking, lithography, and etching processes. These steps are complicated and need expensive equipment, which makes the final products expensive.[3,4] On the other hand, the printing method involves only two steps, printing inks on the substrates and sintering, which allows the manufacturing of electronic devices to be more cost-efficient. Therefore, if the printed electronics technique can replace traditional photolithography, it will have a significant impact on the consumer electronics market. However, there are several issues that must be resolved before the printed electronics technique can be used for real applications. One important issue is the development of appropriate conductive inks. Currently, silver-based inks are most commonly used for printed electronics[1,4] mainly because they have the lowest resistivity among all materials (1.59 μΩ·cm) and a high redox potential, which enables them to be handled more easily and to be stable in air. However, silver also has two drawbacks: low electromigration resistance[5] and high cost.[1] The high cost is a critical problem because it removes the main advantage of the printed electronics technique (low-cost products). In this respect, copper has gained significant research interest in the printed electronics field, not only because it is a low-cost material but also because it possesses excellent electronic properties, such as low resistivity (1.72 μΩ·cm, similar to silver) and higher electromigration resistance.[6] Several methods for the synthesis of copper-nanoparticle-based inks for printed electronics have been published.[6−10] However, because of the low oxidation resistivity of copper, these inks inevitably contain copper oxides and yield low-quality films.[4]

To overcome this problem of easy oxidation, copper-based metal–organic decomposition (MOD) inks are also being researched.[11−14] MOD inks consist of metal–organic compounds, solvents, and some additives. These types of inks have their copper source in a monovalent or divalent state in the metal–organic compounds, so there is no possibility for similar problems such as the formation of undesired copper oxide or precipitation of the metal source to occur. Despite their

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strengths as conductive inks, there have been limited studies on copper-based MOD inks, and these inks have two shortcomings that make them hard to apply commercially. First, most of them require a reducing atmosphere (e.g., hydrogen gas or formic gas), which should be avoided for the industrial production of printed electronics because of safety and cost concerns. Second, these inks are not generally based on alcohol solvents. As far as mass production is concerned, the inks should work well for commercial printing processes, especially reverse offset printing, which is regarded as a suitable technique for mass production with high resolution.[15] Because such printing processes commonly use poly(dimethylsiloxane) (PDMS) as a blanket layer,[16] inks that have good compatibility with PDMS should be selected carefully. Alcohol-solvent-based conductive inks might be good candidates for commercial printing processes because, unlike nonpolar solvents, alcohol solvents do not lead to damage on PDMS (swelling).[17] In this regard, it is necessary to develop alcohol-soluble and self-reducible copper-based MOD inks for commercialization of printed electronics.

Herein, we report a new method for the synthesis of a self-reducible and alcohol-soluble copper-based MOD ink for printed electronics. To synthesize the ink, copper(II) formate is chosen as the starting material because it can be thermally decomposed to metallic copper and no residuals remain after calcination. Furthermore, to make copper(II) formate soluble in alcohols and to lower its decomposition temperature, we used an alkanolamine called 2-amino-2-methyl-1-propanol (AMP) as a ligand for copper(II) formate. In addition, to achieve an even better copper film after heat treatment of the MOD ink, we introduced octylamine and hexanoic acid to the MOD ink as a co-complexing agent and a sintering helper, respectively. These agents were added based on several examples of solventless nanoparticle synthesis. To the best of our knowledge, this is the first use of the concept of solventless nanoparticle synthesis to improve the performance of the MOD ink. The specific resistivity of the heat-treated MOD ink was measured as a function of the temperature, and a simple stamping transfer using PDMS as a stamping mold is briefly discussed.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Materials. Copper(II) formate tetrahydrate (98%) was obtained from Alfa Aesar. Methyl alcohol (99.8%), isopropyl alcohol (99.8%), benzyl alcohol (99%), ethanolamine (MEA; 99%), diethanolamine (DEA; 99%), and toluene (99.8%) were obtained from Samchun. 2-Amino-2-methyl-1-propanol (AMP; 95%), *tert*-butyl alcohol (>99%), octylamine (99%), amino-2-propanol (A2P; 93%), and oleic acid (technical grade) were obtained from Aldrich. Hexanoic acid (98%) and diisopropanolamine (DIPA; 98%) were obtained from Junsei. All reagents were used as received without further purification.

2.2. Synthesis of Copper(II) Formate Based Metal−Organic Compounds. A copper(II) formate/AMP (Cuf-AMP) complex based ink was synthesized as follows. First, 30 mL of methyl alcohol and 260 mmol of AMP (complexing agent) were added to a 250 mL flask and magnetically stirred for 30 min. Then, 130 mmol of a copper(II) formate tetrahydrate powder was introduced to the mixture (the molar ratio of copper(II) formate to the complexing agent was fixed to 1:2). An instant color change to transparent blue occurred as soon as copper(II) formate tetrahydrate was added. This solution was stirred for 1 h to ensure complete formation of the Cuf-AMP complexes. The resulting solution was then dried to extract methyl alcohol and water by a rotary evaporator under reduced pressure at 50 °C, after which vacuum drying was carried out for 8 h at the same temperature. Finally, a high-viscosity liquid with a dark-blue color was obtained (called the Cuf-AMP complexes), and 3 g of it was dissolved in 1.29 g of isopropyl alcohol by sonication and vortexing to form Cuf-AMP ink. Modified ink (Cuf-AMP-O ink) was synthesized in the same manner as the Cuf-AMP ink, except a mixture of 130 mmol of AMP and 130 mmol of octylamine was added instead of 260 mmol of AMP. Additionally, sintering-promoted modified ink (Cuf-AMP-OH ink) was also prepared by adding 40 μL of hexanoic acid to 4.29 g of Cuf-AMP-O ink.

