Development of a Gold Nanoparticle Conductive Ink with a Relatively Low Sintering Temperature

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ABSTRACT

We developed a conductive gold nanoparticle ink with a relatively low sintering temperature that can be used to print different kinds of conductive tracks or electrodes on low-cost polymer substrates. The dependence of the specific resistivity ρ on the sintering temperature was investigated and it could be concluded that the sintered layers exhibit a good conductivity already at temperatures as low as 140 °C, much lower than commercially available products. Using this ink it was possible to print high resolution conductive patterns on the micrometer scale with thicknesses of around 70 nm. Hence, this ink can be used for printing interdigitated electrodes (IDEs) as well as microelectrode arrays (MEAs) to perform electrochemical measurements and experiments with living cells.

Keywords: gold nanoparticles, gold ink, low sintering temperature, inkjet printing

1 INTRODUCTION

Inkjet printing is a widely used and a well-known technique, which is used for deposition of functional materials, such as conductive inks for the fabrication of low-cost electronic systems. Nowadays, a variety of conductive inks (e.g. silver, gold and copper inks) are commercially available. While copper is a relatively cheap material, the metal has the disadvantage of being prone to oxidation in air, thereby changing its conductive properties over time. On the other hand, silver is less susceptible to oxidation, however, the electric properties of printed silver structures are usually altered upon formation of silver oxides. Additionally, it is significantly more expensive than copper. While bearing an even higher price tag than silver, gold has the advantage of being resistant to oxidation and therefore is useful for printed functional systems in which electrode oxidation might pose an issue. Such applications include devices exposed to harsh environments, such as wearables that can see high salt concentrations from sweat or electrochemical sensors, where, noble gold could serve as an electrode material. As well as, for systems with a strong performance drop due to slight changes in resistance as it is the case with organic transistors.

Nevertheless, the down-side of currently available commercial gold inks is the high sintering temperature required for good conductivity. As opposed to common silver inks [1] having a curing temperature of 120-150°C, available gold inks [2] require curing temperatures of >190°C. Such high curing temperatures limit the application to substrates with a melting temperature > 200°C, leaving out many of the common cost-saving polymeric substrates.

In this context, a conductive gold nanoparticle ink with an extremely low sintering temperature that matches that of standard silver inks was developed.

2 MATERIALS AND METHODS

2.1 Inkjet Printer

For printing experiments, an OmniJet 300 inkjet printer (UniJet Co., Republic of Korea) was used that is compatible with Dimatix material cartridges (DMC, Dimatix Fujifilm, USA). These cartridges use piezo-driven printheads and are capable to work in a drop-on-demand mode, addressing every of the 16 nozzles individually. This system is able to deposit drops in a planar, two-dimensional pattern P(x,y) with 1 μm accuracy. For printing a pattern, first a pixel-based bitmap file is created displaying the structure to be printed, which is then converted by the printer software into single-printed drops. The drop deposition is done using a so called raster-scan method. Here, the drops are first placed along the y-direction. The distance between these drops is fixed. In this way, one can print single lines as well as continuous films.

The cartridges (1 pL DMC cartridges from Fujifilm Dimatix Inc., USA), inserted into the print head, consist of 16 nozzles with a nozzles spacing of 254 μm and a nozzle diameter of 9 μm. The frequency was fixed to 1 kHz for all experiments.

2.2 Gold Nanoparticle-based Ink

The gold nanoparticles (AuNPs) were synthesized following the well-known *Brust-Schiffrin-Method* (BSM), in which thiols are used as a capping agent [3]. These AuNPs are then suspended in a mixture of organic solvents, e.g. terpene alcohols and hydrocarbons, to match

