Development of Conductive Carbon Coated Copper Nanoparticle Inkjet Fluid

Kim Eiroma, Ari Auvinen, Johanna Forsman, Eva-Lena Hult, Jorma Jokiniemi, Pirjo Koskela, Juha Sarlin, Thea Sipiläinen-Malm, Unto Tapper; VTT Technical Research Centre of Finland; Espoo, Finland

Abstract

An aqueous inkjettable conductive fluid based on carbon coated copper nanoparticles has been developed. The fluid can be handled in atmospheric conditions and processed at low temperature (105 °C) with no thermal annealing. A layer conductivity exceeding 600 S/cm has been demonstrated. The particles were produced in a continuous flow reactor from copper chloride powder by hydrogen reduction at high temperature (950 °C). Results indicate that conductivity is enhanced through the formation of carbon nanotubes by addition of ethene and water to the reaction flow. The type and concentration of dispersing additive and co-solvents had a significant impact on dispersion stability and electrical conductivity of the deposited layer. Applicability of the fluid for direct patterning of coatings for e.g. antistatic purposes was demonstrated by inkjet printing of a conductor electrode pattern.

Introduction

There is currently a strong drive towards the development of low cost conductive metallic nanoparticle based fluids for printed electrically functional devices. Significant interest has lately been directed towards replacing silver with copper due to its relatively low price and high conductivity. A major challenge in the development of copper based fluids is the tendency of copper to spontaneously oxidize in ambient conditions. Several ways of protecting the copper nanoparticles from oxidation have been proposed [1]. For example, graphitic coatings have been used to stabilize metallic nanoparticles and to minimize their size in conductive and magnetic fluids [2, 3]. Conductivity levels in the order of 1 S/cm have been demonstrated in [2] for inkjet printed layers of a fluid based on graphene coated copper nanoparticles. Metallic nanoparticles having a relatively high specific gravity (compared to e.g. carbon black) are challenging to disperse in a fluid base, and typically require a polymeric stabilizing ligand which will hinder inter-particle contact and hence conductivity unless removed in a subsequent sintering step.

This paper presents an alternative approach for synthesis of copper nanoparticles with a graphitic layer providing stability towards oxidation and carbon nanotubes that enhance the conductivity of the dried fluid layer. The effect of dispersing additive and co-solvent composition on dispersion stability and conductivity of deposited layers is investigated.

Materials & methods

Particle production

Carbon coated copper nanoparticles were produced by a gas phase synthesis technique developed previously for production of metallic nanoparticles [4]. Copper chloride precursor powder (Sigma-Aldrich) was fed using a powder feeder on alumina (Al_2O_3) pellet bed within a quartz glass nanoparticle reactor. The bed was made of 8 g of porous aluminium oxide pellets with 3mm diameter (Sigma-Aldrich). From the pellet bed the precursor was evaporated at 800°C into a nitrogen flow. The gas flow carried copper chloride vapour into the reaction zone, where reaction with hydrogen (13.8 vol-%) at 950°C produced copper nanoparticles and hydrogen chloride.

In order to prevent oxidation and sintering of particles during handling, transport and storage, copper particles were coated during their synthesis with a graphitic carbon layer. In these experiments ethene served as precursor for the coating. In the reaction zone 0.9 vol-% of C_2H_4 was mixed to the gas flow together with hydrogen. In order to promote the formation of carbon nanotubes (CNT) some water vapor was fed into the reaction zone as well. The actual formation of CNTs depended on the copper chloride to ethene ratio fed into the reactor.

The flow coming out of the reactor was diluted and cooled with nitrogen to prevent further agglomeration and sintering of particles. Produced powder was then collected in a PTFE filter bag (GORE®). Hydrogen chloride was removed downstream the filter from the exhaust flow using two tanks filled with NaOH-water solution before the flow was directed to a fume hood. Fourier transform infrared spectroscopy (FTIR, Gasmet Dx4000) was applied to measure the concentrations of HCl in order to monitor the particle production rate. FTIR also measured the concentration of water vapor, gas impurities, CO, CO_2 as well as the gaseous degradation products of ethene. The results from FTIR measurements agreed very well with the amount of powder collected from the filters. According to FTIR data approximately 90-95 % of copper produced in the reactor could be retrieved from the particle filters.

