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Testing of novel nano gold ink for inkjet printing

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ABSTRACT

Gold nanoparticles (GNPs) were synthesised by the Ultrasonic Spray Pyrolysis (USP) process and collected in deionised water with the addition of a stabiliser, i.e. PVP (0.1 wt.%). With the use of a rotary evaporator, a highly concentrated GNPs' suspension was achieved (600 ppm concentration of GNPs), which was used directly as novel nano gold ink for inkjet printing. The physical and chemical characteristics of such prepared nano gold ink were explained in detail by the use of Zeta (ζ) Potential, ATR-FTIR spectroscopy, UV/VIS spectroscopy, and nanoparticle size was identified through SEM. With nano gold ink the chosen pattern was printed onto photo paper, which was characterised for confirming the presence of gold with optical and SEM/EDX observations. The observations revealed that the tested printed nano gold ink on the paper provided a new route for the fabrication of paper-based electrochemical immunosensors, colorimetric sensors and nano-metallic biomedical sensors.

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1. Introduction

Metallic nanoparticles (MNP) have completely different properties like electrical, mechanical, optical and magnetic as their identical bulk materials [1-3]. Based on this, they can be used for various types of applications, such as in the medical and electronic industries [4-6], as well as increasingly in the food industry [7]. The preparation of their inks is envisaged as one of the growing applications of MNP [8]. The metallic nanoparticle ink can be prepared as various types of ink, namely, single element, alloy metallic, metallic oxide and core shell bimetallic nanoparticle inks [9]. These metallic inks, available on the present market, are prepared from Silver, Copper, Gold, Aluminium, Cobalt, Zinc, Palladium, Nickel and Platinum. Nowadays, many conventional methods are being used for the printing of MNP inks on different substrates for different applications [10,11]. Inkjet printing is, namely, a rapidly evolving technology of loading functional inks onto various substrates, and also one of the excellent approaches for the printing of MNP inks, as it deposits the required patterns on the surface with accurate and non-contact writing [12-14]. The described inkjet printing method is operated at room temperature and pressure [8], controlled by data from images or a pattern in conjunction with a computer, and transferring the ink in the form of microdroplets onto the chosen substrate. Inkjet printing has high precision, as well as control of homogeneous microdroplets' loading, and the main advantage is that we can print complex schemes without chemical waste after the printing process, which makes the process environmentally friendly and economical [15].

In the last decade, inks composed of gold nanoparticles (GNPs) – so-called nano gold inks – had a lot of attention towards printed electronics due to the GNPs' properties, like high thermal conductivity, excellent resistance to oxidation and tuneable optical properties [16]. Based on

this, nano gold inks play an important role in the fabrication of printed electronics, biosensing applications (e.g. microelectrode arrays) and electrochemical sensors [17]. The recent literature shows that the preparation of nano gold inks and ink formulations were applied by different approaches [18-21], but these approaches are not beneficial for the production of larger quantities of nano gold ink. The currently available nano gold inks on the market are limited, and cost ineffective when compared to other MNP inks. The aim of this research work was the preparation of novel nano gold ink for the inkjet printing process. The synthesised gold ink presented in this work is cost-effective for the fabrication of paper-based sensor applications.

The rest of this article is arranged as follows: Section 2 describes the synthesis and inkjet printing of GNPs, with the carried out comprehensive characterisation of nano gold ink, including physical and chemical properties, by using different techniques like Zeta (ζ) Potential measurements, ATR-FTIR, UV-VIS spectroscopy, and SEM/EDX observations. Section 3 discusses the results of preliminary testing of printing the patterns by using a Fujifilm Dimatix DMP-2831 inkjet printer. The printed patterns were characterised through Optical Microscopy and SEM/EDX observations. The conclusions and future perspectives are presented in section 4.