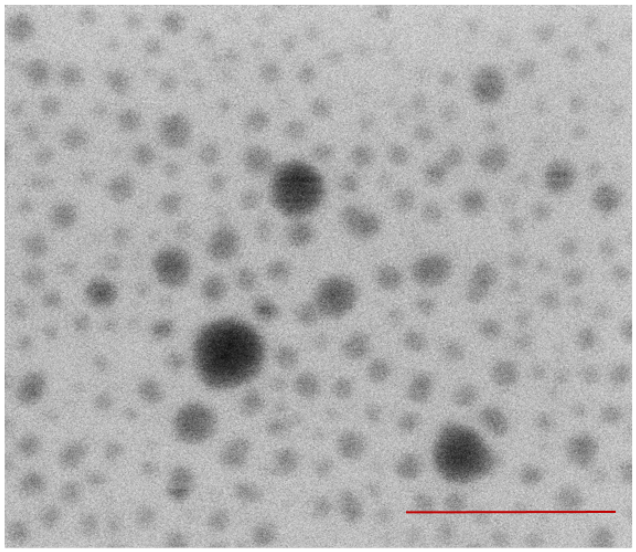

Figure 1: .
STEM image of gold nanoparticles with a diameter of 2.14 nm ± 0.15 nm. (Scale bar: 20 nm)

the viscosity and surface tension ranges of the ink needed for inkjet printing. Finally, this solution was filtered through a 0.2 μm polytetrafluoroethylene (PTFE) filter to obtain the final ink.

3 RESULTS AND DISCUSSION

3.1 Ink Characterization

Here, nanoparticles stabilized with branched thiols having diameters of 2- 3 nm were synthesized (figure 1). Owing to a small size and a branched capping agent, the melting temperature of the nanoparticles lies around 140 °C, which is 160 °C - 260 °C lower than the melting temperature of most other AuNPs [4].

In general, one can say that the melting temperature decreases with longer carbon chains of the thiol. This can be seen in table 1 that shows the melting temperature for different thiols as capping agent.

Consequently, this, leads also to decreasing sintering temperatures, which is in case of this ink around 50-80°C lower than any known gold ink [2]. The gold nanoparticle concentration in the ink was varied between 25-30 wt% and this results in conductivities 30-40 times less than that of bulk gold depending on the used sintering temperature. Using this gold ink, the dependence of the electrical resistivity on the sintering temperature of the gold structures was investigated. The sheet resistance was measured using a four-probe device with a pin distance of 2.5 mm (Schuetz Messtechnik). Since the sheet resistance is related to the specific resistivity via one over the thickness of the measured layer, one can determine the first by measuring the other two

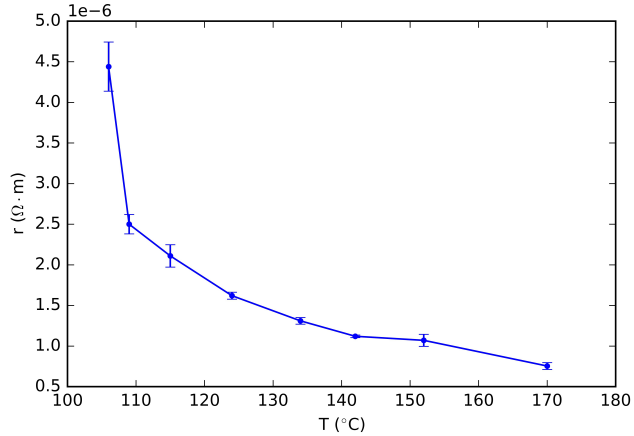

Figure 2: .
Specific resistivity ρ decreases drastically with increasing sinter temperature.

quantities. Equation 1 shows the relationship of sheet resistance and specific resistivity.

$$R_{Sheet} = \frac{\rho}{d} \Longleftrightarrow \rho = R_{Sheet} \cdot d \tag{1}$$

Therefore, it is enough to use printed squares for measuring the sheet resistance and heat the squares up with a heating rate of 5 K min^{-1} and keep the temperature constant for 15 min. Here, an ink with 25 wt% nanoparticles were used for printing. The temperature steps were varied from 100 °C in 5 °C steps to 105 °C, 110 °C, 115 °C and 120 °C. Continuing from 120 °C, the temperature was increased in steps of 10 °C up to 160 °C. Finally, the temperature was further increased to 180 °C. The thickness of these squares are around 66 nm ± 5.5 nm.
At a temperature of 100 °C, the resistance R is somewhere in the high kΩ to the low MΩ range, but decreases very fast to the ohmic range with increasing temperature. As figure 2 shows, for 106 °C, the sheet resistance is 67.3 Ω ± 4,6 Ω, which results in a specific resistivity of $4.44 \cdot 10^{-6}$ Ωm and decreases to 37,9 Ω ± 1.8 Ω or $2.50 \cdot 10^{-6}$ Ωm for 109 °C, respectively.

