Copper Nanoparticle Conductive Inks: Characterization and Fabrication of Inkjet Printed Flexible Electrodes

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***Abstract*—** In this article, multiple commercially available copper (Cu) nanoparticle conductive inks have been investigated – both as received and in modified form, for future flexible printed electronic device fabrication and their applications. Critical fluid properties such as viscosity, surface tension, particle size measurement, and pH values have been analyzed thoroughly along with their temperature dependence for three commercial formulations, Ink 1: DM-CUI-5002 (Dycotec Materials Ltd. UK), Ink 2: Metalon® CI-004 (NovaCentrix, USA), Ink 3: Metalon® CI-005 (NovaCentrix, USA), and a fourth custom diluted version of DM-CUI-5002 (Ink 4). The mean particle sizes of the different Cu nanoparticle inks are 56.2 nm for Ink 1/ Ink 4, 8.62 nm for Ink 2, and 11.5 nm for Ink 3. The viscosities for Inks 1 – 4 are 17.14, 31.30, 13.52, and 15.02 cP respectively (20°C). The resistivity obtained for each nanoparticle ink varied from 8.89 μΩ-cm to 39.5 μΩ-cm. Fluid properties of the nanoparticle Cu inks have been optimized for inkjet printing using Fujifilm Dimatix Materials Printer – DMP 2850 based on legacy printheads and recently launched (2021) Samba G3L printheads. The electrochemical characterization of the ink/flexible inkjet printed electrodes has also been reported based on electrochemical impedance spectroscopy (EIS) measurement (phosphate buffer saline – PBS; pH 7.43). This article indicates the potential viability of utilizing commercially available Cu ink (Ink 3) for printing flexible electronics with both inkjet printheads. However, Ink 4 showed excellent performance with the lowest impedance (~ 400 Ω at 1kHz) making it a promising formulation for flexible inkjet printed Cu electronics.

***Index Terms*—** Electrochemical impedance spectroscopy, flexible electronics, inkjet printing, nanoparticle conductive inks.

I. INTRODUCTION

Recently, inkjet printing has been widely accepted and popularized by researchers in the areas of flexible printed sensor fabrication and its applications. Inkjet printing is an additive manufacturing technology where sensors are printed/fabricated using layer-by-layer deposition of the materials and then the printed patterns are converted into conductive films [1]. Inkjet printing offers quick and simple fabrication, cost-effectivity, high-resolution, low-material waste, and range of usefulness of materials [2-8]. In this process, nanoparticle conductive inks are stored in a sealed reservoir and an exact amount of ink is ejected using piezoelectric cartridge nozzles [9]. It has been reported and observed that inkjet printing outperformed other traditional sensor fabrication technology i.e., lithography, screen printing, and drop casting or stamping in terms of cost-effectivity, resolution, uniformity, and scalability [10-12].

Recently conductive nanoparticle inks i.e., copper (Cu), silver (Ag), and gold (Au) have received intense attention for printed electronic device fabrication due to their high electrical and thermal conductivity, low-production cost, chemical stability, reproducibility, and non-hazardous nature [13-15]. Specially Cu gets huge acceptance and popularity due to its high conductivity (compared to Ag) as well as cost-effectivity [13]. It has been reported that Cu costs only 1% of the most conductive metal Ag [13]. However, one major issue regarding Cu is its low resistance to oxidation i.e., cuprous oxide (Cu_2O) and cupric oxide (CuO) formation. This causes instability and unreliability for Cu printed/fabricated electronic devices in the long-term period [16]. Due to other advantages including extremely low-cost, researchers have been investigating a large amount of time to solve the oxidation issue i.e., developing advanced next generation Cu inks formulations, and effective sintering/post processing techniques for long term reliability [17, 18]. Hence, during the last decades, a huge development in case of Cu chemistry and nanotechnology to improve the Cu nanoparticle conductive inks have been reported/introduced [19, 20]. The agglomeration (one of the major issues) of the Cu nanoparticles have been prevented by adding stabilizing agents (i.e., polyvinylpyrrolidone (PVP), 1-amino-2-propanol) to cover the surface [21]. Different synthesis/formation have been reported to accommodate different printing methods such as adding surface tension modifiers, humectants, and binders have been introduced to modify/adjust viscosity, consistency, and wettability of the Cu nanoparticle conductive inks [22].

Inkjet printing Cu nanoparticle inks have been reported previously by different researchers [17, 23, 24]. Dycotec DM-CUI-5002 has been mentioned in the literature several times for printing electronics with Cu nanomaterials [25-27]. The reported diameter for the ink has been ranged from 25 nm to 40 nm. The inkjet printing parameters (DMP 2800 Dimatix Materials Printer) i.e. cartridge temperature – 47 °C and applied voltage – 40V were reported as optimum to achieve 4m/s drop speed [26]. The 10 pL cartridge was reported to print patterns with 10, 20, and 30 µm drop spacings. Some researchers also used Jetlab® IV (Microfab, Plano, TX) – dual printhead setup (60 µm nozzle orifice) for inkjet printing Cu electronics with DM-CUI-5002 [27]. The filtration with 0.45 µm PTFE filter was highly recommended before transferring the nanoparticle Cu ink for printing. For Jetlab® IV the reported parameters were 40 °C for cartridge and printhead temperature to achieve line with specific thickness (0.298 to 1.796 mm) and width (0.75 to 0.825 mm). Another commercially available Cu nanoparticle ink i.e., Novacentrix product (ICI - 020) has been reported to fabricate RFID antennas on cotton fabric, PCB repair applications, and different electronic applications [28, 29]. In addition, Cu nanoparticle conductive inks have also been employed for devices i.e., vertical interconnects, 3D antenna cover, contact grids on gallium arsenide GaAs, etc. [30-33]. Different types of sintering and cleaning processes have also been reported in different literatures i.e., thermal sintering, photonic sintering - IR sintering, UV sintering, laser sintering, and intense pulsed light sintering, plasma sintering, and chemical sintering [34-47].

It is clear from the literature review that over the past few years several developments have been taken places in case of effective Cu nanoparticle ink formulations, commercialization, incorporating efficient post-processing techniques to get rid of oxidation, etc. However, most of the time detail implicit processes/recipes have not been shared/reported for the inkjettable formulations of Cu nanoparticle conductive inks. In addition, Fujifilm Dimatix has just changed their inkjet heads from Legacy (DMC 11610/DMC 11601) to Samba G3L line. This newly launched printhead requires a lower viscosity (4 to 8 cP) and hence, a completely different printing parameters (cartridge temperature, platen temperature, jetting voltage, jetting frequency, and meniscus set point) to operate. With that in mind, this research aimed to develop the effective and efficient inkjet printing processes/recipes for both Legacy (DMC 11610) and the newly launched Samba G3L printheads in case of all 4 types of reported conductive nanoparticle inks i.e., Ink 1: DM-CUI-5002 (Dycotec Materials Ltd. UK), Ink 2: Metalon® CI-004 (NovaCentrix, USA), Ink 3: Metalon® CI-005 (NovaCentrix, USA), and a fourth custom diluted version of the Dycotec ink (Ink 4). The research thoroughly investigated and reported the fluid properties of the commercially available and modified/optimized Cu nanoparticle conductive inks (Ink 1 through Ink 4). The performance of the reported fabrication processes and the application as electrodes based on electrical impedance measurement using a buffer solution have been outlined in detail with description as well as graphical representations. Section II describes materials, characterization, deposition (based on Fujifilm Dimatix DMP 2850), sintering processes, and electrochemical impedance measurement of Cu nanoparticle conductive inks, section III illustrates results and discussion including graphical/data representation, and section (IV) provides the conclusion along with a viable consideration to utilize flexible Cu electrodes for future chemical and biosensing applications.