2.3. Preparation of Conductive Copper Films. To prepare the conductive copper films, 200 μL of ink was dropped to a 1.5 cm × 1.5 cm glass substrate and spread out on the entire substrate using a pipet tip. This ink-coated glass substrate was baked at a temperature range from 200 to 350 °C for 30 min under a nitrogen (99.99%) atmosphere.

2.4. Stamping Transfer Test. Copper-based MOD ink (Cuf-AMP-OH ink) was spin-coated on a PDMS substrate at 1200 rpm for 120 s and dried for 10 min under vacuum. This spin-coated MOD ink on the PDMS stamp was transferred onto an ultraviolet ozone (UVO)-treated glass substrate (the glass was exposed to UVO for 20 min). This transferred MOD ink on a glass substrate was heat treated at 300 °C for 30 min under a nitrogen atmosphere.

2.5. Characterization. The surface morphology of the films was characterized by scanning electron microscopy (SEM; Hitachi S-4800). For thermogravimetric analysis (TGA), a TGA/DSC 1 star system (Mettler Toledo) was used with a heating rate of 10 °C/min under a nitrogen (99.9999%) atmosphere. X-ray diffraction (XRD) patterns were obtained on a New D8 Advance diffractometer (Bruker) in the reflection geometry using Cu Kα radiation (1.5406 Å). Elemental analyses were performed using a ThermoFinnigan Flash1112 (CE Instrument, Italy). The surfaces of the copper films after heat treatment of ink were investigated by X-ray photoelectron spectroscopy (XPS; Sigma Probe, ThermoVG, U.K.). The sheet resistivity was measured using a four-point probe (CMT-SERIES, CHANG MIN), and the thickness of the point where we measured the sheet resistivity was measured by a surface profiler (Alpha-Step IQ, KLA Tencor) before the specific resistivity was calculated. This step was repeated more than five times, and average values are reported in this paper.

3. RESULTS AND DISCUSSION

In this study, the copper-based MOD ink is prepared by complexing copper(II) formate with AMP and octylamine and then dissolving them into an alcohol solvent. A small amount of fatty acid (hexanoic acid) was also introduced to produce a well-sintered copper film after heat treatment. To elucidate the exact calcination and sintering mechanisms and to achieve the best performance in the final results, the following experiments were conducted carefully. First, the role of the alkanolamine (especially AMP) is examined and discussed. Second, the co-complexing agent (octylamine) and sintering helper (hexanoic acid) are introduced to produce a better metallic copper film. Third, the resistivities of the copper films sintered at various temperatures and a simple experiment demonstrating the potential use of our copper-based MOD ink for commercial printing processes are presented.

3.1. Roles of AMP. Copper formate is a promising material for copper MOD inks because it can be thermally reduced to metallic copper without a reducing atmosphere and because it leaves no byproducts after thermal decomposition. However, copper formate itself is not a suitable copper source for conductive inks because it is not soluble in most organic solvents. Thus, to employ copper(II) formate as a copper precursor in a conductive ink, it must be modified to be soluble in an appropriate solvent. For this purpose, Yabuki et al. suggested a way to change its solubility.[14] They introduced alkylamines to copper(II) formate to generate copper(II)

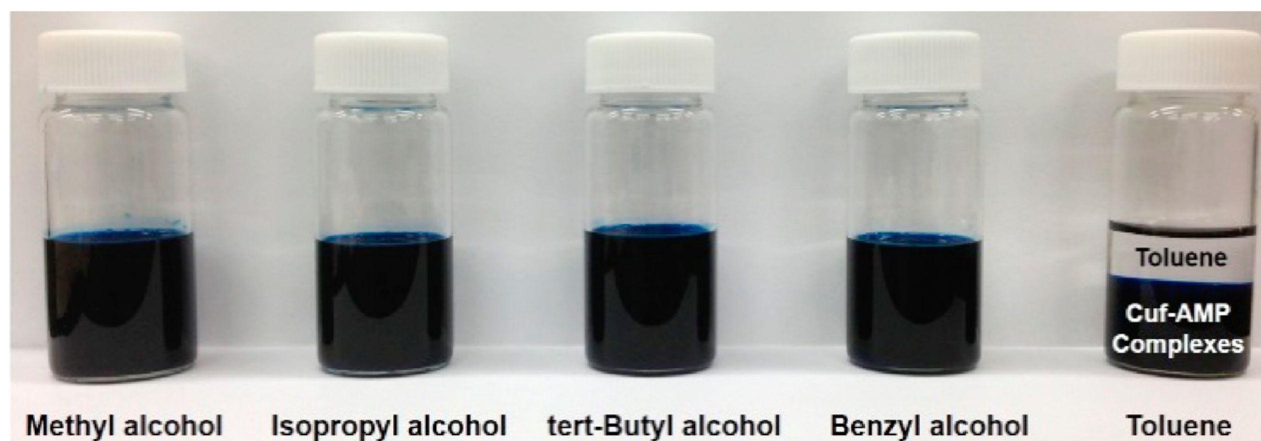


Figure 1. Photograph of Cuf-AMP complexes dissolved in various alcohols and toluene. In the latter case, phase separation between an upper toluene-rich phase and a lower Cuf-AMP complex phase takes place.