2. Materials, methods and design of experiments

2.1 Materials

Synthesis of GNPs

GNPs were synthesised with an Ultrasonic Spray Pyrolysis (USP) device located in Zlatarna Celje d.o.o. (Slovenia), Fig. 1. The USP is composed of an ultrasonic generator (with f = 2,4 MHz), a reactor furnace (with 3 temperature zones) and a system for nanoparticle collection (3 collecting bottles). In the USP, with the ultrasound, the precursor solution with the dissolved material is dispersed into droplets. These droplets are then transported with a carrier gas to a high temperature reactor, where the target material inside the droplet is decomposed chemically via pyrolysis, and nanoparticles of pure elements are formed. In this study, the selected raw material for preparing Au-precursor solutions was Au acetate salt (AuAc, gold (III) acetate ($Au(CH_3COO)_3$), Alfa Aesar), which was dissolved in deionised water and hydrochloric acid (HCl, 37 %, Sigma Aldrich) with a final concentration of Au 1 g/L [22-26]. The pH value of the prepared solution was about 1-2. The high acidity of this solution may be unfavourable for some of the USP elements during synthesis, as observed from previous practical experience. In order to increase the pH value to 5-6, the solution was stirred magnetically and pellets of sodium hydroxide (NaOH, Fisher Chemicals) were added, obtaining a clear yellow solution,suitable for use with USP. The following parameters were used in the USP synthesis: The flow of carrier gas N_2 was 4 L/min, the flow of reduction gas H_2 was 2 L/min, reactor temperatures were T_1 = 120 °C, T_2 = 400 °C, T_3 = 400 °C, the collection medium was ethanol with stabiliser Polyvinylpyrrolidone (PVP) with a concentration of 2.5 g/L. With USP the formed GNPs were collected in the described collection system.

Preparation of nano gold ink

The nano gold ink was prepared directly from GNPs ethanol/PVP suspension which was, after USP synthesis completion, immediately subjected to a concentration process by using a rotary evaporator. The parameters of the rotary evaporation process were: Rotation: 240 rpm, Pressure: 40 mBar, Bath temperature: 40 °C, Initial volume: 250 mL, Distillation time: 45 min, Final volume: 5 mL. The concentration of GNPs in suspension was measured with Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The spectrometer used was an HP, Agilent 7500 CE, equipped with a collision cell (Santa Clara, CA, USA). The following conditions for ICP-MS were used: The power was 1.5 kW, Nebuliser-Meinhard, plasma gas flow was 15 L/min, nebuliser gas flow was 0.85, make up gas flow was 0.28 L/min, and reaction gas flow was 4.0 mL/min. The instrument was calibrated with matrix matched calibration solutions. The relative measurement uncertainty was estimated as ±3 %. The concentration of GNPs in highly concentrated suspension as novel nano gold ink was 600 ppm.

Fig. 1 Ultrasonic Spray Pyrolysis (USP) device located in Zlatarna Celje d.o.o.

Inkjet printing of nano gold ink

The Inkjet printer used for the printing of nano gold ink, was the Fujifilm Dimatix DMP-2831 (FUJIFILM Dimatix, USA) with a piezoelectric Inkjet cartridge. The printing of patterns on a substrate using prepared nano gold ink was under the following parameters: Waveform: low-viscosity (the uniformity of the droplets was the best); Jetting Voltage for all nozzles was 14 V; Tickle control was 23 kHz; Head Angle was 9.5°; Cartridge temperature was 23.5 °C and the Printing plate temperature was 24.5 °C. The print pattern was composed of vertical lines with a thickness of 3 mm and a length of 60 mm. The selected pattern was printed on a commercially obtained glossy photo paper. The pattern was printed in 15 layers in order to ensure a more continuous distribution of GNPs from the nano gold ink.

2.2 Characterisation of nano gold ink and GNPs

Zeta (ζ) Potential measurement

The Zeta (ζ) Potential of nano gold ink, using the Dynamic Light Scattering (DLS) technique, was measured with the Malvern Zetasizer Nano ZS (Malvern Panalytical, UK), and a folded capillary zeta cell. The selected measurement parameters were: Refractive Index (R.I.) for the gold particles was 0.2, absorbance was 3.32, dispersant was ethanol, temperature was 25 °C, R.I. for ethanol was 1.36, viscosity was 1.10 cP, dielectric constant was 22.4.

ATR-FTIR spectroscopy

Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR) analysis of the nano gold ink and pure PVP – as control – was performed with a Perkin–Elmer FTIR Spectrophotometer and a Golden Gate Attenuated Total Reflection attachment with a diamond crystal. The ATR-FTIR spectra were accumulated within 16 scans at a resolution of 4 cm^{-1} within a range of 4000 cm^{-1} to 650 cm^{-1}.

UV/VIS spectroscopy

The UV/VIS absorption of nano gold ink was measured with a Tecan Infinite M200 UV/VIS Spectrophotometer (Tecan, Austria), using a quartz cuvette. The absorbance measurements were made over the wavelength range of 300-700 nm, with no. flashes = 5x and time per measure = 20 ms.