Fluid preparation

The dispersing capability of the nanoparticles was evaluated using three dispersing additives suitable for water-based carbon black pigment dispersions which were kindly provided by BYK Chemie Gmbh: DISPERBYK-190 (Solution of a high molecular weight block copolymer with pigment affinic groups), DISPERBYK-198 (Solution of a copolymer with basic pigment affinic groups) and DISPERBYK -2012, (Solution of a structured acrylate copolymer with pigment affinic groups) hereafter denoted (1), (2) and (3), respectively. Ethylene glycol monomethyl ether (EGME) (Sigma-Aldrich), ethylene glycol monobutyl ether (EGBE) (Merck) and n-propanol (Honeywell Riedel-de Haen) were used as co-solvents for improving the fluid jetting and layer forming properties. The viscosity (at 20 °C), surface tension and boiling point of EGME, EGBE and n-propanol are 2.0 mPas/33 mNm^{-1}/125 °C, 6.4 mPas/27 mNm^{-1}/171 °C and 2.2 mPas/ 24 mNm^{-1}/97 °C, respectively.

The nanoparticles were mixed with the dispersing additives, co-solvents and de-ionized water (DIW), and the suspension was sonicated for 10 minutes in an ice bath at an intensity of 30% (1.0 cycle) using a UP400S ultrasonic processor (Hielscher Ultrasonics). Thereafter, the suspension was left to settle for an hour followed by decanting. Prior to spin coating or printing the suspension was sonicated in an ultrasonic bath for 10 minutes.

Layer deposition

Inkjet printing of the conductive carbon coated copper fluid was carried out with the Dimatix DMP-2831 laboratory scale piezoelectric drop-on-demand printer (Fujifilm Dimatix). The printer utilizes printhead cartridges with 16 nozzles arranged linearly at a pitch of 254 µm. Cartridges generating a nominal drop volume of 10 pL were used. Printing was performed at a jetting frequency of 1 kHz. Printing of solid fill layers for electrical characterization as well as electrode patterns for demonstration was carried out at 20 µm inter-drop spacing (1270 dpi). Spin coating of the nanoparticle dispersions was carried out using an EC101D series spin coater (Headway Research) at 1000 rpm for 1 minute.

Layers were deposited on microscopic glass slides (Thermo Scientific) and heat stabilized Teonex Q65FA polyethylene naphthalate (PEN) film (Teijin DuPont Films) with a thickness of 125 µm. Both substrates were cleaned by immersion in acetone under ultrasonication for 10 minutes followed by immersion in isopropanol under ultrasonication for 10 minutes and drying under nitrogen flow. A single layer for both inkjet printing and spin coating was applied. The spin coated and printed layers were immediately dried on a hot-plate for 60-90 seconds at 60 °C and then transferred to an oven for 1 hour at 105 °C.

For electrical characterization, gold electrodes having a layer thickness of 100 nm, channel length and width of 800 µm and 10000 µm, respectively, were grown by thermal vacuum evaporation on the deposited copper-carbon layer. After oven drying, and prior to electrical characterization, samples were stored in a nitrogen glove box.

Characterization methods

Particle size distribution and structure of the dry particle powder was studied using transmission electron microscopy (TEM, Philips CM200 FEG/STEM). In addition, the specific surface area (SSA) of powder samples was measured using BET (ASAP2020, Micromeritics Instruments). The elemental composition of the particles was analyzed using x-ray fluorescence (XRF, Philips PW2404 X-ray spectrometer) using semi-quantitative SemiQ-program. The weight changes in materials were measured by thermo-gravimetric analysis (TGA, Mettler TGA 851e).

Fluid viscosity was measured using an mVROC viscometer (RheoSense). Fluid surface tension was measured using an EZ-Pi tensiometer (Kibron). Dispersion stability was evaluated qualitatively by visual inspection at intervals of 1 day and 4-5 days.

The topography of the dried spin coated and printed layers was characterized by optical microscopy (BX60, Olympus), stylus profilometry (Dektak 150, Bruker AXS) and SEM imaging (LEO DSM 982 FE-SEM). Electrical characterization of the dried copper-carbon layers was performed by 2-point probe resistance measurements from the thermal vacuum evaporated gold electrodes. Layer conductivity (σ) was calculated using measured values for resistance (R), electrode gap length (L) and width (W) and layer thickness (d).