II. Methods

A. Materials

Dycotec copper ink (DM-CUI-5002), Dycotec copper ink diluent (DM-CUI-5002-DT), Novacentrix copper inks (Metalon® CI-004 and Metalon® CI-005), diethylene glycol monoethyl ether, 1 methoxy- 2 propanol were all used as received. The 1×phosphate-buffered saline (PBS; pH 7.43) was prepared combining 0.1 M sodium chloride (Sigma Aldrich, ≥99.0%), 0.1 M potassium chloride (Sigma Aldrich, MW = 74.55), 0.1 M disodium hydrogen phosphate (Sigma Aldrich, MW = 141.96), and 0.1 M potassium phosphate monobasic (Sigma Aldrich, MW = 136.09).

B. Characterization of Copper Nanoparticle Conductive Inks

Four different types of Cu nanoparticle conductive inks (Ink 1 through 4) have been characterized based on their fluid properties i.e. viscosity, surface tension, particle size, and pH value. All the characterization experiments have been performed at room temperature (~20 °C). Ink viscosity was analyzed using a Brookfield Ametek LV-DVE viscometer (spindle 00 and 30 rpm). The Enhanced UL Adapter accessory and a recirculating water bath were utilized to allow for 16 ml sample volumes to be measured with viscosities down to 1cP. The viscosities of the various inks were then studied as a function of temperature. Ink 4 was synthesized (20ml of Ink 1 + 4ml diethylene glycol monoethyl ether) for the Samba G3L heads and compared. 50 °C was selected as the upper temperature bound, as this is the upper limit of the Samba G3L temperature control capability. Surface tension measurements were performed on a BZY-201 tensiometer using the Wilhelmy platinum plate technique. Prior to each measurement, the plate was cleaned in solvent (isopropanol) and then heated using an alcohol burner. In this method, dynamic contact angle is measured while immersing and withdrawing the vertically suspended platinum plate. Dynamic light scattering (DLS) measurements were performed using a Precision Detectors PD2000LS dynamic light scattering system using a quartz cuvette for particle size measurement of each ink. The observations were obtained using a 10^6x dilution of each ink formulations. Ink 1/Ink4 and Ink 2/Ink 3 were diluted using diethylene glycol mono ethyl ether and 1-methoxy-2-propanol respectively. Prior dilution the inks were filtered through a 5 μm PTFE syringe filter to remove large agglomerates. The DLS measurements were performed at 20 °C. The adhesion test for all four types of reported Cu nanoparticle conductive inks have been performed using ASTM D3359 (ASTM 2009) on Kapton and glass substrate. All the inks showed excellent adhesion property for both substrates. In this research, Kapton has been chosen as the printing substrate for further processes i.e., deposition, printing patterns, and sintering. The initial sintering experiments and resistivity measurements were conducted on glass microscope slides.

C. Deposition of Copper nanoparticle Conductive Inks

The performance of each Cu nanoparticle inks including the diluted/optimized version were evaluated based on inkjet printing using Fujifilm Dimatix DMP-2850 except Ink 2 due to high viscosity compared to optimum value for inkjet printing without reformulation. The jetting parameters were investigated and developed for all three types of nanoparticle inks – Ink 2 was ignored deliberately due to its high viscosity which is incompatible with both inkjet printheads – legacy and newly launched samba G3L printhead. During the study, it was learned that the manufacturer had discontinued their older style printheads – legacy (DMC-11610/11601) and were migrating all systems to their newer samba G3L printheads. Hence, initial development began on the legacy printheads, and then migrated to the newer style printheads. The legacy printhead used for inkjet printing copper was DMC-11610 (10 pL) which has 16 nozzles spaced 254 μm apart. On the other hand, the samba G3L printhead has 12 nozzles spaced 338.67 μm apart. The Cu inks were initially allowed to reach at room temperature – storing temperature for Ink1/Ink 4 is 4 °C. The nanoparticle inks were agitated for 1 minute and desiccated for about 20 minutes to avoid agglomeration and bubbles respectively. Finally, before loading the inks into a syringe (3ml) and performing the printing tests, the inks were filtered with 0.45μm 25mm diameter PTFE filter. Kapton was used as a printing substrate to print the nanoparticle conductive inks. The viscosity requirement of the new head is much lower than the DMC-11610. To use the new heads, after upgrading DMP 2850 printer, one needs to follow the same procedure as with the old heads but be sure to select the Samba 12 nozzle head when loading the cartridge.

Also, these new heads appear to have wetting issues if wiped with isopropanol, so this was avoided. Inkjet printing parameters varied based on different print heads and formulations of inks i.e., platen temperature for both printheads were chosen as 35 °C, cartridge temperature varied from 40 - 50 °C, jetting voltage ranged from 28 to 35 V, jetting frequency and meniscus set point for legacy and samba printheads were chosen as 5KHz and 0.5 as well as 3.5KHz and 5 respectively. The cartridge print height was chosen as 1 mm. The drop spacing used for printing different patterns with both print heads and all the types of Cu inks was 15 µm (1693.3 dpi) – drop diameter of Cu inks on Kapton was ~50 µm.

D. Sintering Process

After inkjet printing different patterns with Cu nanoparticle conductive inks, the ink decomposition and reduction processes were evaluated by pipetting ink samples on a glass microscope slide patterned with polyimide wells. It is expected that the ink can be thermally decomposed at 200 °C into Cu/CuO. It has been reported previously that a 5 minute, 200 °C (15% Hydrogen, 85% Nitrogen) reduction was utilized to achieve conductive copper films [22]. In this research, the resistivity of the inks was measured using four-point probe method. This parameters for four different types of inks were collected from glass microscope slides. The resistivity measurement was performed on the glass slide following drop casting method. Kapton was used to create a test structure on the glass in order to make a ~30 µm thin film of Cu inks. After Cu ink deposition, a tube furnace with a gas manifold to control the gas and pressure mix in the furnace was used to sinter the deposited Cu nanoparticle inks. This, in conjunction with a PID controller allowed for tight control on the heating and cooling of the microscope slides. 300-400 °C were required to reliably sinter all the four types of Cu inks. To reduce the copper oxides and produce clean copper materials 3% hydrogen gas with balance argon at slow rates under vacuum conditions of around ~4 torr was flowed for the duration of the sintering runs. The temperature was increased to and dropped from 400 °C slowly following a slow ramp up, bake at constant temperature, slower ramp down temperature profile.