2.3 Optical and SEM/EDX observations

Optical microscopy

The Inkjet printed layers were examined on the Nikon EPIPHOT 300 light microscope (Nikon, Japan).

SEM microscopy/EDX analysis

A Scanning Electron Microscope (SEM), Sirion 400 NC (FEI, USA) with an Energy-Dispersive X-ray spectroscope (EDX) INCA 350 (Oxford Instruments, UK), was used for the SEM investigations of nano gold ink and printed patterns. Droplets of the nano gold ink were put on SEM holders with conductive carbon adhesive tape and left to dry under vacuum, while the printed patterns were located directly on the SEM holder with conductive carbon adhesive tape without any additional treatment.

EDX was used for the determination of qualitative and semi-quantitative chemical composition.

GNPs' size measurements

GNPs' size measurements in nano gold ink were performed from SEM micrographs. The sizes were measured with the microscope software and with manual measurements from the SEM micrographs, measured with the ImageJ analysis software. The particle size distributions show the manual measurements from the ImageJ software. The GNPs' size distributions were made from 1,000 nanoparticle measurements for each measurement sample. Two types of GNPs' measurements were done: Firstly, on the prepared nano gold ink before filtration, and secondly after manual filtration of nano gold ink through the injection filters with 0.1 μm pore sizes. These measurements were made to determine if the ink was adequate to prevent clogging of GNPs in the nozzle during printing.

3. Results and discussion

3.1 Zeta (ζ) potential measurement

Zeta (ζ) Potential measurement is a significant characterisation technique to determine the surface charge of GNPs in nano gold inks, where the ζ potential can be employed for understanding the physical stability of GNPs [27]. It is generally considered that the GNPs with high negative or positive ζ potential are electrically stabilised, while GNPs with low ζ potentials tend to coagulate [28]. There are many other factors, such as the presence of stabilisers, that affect the physical stability of nano gold inks. The measured ζ potential of GNPs in the studied nano gold ink was -1.89 mV, and the ζ potential distribution can be observed from Fig. 2. A negative ζ potential indicates that GNPs were negatively charged, and this is most likely because GNPs are capped with the PVP stabiliser, which lowers the magnitude of ζ potential. The GNPs capped with PVP stabiliser remained dispersed in the nano gold inks most likely due to the steric hindrance created by the large PVP layer coating on the surface of the GNPs [29].

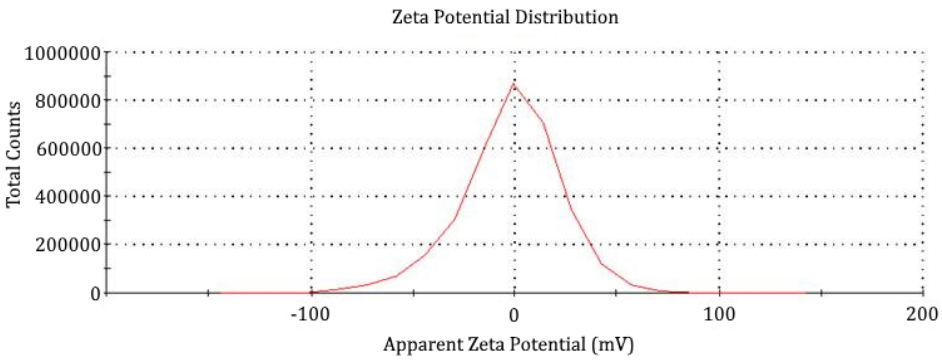


Fig. 2 ζ potential distribution of gold ink

3.2 ATR-FTIR spectroscopy

ATR-FTIR Spectroscopy was used for the determination of PVP stabilised GNPs in nano gold ink – the FTIR spectra of pure PVP and GNPs in nano gold ink are shown in Fig. 3. The FTIR spectra for pure PVP shows characteristic absorption peaks for amide N-H stretch at 3398 cm^{-1}, C-N vibration at 1279 cm^{-1}, C=O stretching at 1667 cm^{-1} and typical peaks for the pyrrolidinyl group of PVP at 1475 cm^{-1} and 1432 cm^{-1}. The characteristic peaks of pure PVP also existed in PVP stabilised nano gold ink, indicating that the adsorption of PVP molecules onto the GNPs' surface was successful [29,30]. The successful functionalisation, most likely via intermolecular hydrogen bonding, was also confirmed with an absorption peak shift of C=O stretching from 1667 cm^{-1} to 1643 cm^{-1}.