formate/alkylamine complexes, and because of the alkyl groups of these complexes' ligands, copper(II) formate exhibited good solubility in toluene. Although their method could allow copper(II) formate to be employed as a copper source for conductive ink, it is not suitable for printing processes involving PDMS blankets because introducing an alkylamine only allows nonpolar-solvent-based inks. To overcome this limitation, we introduced AMP (a kind of alkanolamine) to copper(II) formate and successfully synthesized an alcohol-solvent-based copper MOD ink. In this study, AMP has two roles. First, it helps copper(II) formate to freely dissolve in the alcohol solvent and, second, it lowers the decomposition temperature of copper(II) formate by acting as a mild reducing agent. A photograph of Cuf-AMP complexes [the molar ratio between copper(II) formate and AMP is 1:2] dissolved in various alcohols and a nonpolar solvent (toluene) is shown in Figure 1. Ethyl alcohol, isopropyl alcohol, *tert*-butyl alcohol, and benzyl alcohol were introduced as solvents to confirm the good solubility of this complex in alcohols. The complex could not dissolve in the nonpolar solvent (toluene) but completely dissolved in these alcohols, and no precipitation or separation layer was observed even after storage for 2 months. This result confirms that the method presented here can provide excellent solubility of copper(II) formate in alcohols. The reason for the good alcohol solubility is probably related to the hydroxyl group on the alkanolamine. We hypothesize that only the amino group of AMP seems to coordinate with copper(II) formate and the oxygen in the hydroxyl group does not participate in the coordination because the complexes' color is the same as that of copper(II) formate/alkylamine complexes.[18] Consequently, the uncoordinated hydroxyl group and alkane backbone of the ligands help copper(II) formate to freely dissolve in alcohols, according to the aphorism "like dissolves like." However, when water was added to Cuf-AMP complexes, precipitation occurred (see Figure S1 in the Supporting Information, SI). Water molecules in this case seem to act as additional ligands for Cuf-AMP complexes, and the resulting products are not soluble in both water and alcohols. Hence, water contents in MOD ink in this study should be avoided to maintain the quality of the ink.

In addition to the first role of AMP discussed above, it also acts as a mild reducing agent to lower the thermal decomposition temperature of copper(II) formate. The TGA data clearly demonstrate this second role of AMP (Figure 2). In

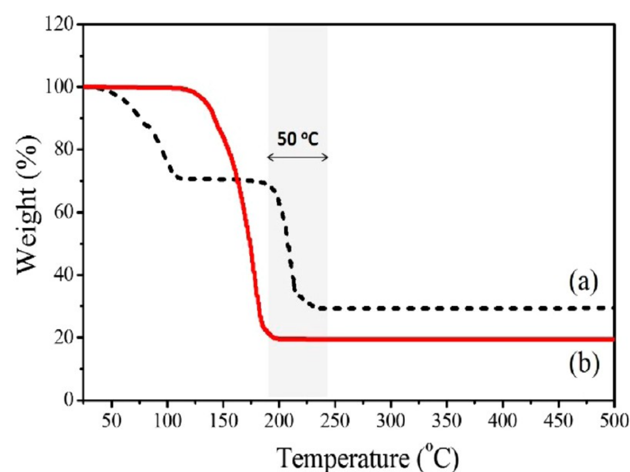


Figure 2. TGA of (a) commercial copper(II) formate tetrahydrate and (b) the Cuf-AMP complexes.

Figure 2a (TGA curve of commercial copper(II) formate tetrahydrate), a two-step weight loss is observed. The first weight loss starts from near 50 °C and finishes at 114 °C and occurs because of dehydration of tetrahydrate.[18] The second weight loss starts from around 188 °C and ends near 240 °C and is caused by decomposition of anhydrous copper(II) formate into metallic copper.[18,19] However, in the case of Cuf-AMP complexes, a one-step weight loss is observed that starts near 125 °C and ends near 190 °C (Figure 2b). The difference between the complete decomposition temperatures of commercial copper(II) formate tetrahydrate and the Cuf-AMP complexes is approximately 50 °C (Figure 2). This difference indicates that AMP can effectively assist in the reduction of copper(II) formate. In addition to TGA analysis, XRD analysis was conducted after heat treatment of the Cuf-AMP complexes at 175 °C for 30 min under a nitrogen atmosphere, to identify whether the Cuf-AMP complexes were completely reduced to metallic copper. The XRD pattern in Figure 3 shows that only metallic copper exists, and no other undesired substances (Cu_2O or CuO) are detected after heat treatment of the Cuf-AMP complexes. This mild reducing ability of AMP may be related to the properties of the alkanolamine. Alkanolamines are subject to oxidative degradation under heating conditions by dioxygen or oxidants.[19−21] Because the thermal treatment of MOD ink in this study is