At 142 °C, ρ reaches a value of $1.22 \cdot 10^{-6}$ Ωm, which is 46 times lower than the specific resistivity of bulk gold ($2.44 \cdot 10^{-8}$ Ωm [5]. Increasing the temperature further, values of $7.5 \cdot 10^{-7}$ Ωm at 170 °C can be reached, which is only 31 times lower compared to bulk gold. Furthermore, it can be seen that the resistivity decreases very fast within 10 °C from $\sim 6.6 \cdot 10^{-2}$ Ωm to $2.5 \cdot 10^{-6}$ Ωm by a factor of 26,400 for increasing the temperature from 100 °C to 109 °C. Consequently, the gold structures already exhibit good conducting properties at low sintering temperatures.

Table 1: Melting temperature of gold nanoparticles with different thiols as capping agent.

Capping agent	$\mathbf{T}_{melt}$ **(°C)**
2-methyl-2-propanethiol	∼ 200 °C
3-methyl-2-butanethiol	∼ 160 °C
2-methyl-1-butanethiol	∼ 160 °C
t-Nonyl mercaptane	∼ 140 °C

3.2 Characterization of inkjet-printed drops on different substrates

Most importantly, these low sintering temperatures allow printing on low-cost polymer substrates, e.g. polyethylene naphthalate (PEN), polyethylene therephthalate(PET), commonly used in printed electronics. For the above described resistivity measurements a PEN substrate (PAQ1 M, DuPont Teijin Films) were used. In the following, the behavior of the ink on different substrates is described. Two different polyethylene naphthalate substrates, namely Teonex®Q83 and Optfine® PQA1, were investigated, in addition to a polyetherimide (ULTEM™ 1000-1000Film, Sabic Innovativ Plastics) and a polycarbonate (LEXAN™8010, Sabic Innovativ Plastics) substrate. The two PEN substrates differ according to their pre-treatment. While Teonex®Q83 has two identical sides, one side of Optfine®PQA1 is planarized which leads to a smooth and defect-free surface.
The behavior of the ink on these substrates is investigated by comparing the size of single printed drops. Furthermore, the surface of each substrate was activated using oxygen plasma (Plasma oven NANO, Diener Electronic, Germany). For all substrates the same conditions were used, namely 0.2 mbar O_2 pressure, 20 % power and 0.2 min treatment time, and a larger drop diameter could be found on all substrates after plasma activation. The most prominent change can be observed for PQA1M substrate. The diameters of the drops on the different substrates are summarized in table 2.

These results lead to the conclusion that the PQA1M substrate is the most suitable for printing small and well defined structures. However, without plasma treatment it is not possible to print continuous structures due to too high a contact angle of the ink on this substrate. Therefore, the surface energy of the substrate was increased by means of oxygen plasma treatment to lower the contact angle and get better wetting of the substrate. Hence, it was possible to print very small and well defined structures with line widths down to 40 μm and thicknesses of 70 nm on PQA1M.

3.3 Applications

As described before, this ink in combination with the 1 pL cartridge is suitable for printing of very small and well defined structures with line widths of 45 μm and thicknesses of 70 nm. These features are needed for printing interdigitated electrode arrays (IDEs) with high specific capacitances or microelectrode arrays (MEAs), which can be used to record action potentials of cardiomyocytes or neurons. Figure 3 shows an IDEs printed on a flexible PEN substrate.