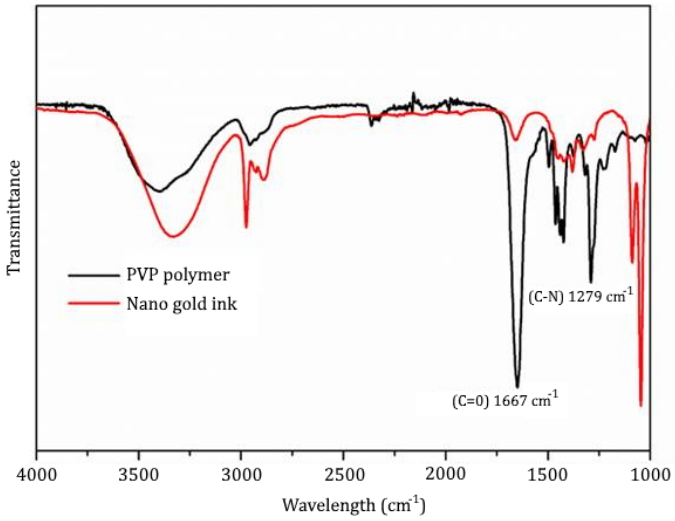


Fig. 3 FTIR spectra of pure PVP polymer (black) and nano gold ink (red)

3.3 UV-VIS spectroscopy

UV-VIS spectroscopy was used for evaluation of the optical and structural properties of nano gold ink, i.e. investigation of the interactions between nano gold ink with different electromagnetic waves. GNPs have unique optical properties, along with a property known as Surface Plasmon Resonance (SPR) [31-32]. With SPR, the absorption of a specific wavelength causes the fluctuation of electrons on the GNPs' surface. SPR is strongly dependent on the GNPs' size, shape and their agglomeration state. It is known that GNPs display a single absorption peak in the visible range between 510-550 nm, and due to the GNPs' size variations, GNPs inks have different colouration [33]. The absorbance spectra of the prepared nano gold ink can be observed from Fig. 4. It was discovered that the maximum absorption band is at ~538 nm, which indicates the stable state of the prepared nano gold ink.

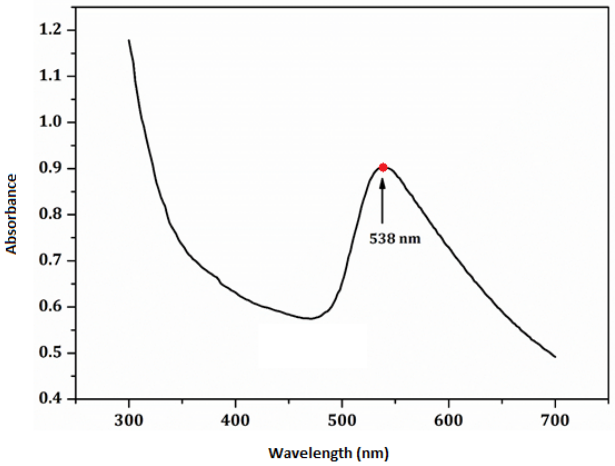


Fig. 4 UV-VIS spectra of nano gold ink

3.4 GNPs' size measurement

GNPs' size measurement was performed using SEM micrographs, firstly on the prepared nano gold ink before filtration (Fig. 5a), and secondly after manual filtration of nano gold ink through injection filters with 0.1 μm pore sizes (Fig. 5b).

The calculated mean GNPs' size in the nano gold ink before filtration was 46.2 nm, with a maximum measured particle size of 332 nm. The smaller GNPs had a mostly spherical shape, while the larger ones had more irregular shapes. After filtration, the mean GNPs size dropped to 16.7 nm. The minimum measured GNPs' size in the filtrated nano gold ink was 5.7 nm, and the maximum particle size was 38 nm. The GNPs' size measurements confirmed that the filtration had removed larger GNPs and clusters of agglomerated GNPs successfully from the prepared nano gold ink, making the ink usable for the printing without clogging of the cartridge nozzles. Mostly spherical and some irregular particles remained in the nano gold ink after filtration, as observed from Fig. 5.