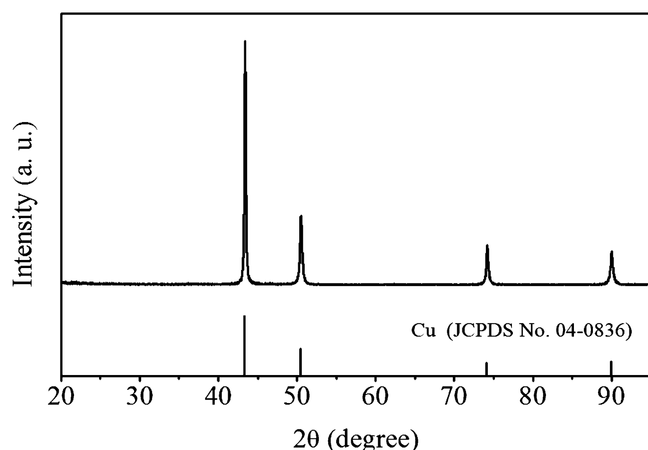


Figure 3. XRD pattern of the copper film after heat treatment of the Cuf-AMP complexes at 175 °C for 30 min under a nitrogen atmosphere.

performed under an inert atmosphere, the partial pressure of dioxygen during calcination is negligible. Thus, oxidative degradation of the alkanolamine by dioxygen is not considered in this study. On the other hand, in the absence of dioxygen, metal ions with a proper redox potential can directly oxidize the alkanolamine and consequently become reduced.[19] This situation matches well with the thermal treatment of MOD ink in this study because the main factors required for oxidative degradation of the alkanolamine by metal ions, namely, the presence of metal ions and alkanolamines, a high temperature, and the absence of dioxygen, are fulfilled. Therefore, it is possible that some AMPs are directly oxidized by copper ions and donate electrons to them during heating of the Cuf-AMP complexes, and this reaction would promote the reduction of copper(II) formate, lowering the decomposition temperature.

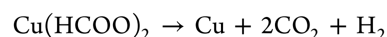
We tried several alkanolamines to synthesize a suitable MOD ink, including MEA, A2P, DEA, DIPA, and AMP. The synthetic procedures for copper(II) formate/alkanolamine complexes with different alkanolamine compounds were similar to the procedure for Cuf-AMP ink described in the Experimental Section, except for synthesis of the MEA complex. Because the Cuf-MEA complexes cannot be synthesized using the procedure for Cuf-AMP ink, we just dissolved copper(II) formate tetrahydrate in MEA (the molar ratio between copper(II) formate and MEA is also 1:2). Table 1 shows elemental analysis data for several copper(II) formate/alkanolamine complexes calcined at 300 °C for 30 min (primary alkanolamines are MEA and A2P, secondary alkanolamines are DEA and DIPA, and the sterically hindered alkanolamine is AMP). Elemental analysis data in Table 1 indicate that, after heat treatment, copper(II) formate complexes with primary and secondary alkanolamines contain a large amount of residuals, whereas the amount of residuals for the copper(II) formate complex with the sterically hindered alkanolamine (AMP) is extremely low. The existence of organic residuals in the film is detrimental to the conductivity because they could inhibit the physical contact between metals in the film. Therefore, chemical compounds that leave small amounts of residuals after heat treatment should be the best choice for MOD inks. In this respect, among the alkanolamines that were examined in this research, AMP is the most appropriate compound for MOD ink.

Table 1. Elemental Analysis of Various Copper Formate/Alkanolamine Complexes Calcined at 300°C for 30 min under a Nitrogen Atmosphere

sample	carbon (wt %)	hydrogen (wt %)	nitrogen (wt %)	total (wt %)
Cuf-MEA	4.4238	0.4645	1.5474	6.4357
Cuf-A2P	2.4482	0.2349	0.6652	3.3483
Cuf-DEA	22.2529	3.0485	6.1482	31.4496
Cuf-DIPA	1.3158	0.1329	0.2197	1.6683
Cuf-AMP	0.3608	0.0469	0.0849	0.4925

Cuf = copper formate, MEA = ethanolamine, A2P = amino-2-propanol, DEA = diethanolamine, DIPA = diisopropanolamine, and AMP = 2-amino-2-methyl-1-propanol.

The reason for AMP's low residual generation after heat treatment is related to its structural characteristics. Copper(II) formate has to be heated under an inert atmosphere to induce the reduction reaction, and during that reaction, one copper(II) formate molecule generates two carbon dioxide molecules. The overall decomposition reaction of copper(II) formate proceeds as follows:[22]



$$Cu(HCOO)_2 \rightarrow Cu + 2CO_2 + H_2$$

The composition of the product gases ($CO_2 + H_2$) was studied in detail by Erofeew and Kravchuk.[23]

Alkanolamine is also known to undergo carbamate polymerization in the presence of carbon dioxide at high temperature.[24,25] When copper(II) formate is thermally reduced to metallic copper, these two main factors necessary for carbamate polymerization of alkanolamine are fulfilled. Thus, the production of high-molecular-weight degradation byproducts from some alkanolamines that have not participated in the reduction reaction during calcination of the Cuf-AMP complexes is possible. If this occurs, some organic species will remain in the copper film rather than evaporate because of their high boiling points, and these remaining organic byproducts will interrupt the metallic contact between the copper metals, resulting in a lower electrical conductivity of the copper film. Therefore, it is axiomatic that, among several alkanolamines, a substance that does not undergo severe carbamate polymerization should be carefully selected as a complexing agent for MOD inks. AMP is a sterically hindered primary amine (the amino group is attached to a tertiary carbon atom).[25] Owing to the steric hindrance near the α-carbon bound to the amino group, formation of stable carbamate ions is inhibited, so carbamate polymerization of AMP is restricted compared to that of other primary and secondary alkanolamines.[24−26] Therefore, one can expect that AMP will leave a smaller amount of carbon residuals than other alkanolamines after calcination of the copper(II) formate/alkanolamine complexes, and this fact is supported by the elemental analysis data shown in Table 1. For this reason, we choose AMP as the copper source for MOD ink to produce a better metallic copper film.