Results

Copper-carbon nanoparticle synthesis and characterization

The produced carbon coated copper particles (figure 1) were non-agglomerated, almost non-sintered and had nearly spherical faceted shape. The particle number size distribution estimated from the TEM micrographs was fairly wide: Approximately normal distribution with number median diameter of 67 nm and standard deviation of 27 nm. As evident in figure 1, when thick multi-walled carbon nanotubes (MWCNT) were present in the samples, they were clearly visible in the TEM pictures. The specific surface area of the produced powder calculated from TEM figures using 390 copper particles was 7.8 m^2/g. The BET measurement from the same powder sample gave 13.7 m^2/g as a result. The difference between these methods indicates that CNTs have a strong influence on the specific surface area of the samples.

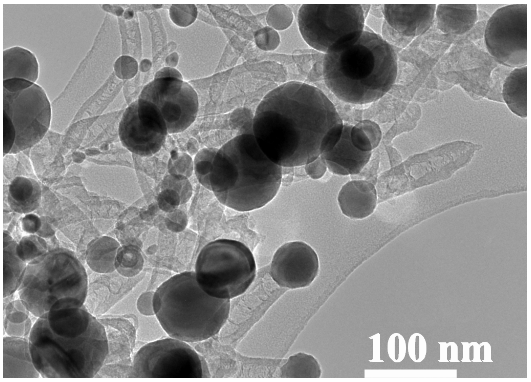

***Figure 1**. A TEM micrograph of copper nanoparticles coated with graphitic carbon layer and CNTs.*

According to the semi-quantitative XRF analysis the copper content of the produced powder was about 90 wt-%. The powder contained approximately 9 wt-% of carbon and 0.95 wt-% of chlorine. Silicon, sulphur and cobalt could be found from the samples as minor impurities with total mass concentration less than 0.5 wt-%.

During the dynamic phase of thermo-gravimetric analysis (heating 25°C → 500°C) the behavior of the sample could be divided into four successive temperature regions during which reactions causing mass changes were detected. During the first stage mass loss of -0.12 wt-% took place probably due to the evaporation of free moisture adsorbed on the surface of the powder. The next three reactions were highly exothermic. During the second and the third phases the mass of the sample increased. Nanoparticles started to oxidize in air atmosphere at about 100°C. Because the oxidation process was slow up to about 135°C, it is fair to assume that all copper particles were coated with carbon. The oxidation process included two main steps and was completed at about 300°C. The weight gain of the reactions 2 and 3 registered in the analysis performed was 16.2 %. It is most likely that the oxide formed was tenorite, CuO. The fourth reaction caused exothermic mass loss. Consequently, it was most obviously due to the burning of carbon contained by the particles.

Assuming that the sample powder contained only metallic copper which oxidized to single oxide and that the burning of carbon took place completely, the weight gain registered in the analysis means that the contents of copper and carbon in the powder were 88.9% Cu and 11.1% C.

Dispersion stability and layer conductivity

Dispersing additive effects on fluids based on copper nanoparticles coated with graphitic carbon layer and CNTs

Three commercially available dispersing additive candidates (1, 2 and 3) were tested for their dispersing properties and compatibility with the preliminary fluid composition consisting of copper nanoparticles coated with a graphitic carbon layer and CNTs (25 wt-%), de-ionized water (50 wt-%) and n-propanol (25 wt-%).

Three levels of dispersing additive based on preliminary testing - 8, 16 and 24 wt-% (relative to copper-carbon particles), hereafter denoted (low), (medium) and (high), respectively - were tested for their effect on dispersion stability and the conductivity of layers fabricated by spin coating on glass. Dispersion stability was evaluated visually by examining fluid samples to determine the degree of particle sedimentation and phase separation at selected time intervals. All dispersions except (1) (low) appeared stable after a period of 5 days. Table 1 shows the dispersion stability and layer conductivity results for all dispersing additives at (low) and (medium) levels.

Table 1: Effect of dispersing additive type and addition level on dispersion stability and conductivity of spin coated copper-CNT layer.