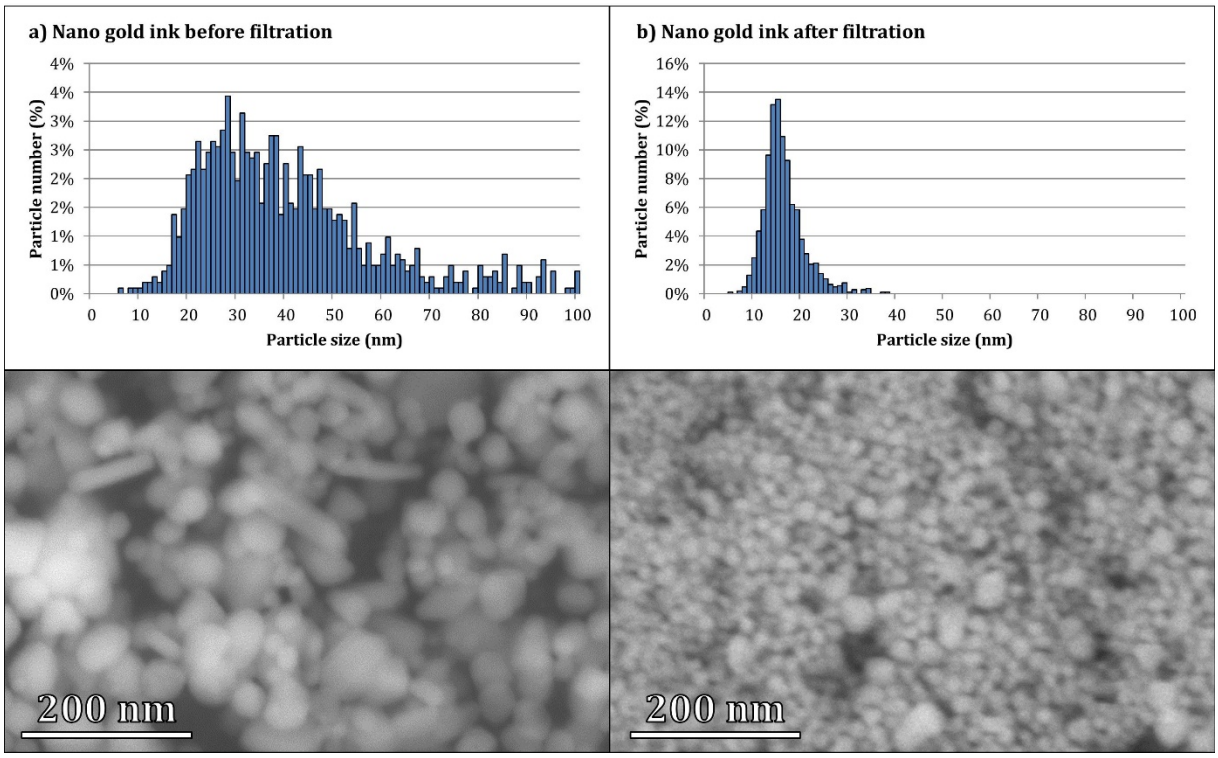


Fig. 5 GNPs' size distributions: a) before and b) after filtration of nano gold ink

3.5 Inkjet printing of nano gold ink

The prepared nano gold ink was injected into the reservoir by means of a syringe and a special metal needle. After the reservoir was filled, a print head was attached to the reservoir, and the assembled cartridge was inserted in the appropriate location in the Inkjet printer. The cartridges used for the printing were Dimatix brand (DMP DMC-11610), with the maximum reservoir volume of 2 mL. The suitable cartridge was first selected in the computer programme. The print head was cleaned by leaking nano gold ink through the nozzles, to make sure that no nozzles were clogged. After the print head was cleaned, a substrate was inserted into the printer and was adhered onto the printing plate at the edges. This prevents the substrate from moving during printing. Before printing, the nano gold ink flow through the nozzles was checked again. With the programme, the individual nozzle and all the nozzles together were checked (Fig. 6a), to ensure that the nano gold ink droplets were homogeneous and uniform. This was achieved with the modification of the ink waveform (Fig. 6b) and with changing the ink droplet parameters.