3.2. Effects of Introducing a Co-complexing Agent: Octylamine.

Figure 4a shows SEM images of the metallic copper films that were produced by calcination of Cuf-AMP ink at 300 °C for 30 min under a nitrogen atmosphere. In the calcined Cuf-AMP ink, microsized particles were generated with many void spaces. These phenomena led to a reduction in the physical contact between the copper particles, resulting in bad conductivity of the metallic copper films. Therefore, to obtain uniformly coated metallic films with good conductivities

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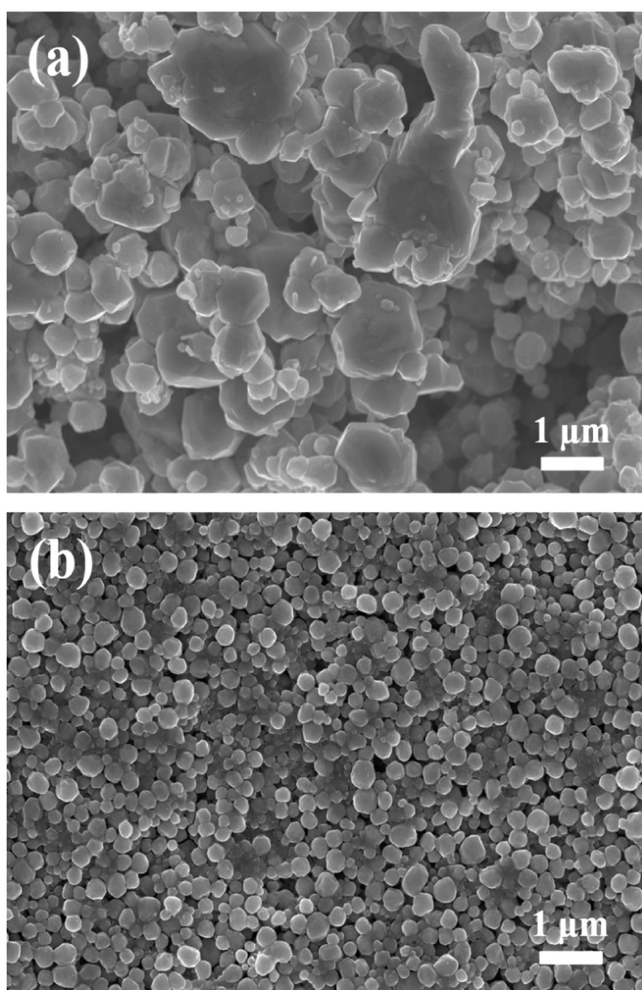

Figure 4. SEM images of (a) Cuf-AMP ink and (b) Cuf-AMP-O ink after heat treatment at 300 °C for 30 min under a nitrogen atmosphere.

on the substrates, Cuf-AMP ink was modified. For this modification, octylamine was introduced as a co-complexing agent. We introduced equal molar amounts of AMP and octylamine to copper(II) formate, and the resulting ink is called Cuf-AMP-O ink [the molar ratio of copper(II) formate to the complexing agents in Cuf-AMP-O ink is also fixed to 1:2, as in Cuf-AMP ink]. Calcined Cuf-AMP-O ink (Figure 4b) has little void space, with smaller, more densely packed particles compared to Cuf-AMP ink. Thus, better physical contact between copper particles was obtained in this film than in the film obtained from Cuf-AMP ink. Furthermore, as shown in Figure S2 in the SI, the Cuf-AMP-O complexes also have good solubility in alcohols and can also be changed to metallic copper completely at 175 °C (Figure S3 in the SI). These results demonstrate that employment of octylamine as a co-complexing agent can enhance the quality of MOD ink without changing the roles of the alkanolamine such as providing alcohol solubility and assisting reduction.

The use of MOD inks can be considered a type of solventless particle synthesis method because particles are generated in situ in the absence of solvent when the decomposition of ink starts near 125 °C, which is above the evaporation temperature of the solvent (isopropyl alcohol). In solventless particle synthesis, shape- and size-controlled nanoparticles can be synthesized if the metal−organic precursors have proper ligands. For example, Kang et al. synthesized copper, iron oxide, and silver nanoparticles without solvent by just heating metal oleate under low pressure.[27,28] Recently, our group reported a one-step synthesis method for ferrite/carbon hybrid nanosheets, which is another example of solventless particle synthesis because uniform iron oxide or manganese ferrite nanocubes are generated first on the solid templates (without solvent) before carbonization of their surfactant layers at 400 °C.[29] From these examples, it can be anticipated that the shape- and size-controlled particles can be synthesized even in the absence of solvent if the metal precursors have appropriate ligands that can control the particle growth.