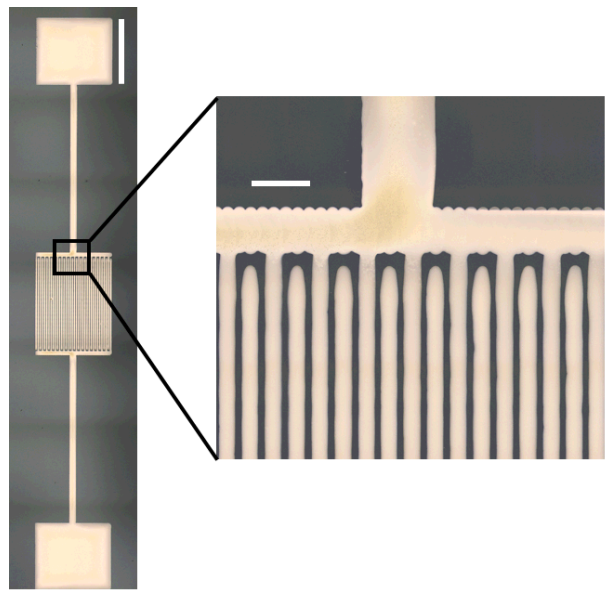

Figure 3: .
Printed gold IDE on a flexible PEN substrate (left) and a 50x magnification of the fingers (right). (Scale bar, left: 2000 μm; scale bar, right: 100 μm)

The distance between the single fingers was 17.6 μm ± 1.6 μm and the width of each finger was on average 45.5 μm ± 1.5 μm, while the thickness of the fingers was 69.1 nm ± 9.6 nm. The capacitance of IDEs in air was measured to be ∼1 pF, which is a value that corresponds to a theoretical calculation. Such electrodes can be used to develop (bio)sensors and do electrochemical investi-

Table 2: Diameters of single printed drops on different substrates without and with oxygen plasma treatment (0.2 mbar, 20% power, 0.2 in).

Substrate	**d (μm) without O_2 plasma**	**d (μm) with O_2 plasma**
LEXAN	59.44 ± 2.76	65.75 ± 0.38
ULTEM	63.38 ± 2.83	69.06 ± 1.50
Q83	64.14 ± 0.28	65.05 ± 0.44
PQA1M	27.76 ± 0.11	51.19 ± 0.30

gations, e.g. impedance, capacitance and conductivity measurements. In the area of biosensing, IDEs are used to detect the binding of antibodies to antigens or binding of DNA to probes. However, these events take place near the surface of the sensing layer and therefore, electrodes with high specific capacitances are needed [6].
Beside IDEs, the gold ink can be used to print microelectrode arrays with a different number of electrodes. These MEAs can be used to measure action potential of living cells. Figure 4 shows a MEA with 64 electrodes, printed on PQA1M. The temperature of the substrate holder was elevated to prevent bulging of the ink, therefore, a stacked coin pattern was exhibited.

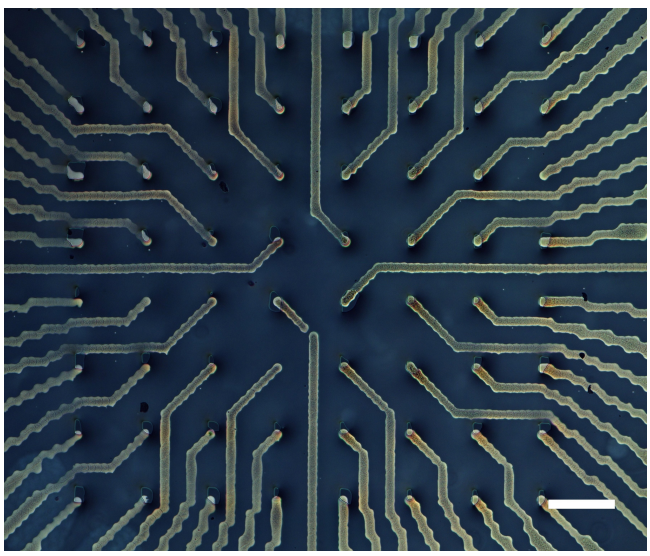

Figure 4: .
DIC image of an all-printed small-scaled MEA with 64 implemented microelectrodes. (Scale bar: 200 μm).

In both cases, detecting binding events and measuring cell action potentials, the electrodes are in contact with solutions with high concentrations of electrolytes, which might have affected prone to oxidation silver or copper tracks. However, using the gold ink stable and reproducible electrodes could be printed.
A third application would be organic field effect transistors (OFETs), which might experience a strong performance drop due to slight changes in resistance. Here, the gold would serve as drain and source electrodes [7].

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