Dispersing additive	Addition level	Conductivity (S/cm)	Stability
(1)	(low)	8.3±3.6	unstable
	(medium)	4.7±2.3	stable
(2)	(low)	470.2±95.6	stable
	(medium)	167.2±87.1	stable
(3)	(low)	50.2±42.7	stable
	(medium)	14.9±4.8	stable

Dispersing additive level (high) is omitted from the results as sufficient stability was obtained for level (medium) or (low) for all dispersing additives, and conductivity results indicate a drastic drop in conductivity as the dispersing additive level is increased. SEM imaging of the spin coated layers did not provide clear indication as to the reasons for the significant differences in conductivity.

It is evident that dispersing additive (2) with addition level (low) gave the most promising results in terms of layer conductivity while providing sufficient dispersion stability. Thus this fluid composition was selected for further studies.

Co-solvent effects on fluids based on copper nanoparticles coated with graphitic carbon layer and CNTs

Preliminary jetting tests indicated that the viscosity of the particle/dispersing additive/DIW/n-propanol composition was too low and the volatility too high for stable and sustainable drop formation. Two commonly used co-solvents for improving inkjetting performance, ethylene glycol monomethyl ether (EGME) and ethylene glycol monobutyl ether (EGBE), were studied for their effect on dispersion stability and layer conductivity. The fluid compositions (A), (B) and (C) containing EGME/n-propanol or EGBE/n-propanol co-solvents at varying levels and resulting conductivities of spin coated layers on glass are presented in table 2. Dispersing additive (2) at 8 wt-% (relative to copper-carbon particles) was added to the total formulation.

Table 2: Fluid compositions with varying levels of co-solvents EGME/n-propanol and EGBE/n-propanol and resulting conductivities of spin coated copper-CNT layers on glass.

Composition	A	B	C
Particle loading (wt-%)	25	25	25
Dispersing additive (2) (wt-% on particles)	8	8	8
DIW (wt-%)	50	50	25
n-propanol (wt-%)	18.7	12.5	25
Co-solvent (EGME/EGBE) (wt-%)	6.3	12.5	25
Conductivity (EGME) (S/cm)	-	-	87.8
Conductivity (EGBE) (S/cm)	108.5	337.9	642.9

For the fluid compositions containing EGME/n-propanol as co-solvent, only composition (C) was stable for 4 days, therefore compositions (EGME) (A) and (EGME) (B) were not studied further. Compositions containing EGBE/n-propanol as co-solvent all exhibited dispersion stability after 4 days.

From the results in table 2 it is evident that the addition of EGBE has the effect of increasing the conductivity of the spin coated layer. This is assumed to be due to the higher boiling point of EGBE (171 °C) compared to EGME (125 °C) which slows down the evaporation rate of the solvents during drying of the layer, possibily promoting a more uniform packing of the copper-carbon nanoparticles. SEM images of the layers, however, do not provide confirmation to this assumption, as no distinct differences could be seen.

Printing and spin coating of compositions based on copper nanoparticles coated with graphitic carbon layer

A fluid composition for inkjet printing was prepared from the final batch of particles coated with a graphitic carbon layer, excluding the CNTs. Fluid formulation (C) (EGBE) containing EGBE as the primary co-solvent (table 2) was repeated.

Analysis of inkjet drop formation of the fluid (C) (EGBE) suggested that the break-up of the trailing ligament of the drop was not stable enough for reliable jetting, in particular at higher frequencies (exceeding approximately 5 kHz). The fluid viscosity at a shear rate of 3000 s^{-1} was measured to be in the range of 7-8 mPas, and surface tension was measured at 27.6 mN/m, which suggests that optimizing the fluid properties towards the range generally considered to give the best jetting performance for industrial printing (viscosity 10-20 mPas, surface tension 30-40 mN/m) could provide enhanced jetting performance. Nevertheless, a respectable drop velocity of 5 m/s was attained in a regime where the trailing ligament of the drop breaks up into satellites which merge with the main drop at a minimum stand-off distance of 1 mm.