E. Electrochemical Characterization of Inkjet Printed Flexible Electrodes

The electrode pairs were designed using computer aided design (CAD) software GIMP 2.10.32. The images were then converted into bitmap (.bmp) images which is compatible for printing with DMP 2850. The pixelation technique has been applied to avoid the coalescence between two adjacent droplets of Cu nanoparticle inks [2-5]. The designs were printed following the above-mentioned inkjet printing processes and parameters. Electrochemical impedance spectroscopy (EIS) measurements were performed for the Cu inks to evaluate their performance in terms of impedance at different frequency range. The nanoparticle inks with excellent electrical and mechanical properties were considered for this electrochemical characterization process i.e. Ink 3 and Ink 4. This process was performed using phosphate buffer saline (PBS with pH 7.43) as an electrolyte. This electrolyte was prepared using 0.1M sodium chloride, 0.1M potassium chloride, 0.1M disodium phosphate, and 0.1M potassium dihydrogen phosphate on July 11, 2022. Measurements were performed using Metrohm Autolab PGSTAT302 potentiostat. The system was connected with the electrodes pairs using a two-electrode setup. A square well (length/width – 3 mm) was created using masking tape to insert solution (10 µL) onto the electrode pairs for the measurement. The impedance response was recorded with 10 mV with the frequency range of 0.1 Hz to 100 KHz. The EIS measurement was performed for both designs (Design 1 and Design 2 – Fig. 1) for the qualified ink solutions (Ink 3 and Ink 4) for the Samba G3L printheads (Dimatix Materials Printer DMP -2850).

III. Results and Discussion

Fig. 1 shows the proposed designs (CAD) of the inkjet printed flexible electrodes. The length and width of the electrode pairs are 10 mm and 5 mm respectively. The gap of the straight and interdigitated electrodes is 0.5 mm for both designs. The performance of the electrode pairs were investigated in terms of resistivity for both designs. The CAD design was converted into bitmap images which is compatible to inkjet print with DMP 2850. Before inkjet printing with commercially available and optimized Cu nanoparticle conductive inks, the fluid properties (i.e., viscosity, surface tension, particle size measurement, and pH value) of all the inks were investigated thoroughly. Table I presents fluid properties of all the considered commercially available Cu nanoparticle conductive inks (Ink 1 through Ink 4) to inkjet print with DMP 2850.

TABLE I

Fluid Properties of Different Copper Nanoparticle Conductive Inks

Copper Nanoparticle Conductive Ink	Viscosity (cP)	Surface Tension (mN/m)	Particle Size (nm)	pH value	Temperature (°C)
Ink 1	17.14	32.55	56.2	9	20
Ink 2	31.30	28.38	8.62	8	20
Ink 3	13.52	26.97	11.5	10	20
Ink 4	15.02	32.59	56.2	10	20

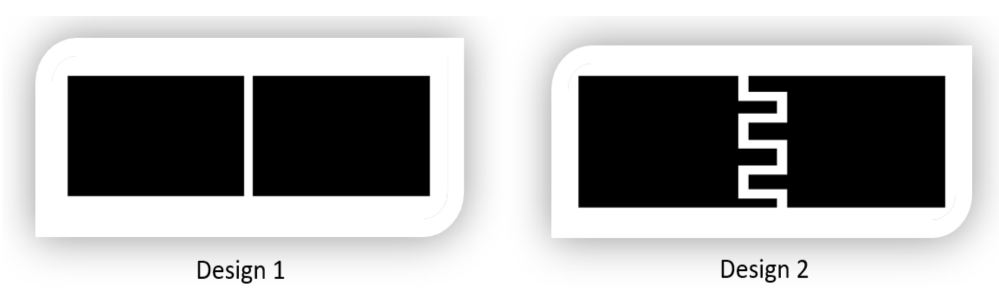

Fig. 1. Electrode shapes designed for the electrical characterization experiment (width: 10 mm; height: 5 mm; gap: 0.5 mm).

It is observed that Ink 3 has all the compatible properties to inkjet print using newly introduced Samba G3L. But, Ink 1 required optimization in order to reduce the viscosity. In this research Ink 4 or the optimized version of Ink 1 was synthesized by adding diethylene glycol monoethyl ether with the fresh Cu nanoparticle ink (Ink 1) with 1:5 ratio. This optimized version (Ink 4) of the commercially available Cu ink passed all the investigation regarding the fluid properties to be compatible with Samba G3L in order to be considered for electrode pairs fabrication. Fig. 2 shows viscosity vs temperature curve for all the considered Cu inks. It is observed that for the new Samba G3L printhead (4 cP to 8 cP) Ink 3 and Ink 4 can be used potentially with the optimization of the cartridge temperature. Due to extremely high viscosity at room temperature (31.30 cP) Ink 2 was ignored for future fabrication processes. The inkjet printing parameters for both Legacy and Samba G3L were developed for Ink 1, Ink 3, and Ink 4. Table II represents optimized inkjet printing parameters for each conductive nanoparticle Cu inks and their drop speed for both piezoelectric cartridges.

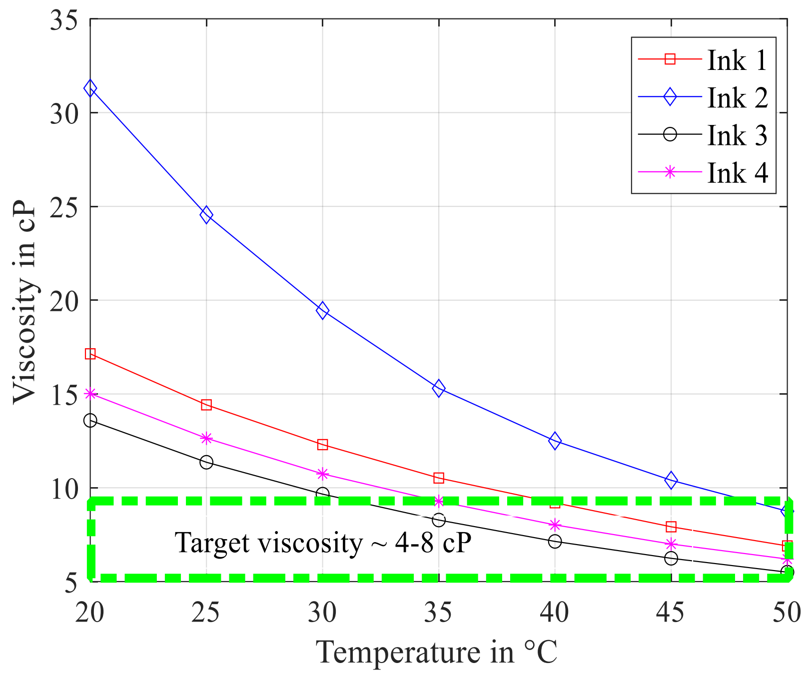

Fig. 2. Viscosity versus temperature for multiple ink formulations. The green region represents where the Samba G3L printheads are designed to operate.

