# Novel Low Temperature Copper Inkjet Inks are a Low Cost Alternative to Silver for Printed Electronics

***Michael J. Carmody; Intrinsiq Materials Inc.; Rochester, NY (USA); Jonathan Tunbridge, Tung Kong; Intrinsiq Materials Ltd. Farnbourough, Hampshire (UK)***

## Abstract

*Demand for the use of metal-based inkjet inks for printed electronic applications is well known. Gold and silver based inks have been produced, but cost and performance limitations are likely to remain major obstacles to widespread adoption. Copper, which is potentially a low cost alternative, readily oxidizes, particularly in highly reactive nanoparticle form, making it unsuitable for ink formulation.*

*However, using a combination of highly specified copper nanoparticles and a proprietary coating and functionalization process, it has been possible to protect the copper from oxidation and produce a stable copper inkjet ink.*

*The ink enables the direct printing of copper circuits via established commercial inkjet technology. After printing, an oxide free conductive copper track is produced via rapid thermal annealing of the deposited ink. The ink has been specifically designed for photonic curing in air via high intensity light sources ie. lasers or broad band flash lamps. This low temperature curing allows the use of low cost, low temperature, flexible, and other, substrates including paper, PET, polyimide, polyester, FR4, and glass. Conductivities are comparable to commercial silver inks with significantly higher metal loadings.*

*Information around applications and performance is presented along with plans to extend the technology to other metals and applications.*

## Introduction

Traditional lithographic processes for creating printed circuits are expensive, wasteful, and have significant environmental impact. Thus, printing with conductive inks is gaining favor as a less expensive, easier alternative [1]. However, metal particles needed for inks must be annealed to become conductive, and this is not compatible with all desired substrates. Nanoparticulate inks can obviate the need for high temperature annealing due to their low melting point. Iradiation with intense pulsed UV light can be effective at annealing such particles [2]. Silver inks have been used for this purpose, but the price of silver can be variable, and it is expensive, often accounting for up to 40 % of the cost of inks.

Copper would be a much less expensive alternative for this purpose since it can also be formed into nanoparticles, but it is prone to oxidation. It has been found that encapsulating the copper in a shell of carbon, polymer, silica, or silver [3] can inhibit oxidation, but these processes can be complicated and can have a negative effect on the conductivity of the resulting printed pattern.

What is required for commercial success is a method of producing inexpensive encapsulated copper nanoparticles that form stable dispersions. These must be formulated into inks, which can be facilely printed onto a range of substrates, and the printed patterns must be cured at room temperature in air. In the present paper we describe a vapor phase method of producing polymer encapsulated copper nanoparticles which are easily dispersed into inkjet or screen printing inks. We show that these are easily printed onto a variety of substrates and cured at room temperature in air resulting in highly conductive, well-resolved lines.

## Experimental

Encapsulated copper particles were prepared using a proprietary method and were encapsulated in an organic shell.

Inkjet ink was prepared by slowly adding encapsulated copper particles to a solution of ethylene glycol:butanol which was rapidly mixed at high shear for 60 minutes. The dispersion was additionally sonicated for 48 minutes and filtered under argon through a 1.2 μ filter.

Inks were printed on a home-built printer using a Spectra 126 inkjet printhead.

The SEM images were obtained at the stated temperatures using a Hitachi S-4800 Ultra-high resolution FE-SEM (resolution to 0.6 nm). The images were obtained under low pressure vacuum.

The XRD data was obtained using a Brucker D500 defractometer at 27$^{o}$C using a step interval of 0.020$^{o}$ and a step time of 4 seconds. An angle range of 25.0$^{o}$ – 95.0$^{o}$ was swept in each instance [4].

Printed patterns were cured on a broad band UV light source, or with lasers.

## Results and Discussion

A STEM image of encapsulated particles that result from the proprietary process is shown in Figure 1. The image shows copper nanoparticles which are unagglomerated and un-sintered as can be

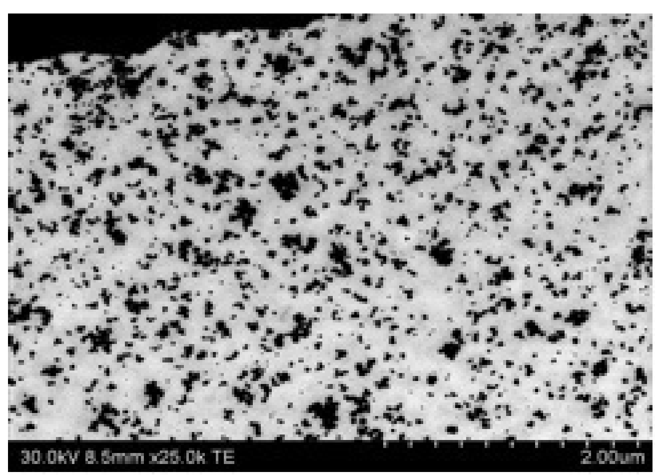


***Figure 1**. Organic encapsulated copper nanoparticles*

seen by the distinctive black dots. The particle size distribution was determined by manually sampling 200 particles of the image and the histogram is shown in Figure 2. The average particle size is approximately 31 nm and 90% of the particles are smaller than 58 nm. Similar particles can be produced using nickel and other metals using a variety of organic encapsulants.