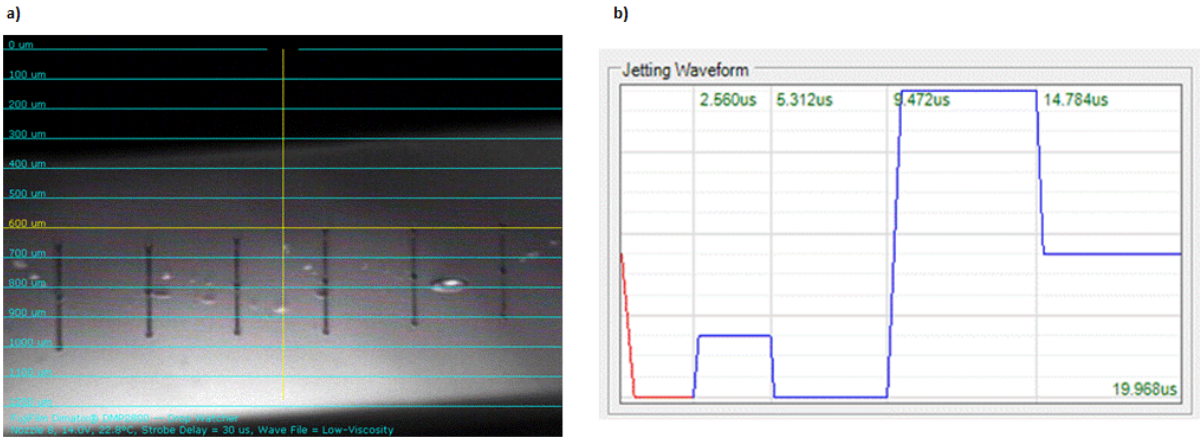


Fig. 6 a) Image of ink jetting through nozzles at the applied voltage of 14 V, which is the threshold for proper drop formation and breakage using the wavefo; b) waveform customised for this study

3.6 Optical microscopy

The nano gold ink Inkjet printing performance of vertical lines printed onto photo paper was observed by optical microscope, as shown in Fig. 7a. It can be seen that the printed line widths between each line do not correspond, most likely due to the overlaying between the spreading of the droplets. The line width becomes smaller with increasing in the drop spacing, which is due to decreasing in the overlapping of the nano gold ink droplets. The measured average printed line width was ~130 μm.