TABLE II

JETTING RECIPES (FUJIFILM DIMATIX DMP 2850) OF DIFFERENT COPPER NANOPARTICLE CONDUCTIVE INKS

Copper Inks	Optimized Inkjet Printing Parameters	Inkjet Printhead	Drop Speed (m/s)
Ink 1	Platen temp – 35 °C Cartridge temp – ~47 °C Jetting Frequency – 5 kHz Jetting voltage – 35V	Legacy	3.3

	Meniscus set point – 0.5		
Ink 3	Platen temp – 35 °C Cartridge temp – ~50 °C Jetting Frequency – 3.5 kHz Jetting voltage – 30V Meniscus set point – 5	Samba	10.603
Ink 5	Platen temp – 35 °C Cartridge temp – ~40 °C Jetting Frequency – 3.5 kHz Jetting voltage – 28V Meniscus set point – 5	Samba	3.673

The waveforms for both legacy and samba printheads were developed successfully to inkjet print the conductive Cu inks. For both printheads the waveforms were successfully used to inkjet print Cu inks with optimized inkjet printing parameters i.e., jetting voltage, jetting frequency, drop velocity/speed, cartridge temperature, and cleaning methodologies. Fig. 3 shows waveform data for both legacy (DMC-11610) and samba G3L printheads. After successfully optimizing the waveforms and inkjet printing parameters, the next challenge was to print the proposed electrodes pairs. But before printing the electrodes, another issue was investigated critically i.e., observe the drop size and shape with camera watching view. The ink drop was optimized in such a way that the tail of the drop was emerged with main drop on the printing substrate. If the tail of the drop breaks it creates lots of satellite drops. This problem was completely resolved after optimizing the drop shape and size by adjusting jetting frequency, jetting voltage, and cleaning cycle. In this research, for both cartridges, 0.2s purge was utilized in every 5 minutes throughout the printing. Fig. 4 represents camera view of the Cu nanoparticle conductive ink (Ink 4) drop from Samba G3L printhead. Fig. 5 shows the drop diameter of Dycotec copper nanoparticle conductive ink on Kapton. It was observed that the approximate drop diameter was ~50 µm. Drop spacing parameter for inkjet printed conductive patterns was based on the drop diameter. It was investigated that 15 µm drop spacing (70% overlap) provided optimum results in terms of resistivity measurement after sintering. Fig. 6 represents the printed patterns (letters with 500 µm in thickness) of the Cu nanoparticle conductive inks (Ink 1 and Ink 4) based on the reported optimized inkjet printing parameters for both legacy and samba printheads.

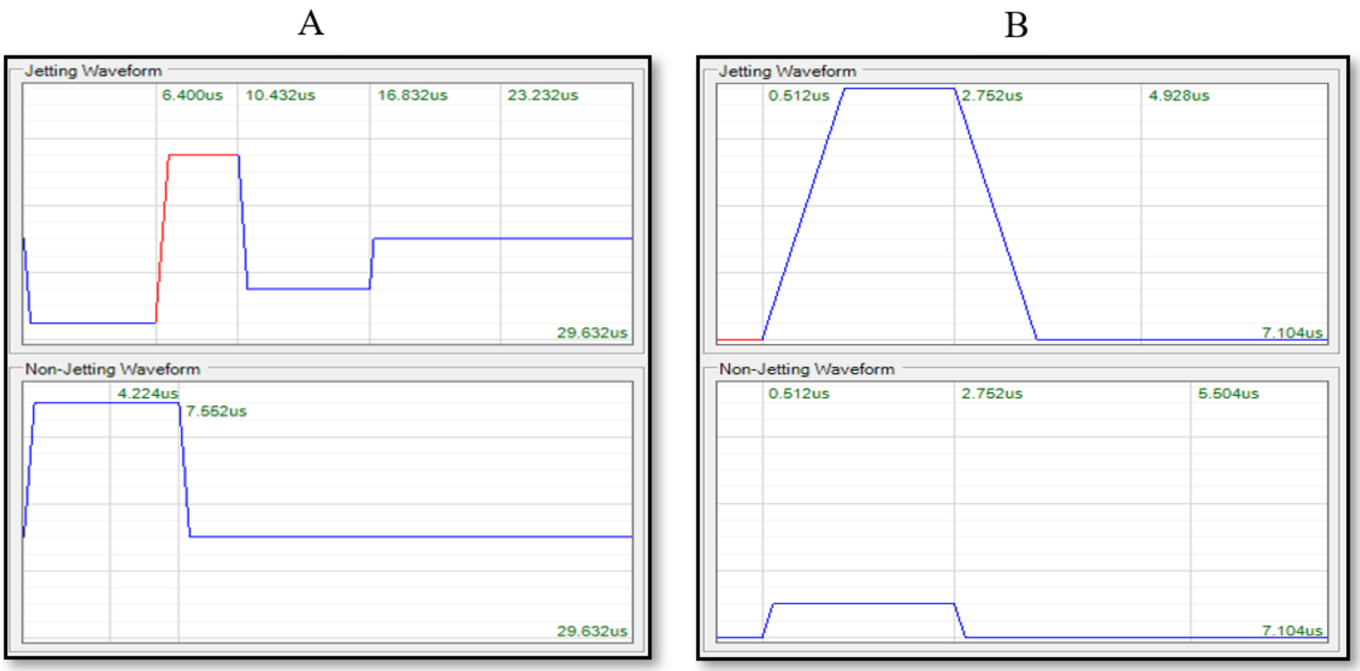

Fig. 3. Waveform data for the copper nanoparticle conductive inks (Ink 1 through 4) on the Legacy DMC-11610 printhead (A) and Samba G3L printhead (B).

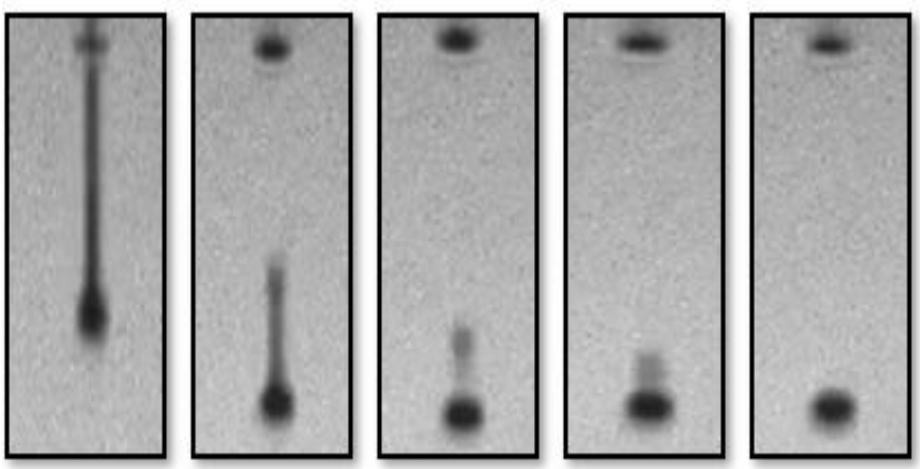

Fig. 4. Camera view of copper nanoparticle conductive ink (Ink 4) drop utilizing Samba printhead.