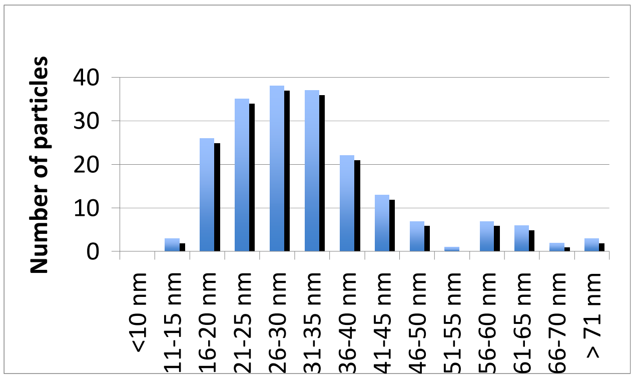


***Figure 2**. Particle size distribution for encapsulated particles*

Inks made from the particles were tested for oxidative stability. The X-Ray diffraction pattern of a sample left open to the air for 30 days is shown in Figure 3 and compared to a freshly prepared sample. Note that the two traces are indistuinguishable, that only pure copper is detected, and that there appears no trace of crystalline Cu(I) or Cu(II) oxide. Additionally, printed samples of the inks were cured for up to one month after printing and the conductivity (see below for curing and conductivity results) was found to be unchanged. No visual settling of the inks was noted after six months shelf keeping.

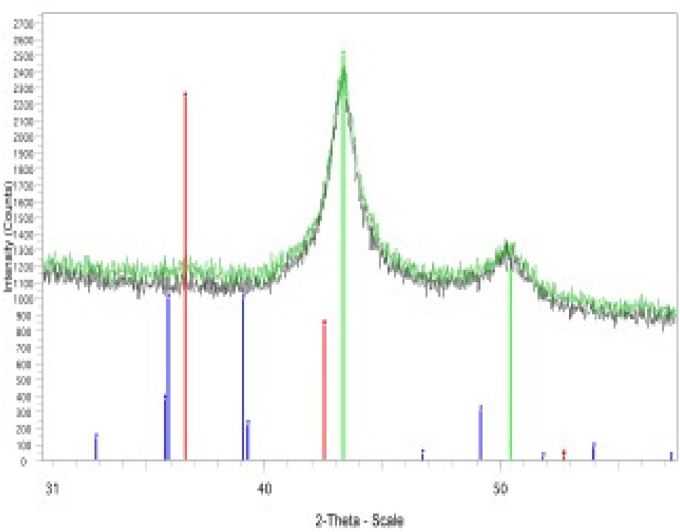


***Figure 3**. XRD traces for fresh (black, lower) and aged (green, upper) samples showing no crystalline copper oxide*

Inks were successfully inkjet printed onto a variety of media and a print on polyimide is shown in Figure 4. Note the sharp boundaries of the lines and their excellent resolution. Similar prints were obtained on polyester, PET, FR4, borosilicate glass, alumina, and carbon fiber. On absorbant paper, a single pass print shows an ink depth of 460 nm while a single pass on polyimide is 277 thick. A second pass on polyimide increases the thickness to 347 nm. Additionally, printed materials can be chemically over-plated for roll-to-roll applications.


*Figure 4. Print of copper ink on various Kapton*

The efficiency of the curing using broad-band UV light is shown in the before and after exposure comparison in Figure 5. The original small round particles form a network of much larger, interconnected particles.

The copper nano inks can be cured in a variety of ways including by laser light. Figure 6 show a sample in which the top half of the text has been treated with a 1064 nm laser, while the bottom has not been cured. Note the metallic, copper sheen in the cured section and the black, matte appearance of uncured section.

Since a key attribute of metal nanoparticles is the ability to be sintered on low Tg substrates, the SEM cross sectional micrograph shown in Figure 7 is extremely telling. This shows the copper ink printed onto polyimide and laser cured. The copper particles form a uniform layer and are well cured, but the polyimide substrate is not deformed at all. Conductivities as high as 20% of that of bulk copper have been obtained by these methods.