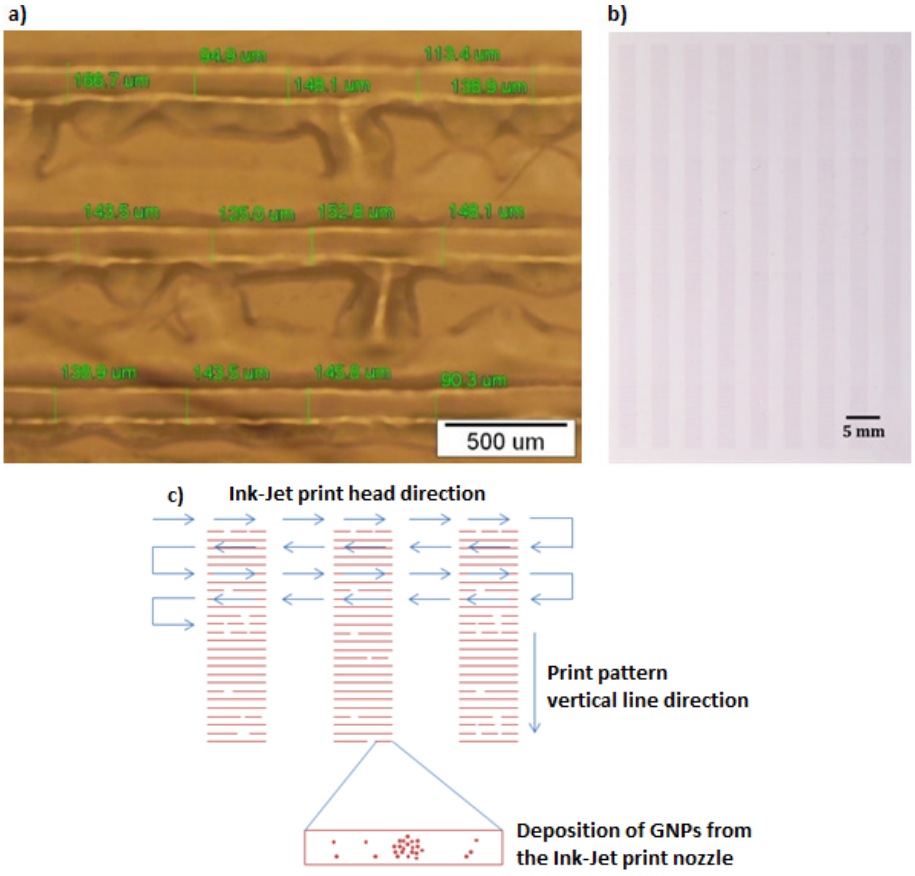


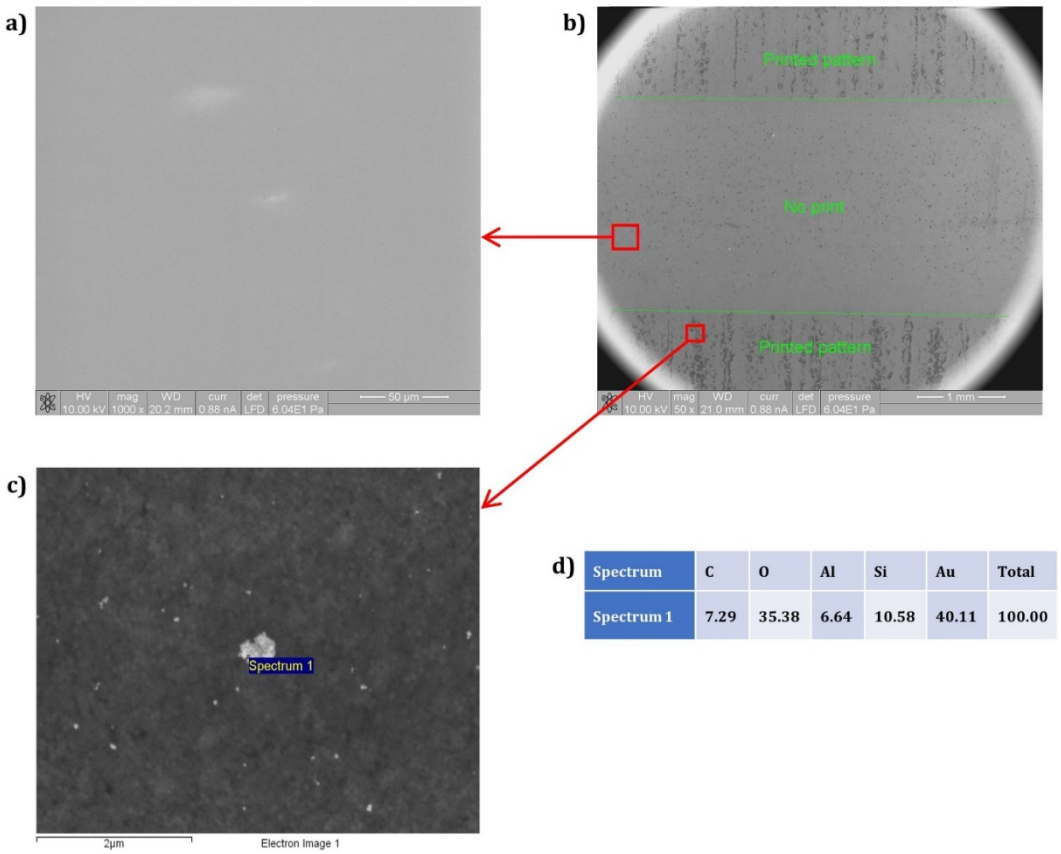
Fig. 7 Optical microscope image of nano gold ink Inkjet printing performance: a) Vertical lines on photo paper; b) Macro image of printed pattern; c) Schematic representation of the pattern printing directions

3.7 SEM microscopy/EDX analysis

A typical SEM micrograph of a nano gold ink printed pattern on pure photo paper is shown in Fig. 8a. The gold printed pattern was investigated thoroughly for determination of the GNPs' distribution (Fig. 8b). The GNPs were clustered together to a greater extent in the optimal region (Fig. 8c). EDX analysis confirmed that the printing with nano gold ink was successful, as the chemical composition of the clusters showed more than 40.1 % of Au (Fig. 8d). The elements C, O, Al and Si were originating from the printing substrate – a commercially obtained glossy photo paper.

The SEM analysed printed pattern does not show a continuous layer of GNPs, but rather visible printing lines, which contain clusters of GNPs and discrete GNPs. These initial results identify that the printing parameters would have to be modified for printing of a more continuous layer of GNPs: Print nozzle size, rheological properties of the nano gold ink (surface tension and viscosity), GNPs' concentration in the nano gold ink, GNPs' sizes, droplet spacing, print overlapping and printing direction [34]. There are some limitations for these parameters that also need to be considered for printing of a continuous layer.