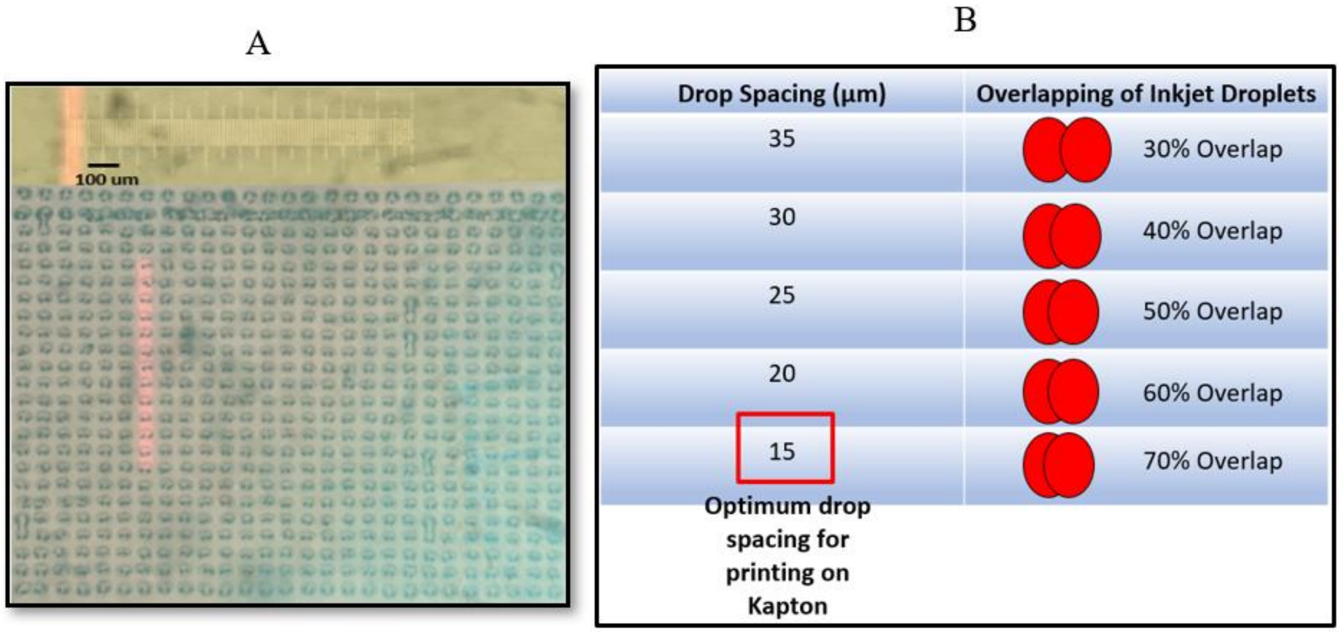

Fig. 5. Drop diameter of Ink 1/Ink 4 on Kapton (A) and optimum drop spacing parameter for inkjet printing conductive patterns (B).

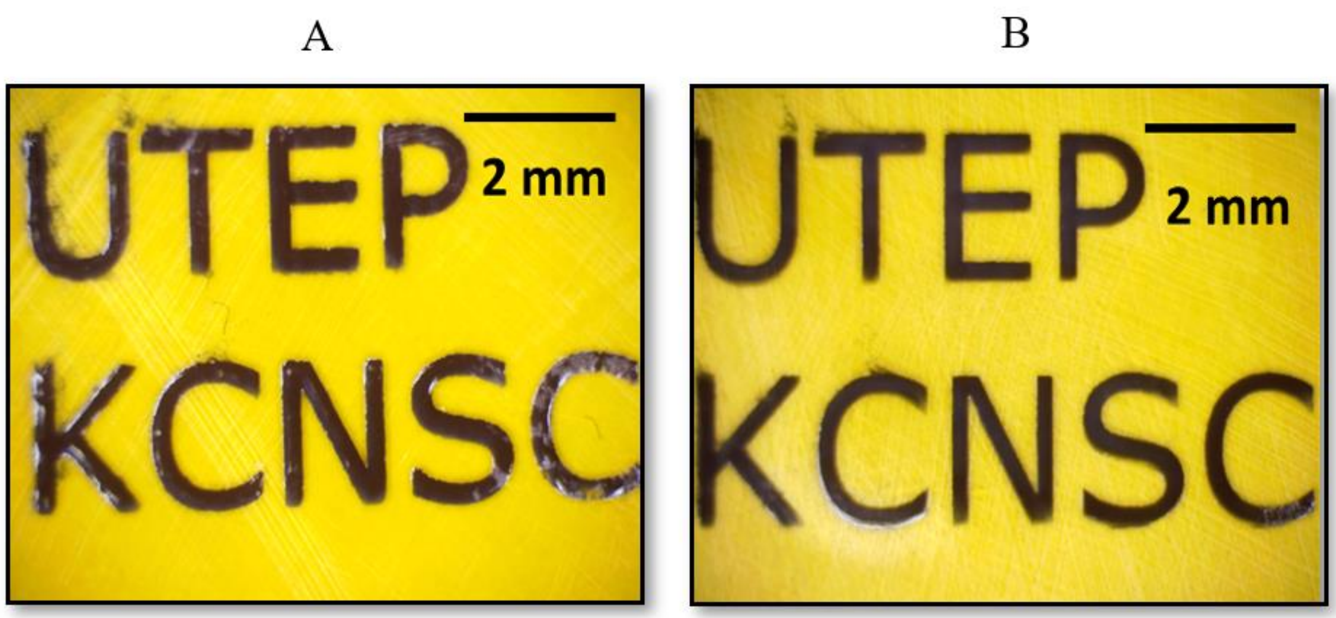

Fig. 6. The letters (500 µm in thickness) with dimension 10 mm by 5 mm were printed with optimized and reported inkjet printing recipes – Legacy printhead (DMC 11610) using Ink 1 (A) and Samba G3L Ink 4 (B).

The sintering process of inkjet printed Cu electrodes was conducted at 300 – 400°C in a furnace tube with 3% hydrogen gas and 97% argon gas. The temperature was increased and decreased very diligently in 8 segments. Fig. 7 presents temperature control program with 8 segments in MTI tube furnace (compact RTP furnace OTF-1200X-4-RTP with 4-inch quartz tube). The reported gas flow is mandatory to avoid oxidation and produce clean Cu films. The gas was flown at low rates under vacuum conditions (~4 torr). The resistivity of the inks was tested using a test coupon utilizing four-point probe measurement technique. Fig. 8 represents the test coupon – both CAD design and fabricated test structure used to measure the resistivity for different Cu nanoparticle conductive inks. The test structure was fabricated using 2 layers of laser cut Kapton tape on a clean soda lime microscope slide ($25\ mm \times 75\ mm$). The layers were cut using Emblaser 2 laser cutter and engraver. The first layer of this coupon was chosen as a test structure with all 4 pads in a row ($2.54\ mm$ spacing) along with some triangle alignment marks. Silver conductive epoxy was placed on the laser cut Kapton tape to create the structure. Silver epoxy was cured at ~70 ℃ for 2 hours. The second layer is cut from Kapton tape for patterning Cu nanoparticle conductive inks (a well of $10\ mm \times 1\ mm$). It also has triangle alignment marks to avoid unnecessary misalignment during fabrication of test structures. This shape was chosen to fit more tests within the margins of the microscope slide. Arbitrary choices were made to the size of this test structure and fabricate four-point probe. Ink resistivity for Ink 1 through Ink 4 have been reported in Table III. The reported resistivity is the mean of the 5 observations for each ink. The adhesion test has been performed for all the considered inks on glass substrate and Kapton. All the inks showed excellent adhesion property for both substrates. Fig. 9 shows scanning electron micrograph (SEM) images for Ink 3 and Ink 4 after sintering. Both pictures show the coagulation of the nanoparticles and decomposition of the organic solvent – 2-methoxy propanol for Ink 3 and diethylene glycol monoethyl ether for Ink 4. These two properties are the evidence of the successful sintering process/reduced resistivity. Fig. 10 represents energy dispersive spectroscopy (EDS) for both Ink 3 and Ink 4. The EDSs show the presence of Cu for both ink formulations. It also proves that no oxidation was formed during the sintering process.