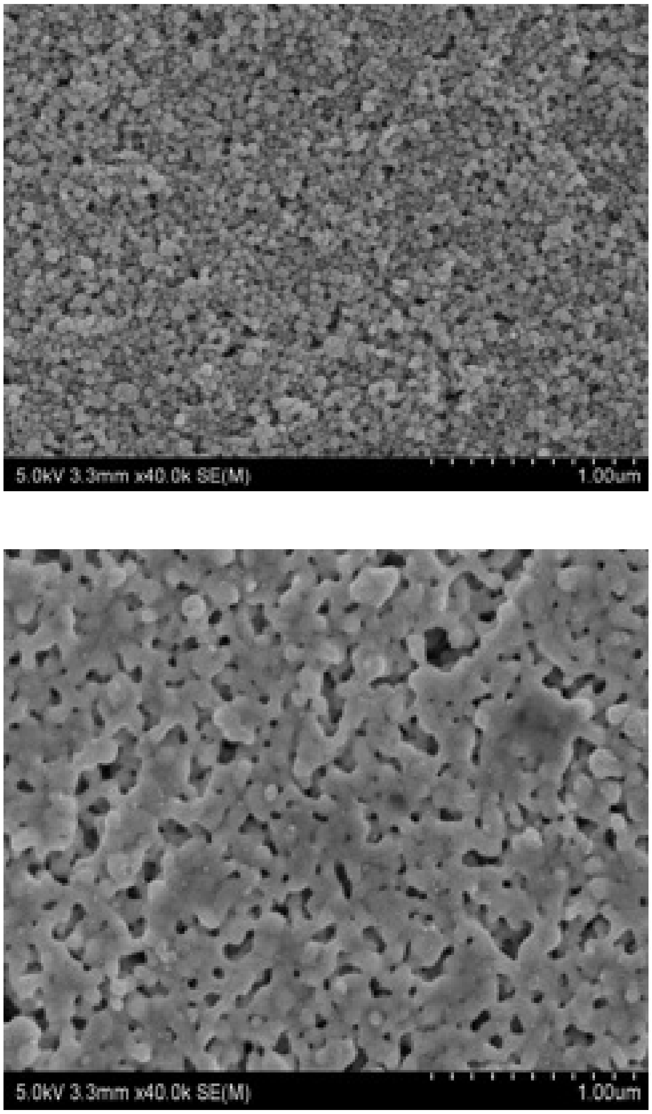


***Figure 5** Micrograph of ink deposit before (top) and after (bottom) photonic curing*


*Figure 6 A comparison of laser cured and uncured samples*

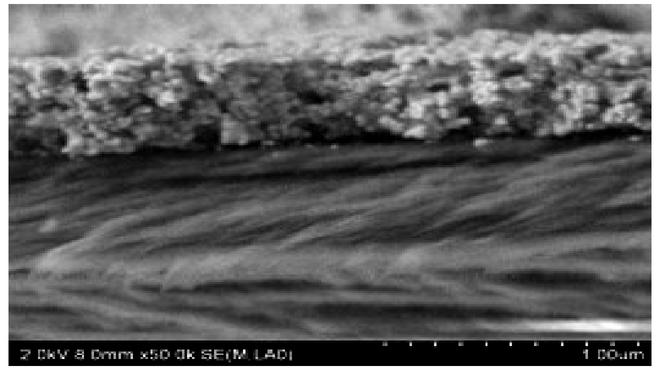


***Figure 7**. Cross sectional micrograph of copper ink on polyimide, photonically cured*

## Conclusions

We have shown that small, uniform copper nanoparticles can be produced by a novel encapsulation method. This has the potential to be very inexpensive since it could be run in a continuous or semi-continuous mode. These particles are very stable to atmospheric oxygen as evidenced by keeping experiments on both the particles themselves and the ability to cure printed patterns even after a month-long atmospheric exposure. Inks made from these particles have been effectively printed from commercial inkjet printers using both Xaar and Spectra printheads, and produce well-defined patterns on a variety of potentially useful substrates. Most importantly, the printed inks can be photonically cured at room temperature (in air) to give highly conductive patterns even on low Tg substrates.

## Acknowledgements

The authors would like to thank Vivien Lee and Luke Townsend for their help in generating data for these experiments, and Paul Reip and Richard Dixon for their help in preparing the manuscript.

## References

[1] B.-J. de Gans, P.C. Duineveld, U.S. Schubert, Adv. Mater. 16, 203 (2004)
[2] J. Ryu, H.-K. Kim, H. T. Hahn, J. Electr. Mater. 40 (1), 42 (2011)
[3] S. Magdassi, M. Grouchko, and A. Kamyshny, Materials 3, 4626 (2010)
[4] A.B. Godfrey, A. Kong, WO2010/073021

## Author Biography

*Michael Carmody received his BS in Chemistry from the University of Detroit (1972) and his PhD in Organic Chemistry from the Ohio State University (1976). He worked 32 years in the Research and Development Laboratories at Kodak in Rochester, NY, and recently joined Intrinsiq Materials. His work has focused on the development of novel materials for imaging systems and properties and development of inkjet inks . He has served as adjunct faculty at the Rochester Institute of Technology, Monroe Community College and SUNY Brockport.*