Layers of said formulation were inkjet printed and spin coated on both PEN film and glass. Conductivity results (table 3) show that spin coated layers on glass provide the highest conductivity, and that fluid formulations based non-CNT containing copper-carbon nanoparticles result in conductivities approximately a decade lower than those containing CNTs, comparable to results reported in [2] for inkjet printing on plastic film. Moreover, results support the assumption that CNTs indeed are contributing to the significant increase in conductivity of the deposited layers.

Table 3: Effect of deposition process and substrate on the conductivity of composition (C)(EGBE) for copper-graphitic carbon containing fluids.

Process	Substrate	Conductivity (S/cm)
Spin coating	Glass	34.1
	PEN	10.9
Inkjet printing	Glass-	12.3
	PEN	3.4

Even though there seems to be a clear difference between spin coating and inkjet printing in terms of layer conductivity based on the results for composition (C) (EGBE), preliminary tests indicate that a further increase in concentration of the highest viscosity component, EGBE, enhances the conductivity to approximately the same level than for spin coated layers, in addition to providing more stable drop formation in the printhead. However, more detailed analysis on the fluid and layer properties are needed to fully understand this behavior.

Figure 2 shows an optical microscope image of an electrode inkjet printed with fluid (C) (EGBE) on glass. The inset shows an SEM image of the printed surface, indicating that particles and clusters thereof are in the <100 nm range. The resulting line width is approximately 100 µm and layer thickness of the single printed layer was measured at 1.4 µm.

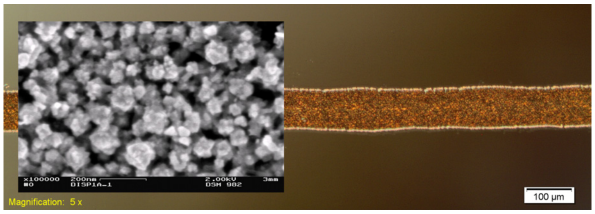

***Figure 2**. Optical microscope image (5X magnification) of an electrode inkjet printed with fluid (C) (EGBE) on glass. Inset shows SEM image (100000X magnification) of the printed surface.*

Conclusions

The formulation of a stable inkjettable conductive fluid containing carbon coated copper nanoparticles has been demonstrated. Inkjet deposition of conductive patterns for e.g. antistatic purposes seems feasible with the developed conductive fluid. Results indicate that the formation of CNTs on the surface of the copper nanoparticles significantly enhances the conductivity achieved for deposited layers dried at low temperature. The conductivity is strongly affected by the polymeric dispersing additive level. Also, the lower evaporation rate of the co-solvent seems to promote more efficient inter-particle packing, which further enhances the conductivity.

Results suggest that further work is needed for understanding the effects of the fluid components on conductivity in more detail, in order to achieve even better performance. The effect on conductivity of various alternative low-temperature sintering methods will be investigated. Further studies and optimization of the fluid jetting performance are also needed to determine the fluid's applicability in an industrial process.

References

[1] S. Magdassi, M. Grouchko, and A. Kamyshny, "Copper Nanoparticles for Printed Electronics: Routes Towards Achieving Oxidation Stability," Materials, 3, 9 (2010).

[2] N. A. Luechinger, E. K. Athanassiou, W. J. Stark, "Graphene-stabilized copper nanoparticles as an air-stable substitute for silver and gold in low-cost ink-jet printable electronics," Nanotech., 19, 44 (2008).

[3] P. Koskela, U. Tapper, A. Auvinen, J. Jokiniemi, A. Alastalo, H. Seppä, M. Aronniemi, J. Juuti, H. Jantunen, Proc. EAC2009, T014A10, (2009).

[4] J. Forsman, U. Tapper, A. Auvinen, J. Jokiniemi, "Production of cobalt and nickel particles by hydrogen reduction," J. Nanop. Res., 10, (2008).

Acknowledgements

The work described in this paper has received funding from the European Community's Seventh Framework Programme under grant agreement n° 228559.

Author biography

Kim Eiroma (M.Sc.) is a research scientist focusing on application of the inkjet deposition process for the fabrication of functional devices. Since the beginning of 2011 he has been pursuing doctoral studies related to upscaling of the inkjet materials deposition process. Mr. Eiroma is currently affiliated with the Printed Functional Solutions Centre at VTT Technical Research Centre of Finland.