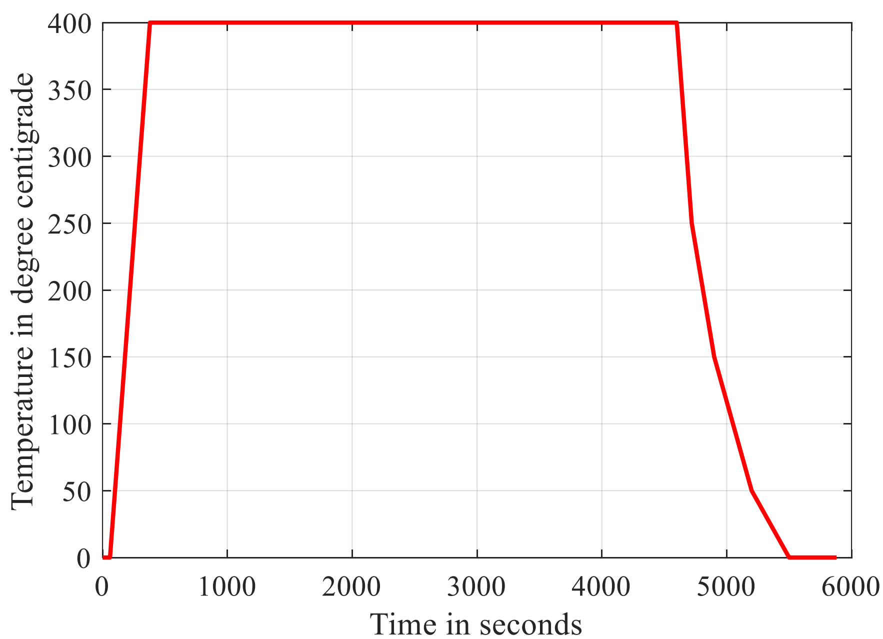

Fig. 7. Temperature control program with 8 segments in MTI tube furnace.

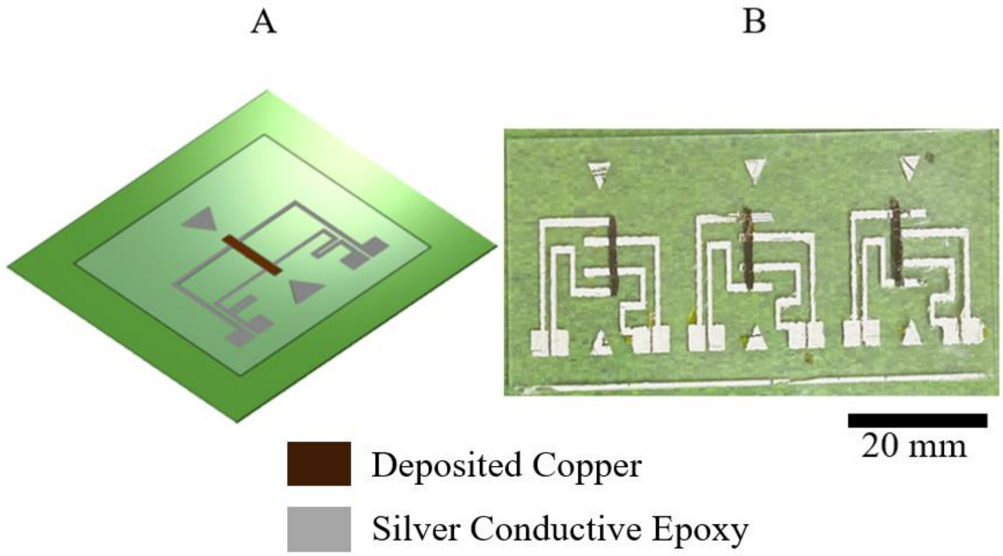

Fig. 8. Test structure for ink resistivity measurement using four-point probe (A) CAD design and (B) fabricated test coupon.

TABLE III

RESISTIVITY (N=10 OBSERVATIONS) AND ADHESION TEST ON DIFFERENT SUBSTRATE (GLASS AND KAPTON) FOR DIFFERENT TYPES OF COPPER NANOPARTICLE INKS. CLASSIFICATION 5 REPRESENTS EXCELLENT ADHESION WITH 0% REMOVED AREA.

Cu Nanoparticle Conductive Ink	Mean Resistivity (µΩ-cm) [n=5]	Glass substrate adhesion	Kapton adhesion
Ink 1	39.50	5	5
Ink 2	22.80	5	5
Ink 3	08.89	5	5
Ink 4	39.50	5	5

A. Electrochemical Impedance measurement

Ink 3 and Ink 4 outperformed all the other considered commercially available Cu inks. So, these two conductive inks were selected for inkjet printing Cu electrodes. The electrodes for each proposed design were inkjet printed on Kapton. 4 electrode pairs (1 for each design) were printed for both inks. Fig. 11 represents inkjet printed electrodes pairs for both designs and their mechanical bending capability. The EIS measurement for each electrode pairs were conducted after carefully running the sintering process and resistivity measurement. Fig. 12 represents impedance vs frequency characteristics for both designs in case of each considered Cu nanoparticle conductive inks. To compare the impedance and understand/analyze the performance of different inks and different designs, the impedance for each case was measured at 1 KHz. Fig. 13 illustrates the performance of each ink and each design precisely. It was observed that Design 2 electrodes pair (interdigitated) inkjet printed with Ink 4 provided lower electrical impedance compared to Ink 3. In the next phase, 10 electrodes pairs were printed with Design 2 using both Ink 3 and Ink 4 copper nanoparticle conductive inks. This demonstrated the repeatability of the flexible printed electrodes with a mean total impedance value of 374.49 ohms with a standard deviation of ±0.4104 ohms for Ink 4 (optimized Cu ink) and 379.40 ohms with a standard deviation of ±48.30 ohms for Ink 3 (commercially available Cu ink).