We introduced this concept to our MOD ink process. When only AMP is used, the interparticle collisions between copper particles and diffusion of reduced copper ions into copper particles are not interrupted because AMP is not a good organic compound for controlling particle growth. In this situation, small particles and reduced copper ions tend to attach and grow on certain bigger particles to achieve a minimum surface energy. As a result, copper particles are not homogenously generated throughout the entire substrate layer, and the formation of many void spaces subsequently occurs. To solve this problem, octylamine was employed as a co-complexing agent based on the concept of solventless particle synthesis. Alkylamines are commonly used in nanoparticle synthesis to control the size and shape of the nanoparticles.[30] Although organic compounds with long alkyl chains show better size- and morphology-control abilities,[31] their boiling points are generally high, so if they are introduced to MOD ink as ligands, a higher curing temperature will be required. With that in mind, we choose octylamine as a co-complexing agent because its boiling point is relatively low, at 179 °C (similar to that of AMP, 165 °C), and it has comparatively good size-control ability.[14] Then, the quality of the resulting copper films was improved compared to that obtained with only AMP as a ligand. Moreover, the wettability of the complexes on the substrate can be tuned by introducing a co-complexing agent. Because we use isopropyl alcohol as a solvent, only a high-viscosity liquid (complexes) remains once the complexes' decomposition temperatures are reached, and the wettability of the complexes on the glass substrate seems to change as the temperature increases. This phenomenon becomes a considerable problem. Figure S4 in the SI shows photographs of Cuf-AMP and Cuf-AMP-O inks after heat treatment at 300 °C for 30 min under a nitrogen atmosphere. Because of their different wettabilities, Cuf-AMP ink underwent severe shrinkage (Figure S4a in the SI) but Cuf-AMP-O ink did not (Figure S4b in the SI). Therefore, Cuf-AMP/octylamine complexes are considered to have better wetting properties on glass substrates. Although this problem is not investigated in detail in this report, we believe that the wetting properties of the complexes can also be engineered by changing the co-complexing agent from octylamine to other suitable organic species, which will allow MOD ink in this study to be applied to various substrates.

3.3. Addition of Carboxylic Acid To Promote Sintering. Even though the particles in calcined Cuf-AMP-O ink are densely packed, so good metallic contacts are formed, the film is still not sufficient for use as electrodes or conductive interconnect lines for printed electronics because its spherical shape inevitably leads to small contact areas. Therefore, to achieve better performance of the printed metallic copper film, the copper particles should be fused into continuous networks.[1] In other words, the copper particles have to be sintered. It is

well-known that a decrease in the size of the metal nanoparticles results in a decrease in their melting points compared to that of their bulk counterpart,[32] so to obtain a well-sintered copper metallic film at a relatively low temperature, the size of the generated copper nanoparticles should be sufficiently small. However, the copper particles of Cuf-AMP-O ink are too large to be sintered at 300 °C (Figure 4b), so the particle size must be decreased to expedite sintering. With the purpose of decreasing the copper nanoparticle size to promote sintering, a fatty acid was introduced. Fatty acids are among the most widely used chemical compounds for size and shape control of nanoparticles in solution-phase synthesis.[33] Furthermore, from several previous reports, it seems that fatty acids can also perform their size- and shape-controlling roles even in the absence of solvents.[34−37] Because our MOD ink method can be regarded as a solventless particle synthesis, as mentioned above, we anticipated that introducing a fatty acid to Cuf-AMP-O ink will reduce the sizes of the particles and thus lower their sintering temperature.

In this work, two kinds of fatty acids, hexanoic acid and oleic acid, were tested to promote sintering. For these tests, 40 μL of fatty acid was added to 4.29 g of Cuf-AMP-O ink, which was then coated onto glass substrates and baked at 300 °C for 30 min under a nitrogen atmosphere. Figure 5a is a SEM image of MOD ink with hexanoic acid (Cuf-AMP-OH ink), and Figure 5b is a SEM image of MOD ink with oleic acid (Cuf-AMP-OO ink) after heat treatment. The copper film formed from Cuf-AMP-OH ink is completely sintered and very well fused to form conduction networks of metallic copper. This clearly demonstrates that the addition of a fatty acid in MOD ink could effectively facilitate the sintering of copper nanoparticles. However, in the Cuf-AMP-OH ink, the nanoparticles were not sintered even though large numbers of small nanoparticles were generated. This difference can be explained on the basis of their boiling points (205.8 °C for hexanoic acid and 360 °C for oleic acid). Because sintering occurs after all organic species are removed and thus after the formation of necks between particles, effective removal of organic species is a prerequisite to achieving better sintering of the particles.[1] A temperature of 300 °C should be high enough to remove the hexanoic acid layer on the surface of the copper nanoparticles but insufficient for removal of the oleic acid layer. The specific resistivity of copper films obtained from Cuf-AMP-OH ink was better than that of the film obtained from Cuf-AMP-O ink (12.79 and 20.02 $\mu\Omega\cdot$cm, respectively, after heat treatment at 300 °C for 30 min under a nitrogen atmosphere). This improvement resulted from sintering of the metallic copper particles in the film. However, the resistivity of the film obtained with Cuf-AMP-OO ink (its sheet resistivity was on the order of megaohms per square) was worse than that obtained with Cuf-AMP-O ink, which must be due to the existence of oleic acid in the film. On the basis of this observation, we selected hexanoic acid as an additional additive to trigger effective sintering of the copper nanoparticles.