The print nozzle size, along with the rheological properties of the nano gold ink, determines the ink flow for printing. These properties need to keep the nano gold ink inside the nozzle without the ink flowing freely from the nozzle when the printing is stopped and provide the flow of the ink and droplet generation when the Inkjet is activated. Stabilisers for GNPs may alter the rheological properties of the nano gold ink, which is something to consider during nano gold ink formulation.



Spectrum	C	O	Al	Si	Au	Total
Spectrum 1	7.29	35.38	6.64	10.58	40.11	100.00

Fig. 8 SEM micrograph of Inkjet printed GNPs with corresponding EDX analysis: a) Pure photo paper; b) Printed pattern with the space between the lines; c) GNPs' distribution; d) EDX analysis

The available nozzle sizes also limit the GNPs' sizes in nano gold ink, which can be used for successful printing. Our experimental results show that GNPs of size around 10 nm are still capable of printing, while larger sizes clog the printing nozzle, making nano gold ink unusable. Since the GNPs in nano gold ink, obtained with the USP technique had a broad size distribution, filtering of nano gold ink was mandatory for printing with an Inkjet printer. Another point to consider is the concentration of GNPs in the nano gold ink and their stability. Using very high concentrations of GNPs (> 600 ppm) leads to unstable dispersions (depending on the stabiliser used), resulting in agglomeration, rendering the nano gold ink unusable. Very high concentrations may also lead to unwanted Inkjet behaviour, interfering with ink droplet sizes and droplet generation intervals. The distribution of GNPs inside the droplet is also a factor, affecting the printed pattern. These combined nano gold ink properties may result in various forms of the printed patterns. One such example is the "coffee-ring effect" [9], where most of the GNPs would be clustered on the droplet outer diameter, while the inside of the printed droplet has a disproportionately low number of GNPs.

Possibilities for improving the printed pattern may be by modifying the droplet spacing, print overlapping and printing direction, in order to produce more favourable results for printing a more continuous layer of GNPs. Several experiments need to be performed in order to find the optimal balance of nano gold ink properties, GNPs' properties and printing parameters. Here, it was shown that USP is capable of providing GNPs to be used in Inkjet printing, while the discussed printing specifications depend on the application of the printed patterns.

Using a printed layer of discretely dispersed GNPs on glass or other transparent substrates produces a spectrally selective surface which blocks infrared radiation due to the plasmon resonance effect. This makes these printed GNPs usable in specialised optical applications, such as light filters or logic gates [35]. An example of exploiting this property is also usage in energy-efficient windows. Note, however, that, nowadays, some other materials are better suited for this particular task [35]. The catalytic properties of GNPs may also be used for CO oxidation into CO_2, using these GNPs in gas masks and some chemical processes, as well as for the removal of CO traces [35]. They may also be used as decorative inks, or as a colouring additive in niche glassware and ceramics. The successful printing of GNPs produced by USP thus shows the possibility of utilising these GNPs for the fabrication of specialised products.

4. Conclusion

Nano gold ink prepared directly from a highly concentrated GNPs' suspension synthesised through USP synthesis, was investigated in the present work. Results of different characterisation showed that the high stability of the nano gold ink was confirmed. ζ potential measurements showed that GNPs were negatively charged, due to the capping of GNPs with PVP stabiliser, and the successful functionalisation of PVP was confirmed with ATR-FTIR. The average size of GNPs in nano gold ink was 16.7 nms after manual filtration through injection filters with 0.1 μm pore sizes. From this case study, we can conclude that the nano gold ink printed patterns are highly stable, while the printing specifics can be modified for different applications. The preparation of nano gold ink with USP and the selected synthesis parameters required filtration of the nanoparticles in order to prevent clogging of the inkjet printing head. The given initial results also show a non-continuous layer of printed GNPs, indicating that the ink and printing parameters would have to be modified for more favourable results. The presented results demonstrate that the preparation of nano gold inks with the USP technique can contribute in the fabrication of specialised products, useful for different types of technological applications such as electrochemical and nano-metallic biosensors.

Considering the successful synthesis of gold nano ink, the preparation of lower concentrations of GNPs with sizes below 10 nm, and an evaluation of their properties, printing characteristics and real-life analysis for their application in paper-based sensors, will be tested in future studies.

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