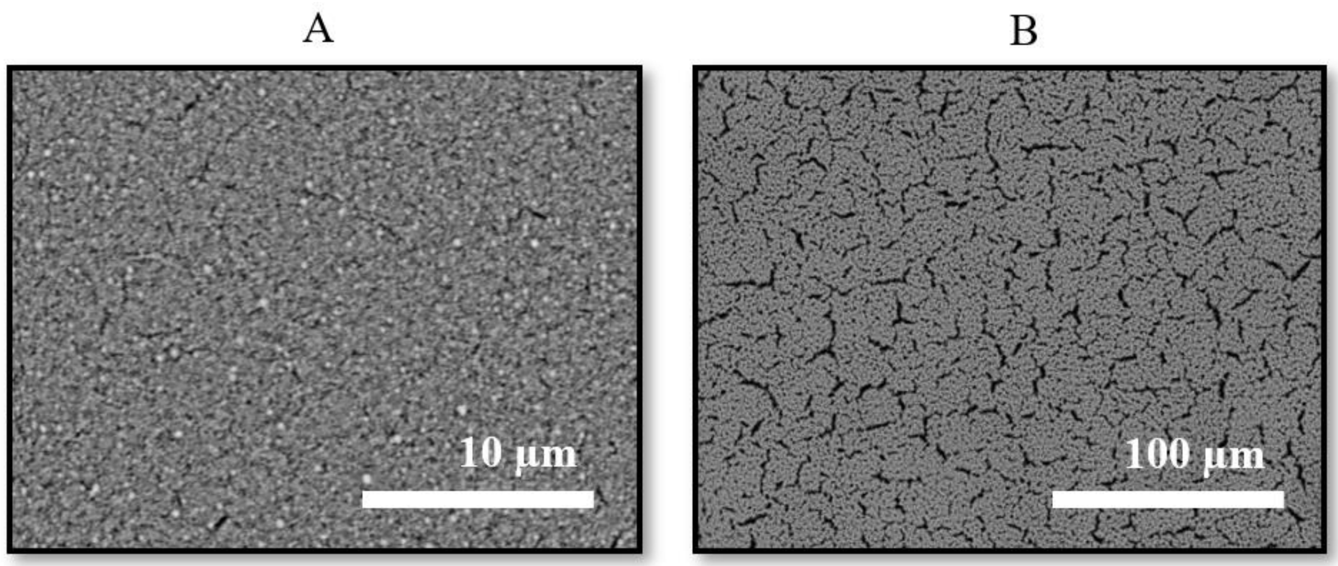

Fig. 9. Scanning Electron Micrograph (SEM) images for Ink 4 (A) and Ink 3 (B) after sintering the copper nanoparticle conductive ink.

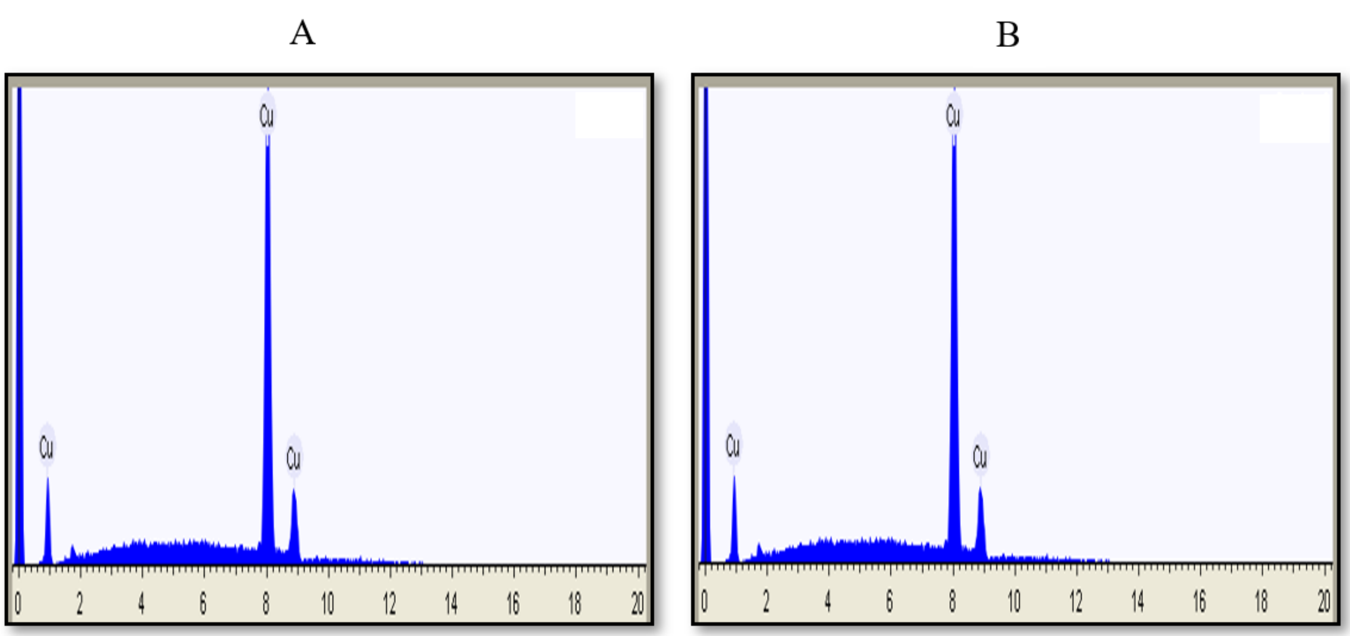

Fig. 10. Energy Dispersive Spectroscopy (EDS) for Ink 4 (A) and Ink 3 (B) after sintering the copper nanoparticle conductive ink.

IV. Conclusion

In this research work, different commercially available Cu nanoparticle conductive inks have been investigated and explored for future flexible printed electronic device fabrication and its applications. Different fluid properties such as viscosity, surface tension, particle size measurement, and pH values were studied thoroughly. The mean particle sizes of the different Cu nanoparticle inks were 56.2 nm for Ink 1/Ink 4, 8.62 nm for Ink 2, and 11.5 nm for Ink 3. The viscosities at room temperature (20°C) for each considered inks (Ink 1 through Ink 4) were 17.14, 31.30, 13.52, and 15.02 respectively. In spite of having low resistivity, due to high viscosity at room temperature and incompatibility with the new Samba G3L printhead, Ink 2 was ignored for future developments/optimization. On the other hand, commercially available ink i.e., Ink 1 has been modified with organic solvent – diethylene glycol monoethyl ether (5:1) to make it compatible with the newly introduced piezoelectric inkjet cartridge Samba G3L. In this research, printed sensors were inkjet printed using Dimatix Materials Printer DMP 2850. Hence, all the developments, optimization, and printing recipes were developed based on DMP 2850. The waveforms and optimized inkjet printing parameters have been reported for both legacy and samba G3L. All the considered nanoparticle inks have shown excellent adhesion property for both glass substrate and Kapton. Kapton has been chosen as a printing substrate for this research as it offers excellent mechanical stability and flexibility over a wide range of temperature i.e., -269 °C to 400 °C.