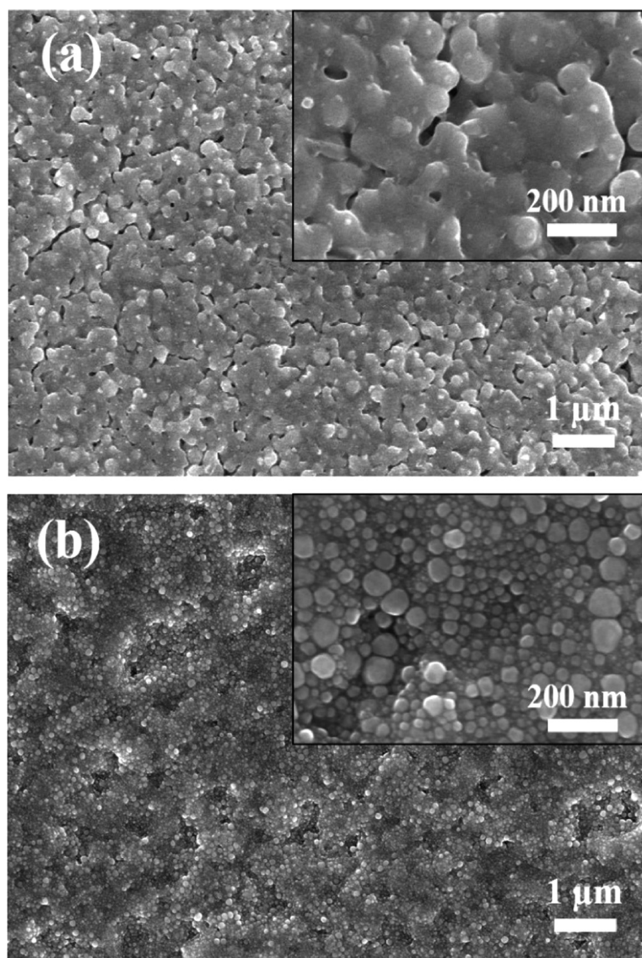

Figure 5. SEM images of calcined Cuf-AMP-O ink with sintering helpers: (a) addition of hexanoic acid; (b) addition of oleic acid. The insets show high-magnification views.

Sometimes, XRD analysis is unsuitable for identifying the existence of an oxide layer on the metal particles because the oxide layer can exist in an amorphous form. Therefore, we also conducted XPS analysis of the surfaces of copper films that were annealed at 300 °C for 30 min under a nitrogen atmosphere to confirm whether copper oxide really exists on the copper film. Parts a and b of Figure 6 show the peak-fitted Cu $2p_{3/2}$ spectra of the copper films formed from Cuf-AMP-O and Cuf-AMP-OH inks, respectively. Interestingly, only one peak centered at 932.27 eV was observed for Cuf-AMP-OH ink (932.31 eV in the case of Cuf-AMP-O ink), and this value is assigned to copper.[7] These XPS data show that our MOD ink

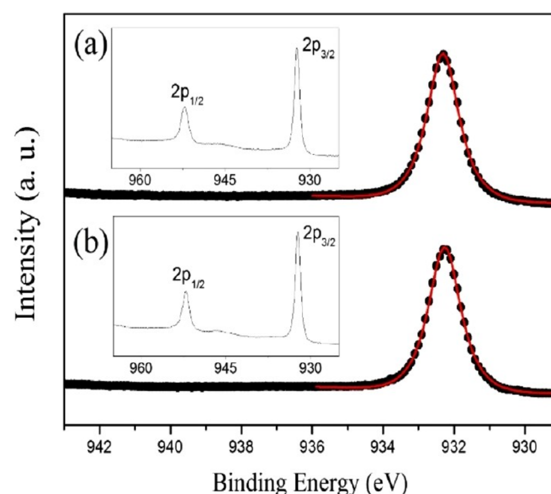

Figure 6. XPS Cu 2p spectra of (a) Cuf-AMP-O ink and (b) Cuf-AMP-OH ink after heat treatment at 300 °C for 30 min. The insets are the Cu 2p doublet spectra.

produces only pure metallic copper, so it is a good candidate material for printed electronics.

3.4. Resistivity of Copper Films Treated at Various Temperatures. Measurement of the specific resistivity was conducted to determine the performance of MOD ink in this study. The obtained specific resistances of Cuf-AMP-OH ink were 23.4, 18.7, 12.79, and 9.46 $\mu\Omega\cdot$cm for heat treatment at 200, 250, 300, and 350 °C, respectively. It should be pointed out that, although the specific resistivity of Cuf-AMP-OH ink was a little bit higher than other previously reported data,[11−13] heat treatment of our MOD ink was conducted under an inert atmosphere, unlike in other previous reports where a reducing atmosphere was commonly introduced to enhance the reduction of copper-based MOD ink. The specific resistivity obtained for heating at 350 °C is 9.46 $\mu\Omega\cdot$cm, which is just 5.5 times higher than the specific resistivity of bulk copper (1.72 $\mu\Omega\cdot$cm). Furthermore, the specific resistivity obtained after heat treatment at a relatively low temperature (200 °C) is 23.4 $\mu\Omega\cdot$cm, which is sufficient for Cuf-AMP-OH ink to be used in flexible printed electronics when poly(ether sulfone) or polyimide is used as a substrate.[4] The obtained results are plotted in Figure 7 as a function of the heating temperature,

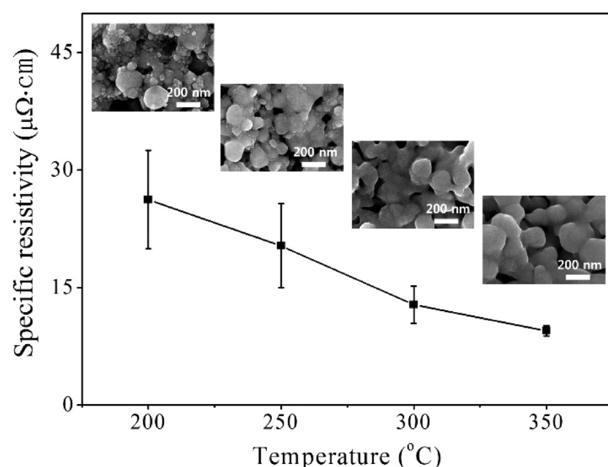

Figure 7. Specific resistivity of the film obtained after heating Cuf-AMP-OH ink for 30 min under a nitrogen atmosphere as a function of the heating temperature. The inset SEM images show the surface morphologies of the corresponding copper films.

and their surface morphologies (SEM images) are also presented. As can be seen in Figure 7, as the curing temperature increases, better conductivity of the copper film is obtained, and the SEM images show that more sintering of the copper nanoparticles occurs. From this result, we confirm that, in addition to removing organic residuals from the copper film, promoting the sintering of the copper nanoparticles is another important factor for obtaining good conductivity.

3.5. Simple Stamping-Transfer Test. To show the potential of our MOD ink for reverse offset printing, we carried out a simple stamping-transfer test using PDMS as a stamping mold. The result is shown in Figure 8. Although some residues remained on the PDMS stamp after transfer (these residues appeared in the pores after sintering; see Figure 8b), our Cuf-AMP-OH ink can be transferred fairly well from the PDMS stamp onto the glass substrate. This indicates that the Cuf-AMP-OH ink developed in this study is a good candidate for reverse offset printing. It is worth noting that we used Cuf-AMP-OH ink without solvent modification or ink formulation

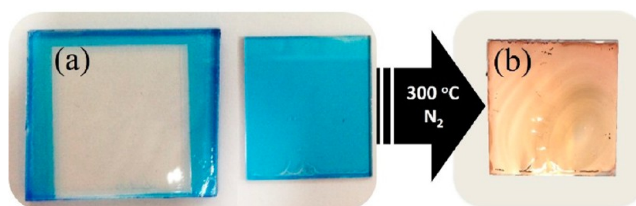

Figure 8. (a) Stamping-transferred Cuf-AMP-OH ink layer on the UVO-treated glass. (b) Copper film from transferred Cuf-AMP-OH ink in part a.

for printing. Therefore, if a professional printing technique and ink formulation are combined with our ink, we are certain that the quality of the imprinted copper film will be improved.

Furthermore, to broaden the potential use of our MOD ink, drawing of conductive patterns by other printing methods such as the pen-on-paper approach and inkjet printing was attempted. From the obtained results (see Figures S5 and S6 in the SI), the possibility of exploiting our ink for various printing methods could be demonstrated.

4. CONCLUSIONS

In summary, an alcohol-soluble and thermally reducible copper-based MOD ink has been successfully synthesized. We choose copper(II) formate as a precursor because of its strong potential for use as a conductive ink. Then, an alkanolamine called as AMP was exploited as a complexing agent to dissolve copper(II) formate in alcohol solvents and to reduce the decomposition temperature of copper(II) formate. In addition, for the purpose of obtaining a well-sintered metallic copper film after heat treatment, octylamine and hexanoic acid were introduced to our system as a co-complexing agent and a sintering helper, respectively. Their introduction into MOD ink was based on the several examples of solventless nanoparticle synthesis. It is believed that this approach can be extended to other MOD inks and will therefore be a positive influence on the field of solution-process-based electronic devices. The resistivity achieved after heat treatment of Cuf-AMP-OH ink at 350 °C is 9.46 $\mu\Omega\cdot$cm, which is only 5.5 times higher than the specific resistivity of bulk copper. To show the potential of Cuf-AMP-OH ink for commercial printing processes such as reverse offset printing, a stamping-transfer test using PDMS as a stamping mold was conducted, and as a result, a positive outcome was obtained. On the basis of the result, we are certain that if a professional printing technique is applied to our MOD ink, it may be found to be very useful in commercial printed electronics.

■ ASSOCIATED CONTENT

Supporting Information

Photographs of Cuf-AMP complexes dissolved in water, Cuf-AMP-O complexes dissolved in various alcohols, Cuf-AMP-O inks with Cuf-AMP-O complex loads of 90, 70, 50, 30, and 10 wt %, Cuf-AMP ink, and Cuf-AMP-O ink after heat treatment, XRD pattern of the copper film after heat treatment of Cuf-AMP-O ink at 175 °C, photographs of copper patterns printed using a pen and an inkjet printer and descriptions of how to prepare copper patterns by each method, and an optical image of an inkjet-printed copper pattern. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +82 31 888 9141. Fax: +82 31 888 9148. E-mail: parkat9@snu.ac.kr.

Notes

The authors declare no competing financial interest.

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