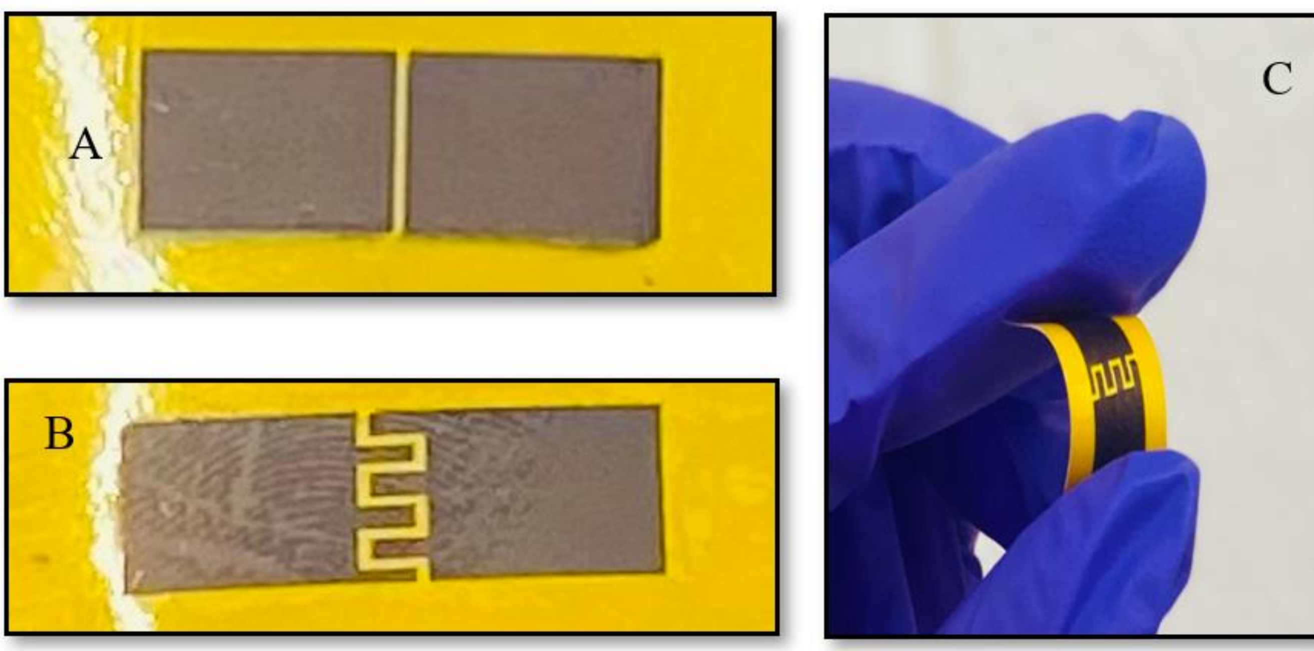

Fig. 11. Design 1 (A) and Design 2 (B) of the printed copper electrodes pairs; (C) mechanical bending outwards using Ink 3/4.

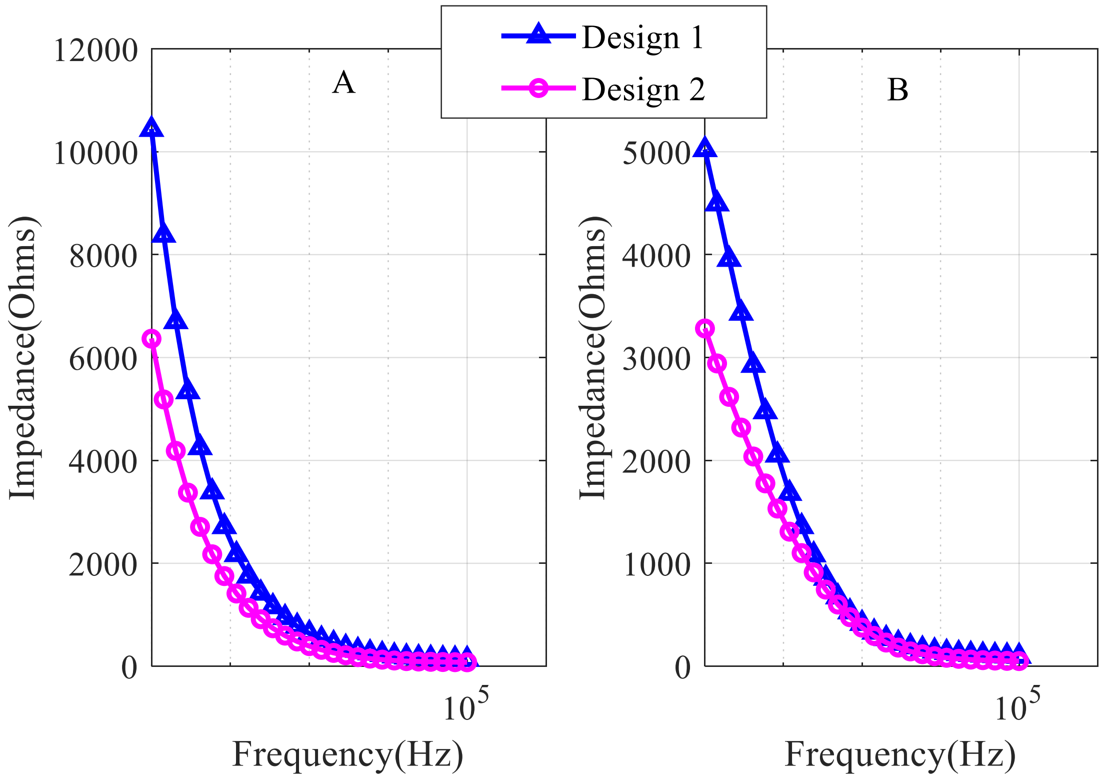

Fig. 12. Electrochemical impedance spectroscopy (EIS) response for a frequency response of 0.1 Hz to 100 KHz of the different printed electrodes pairs using Ink 3 (A) and Ink 4 (B).

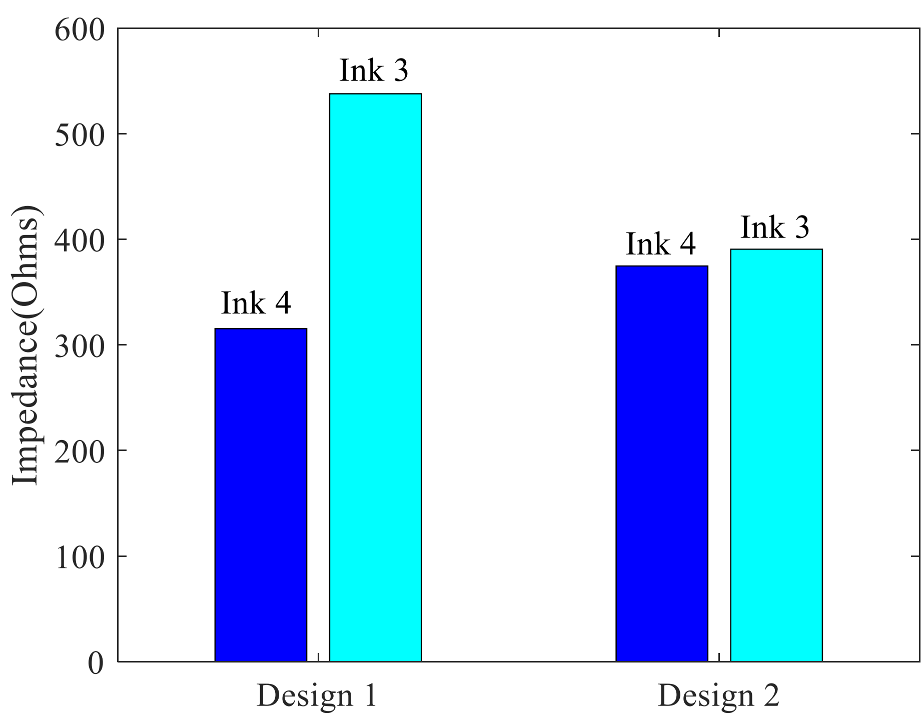

Fig. 13. Electrochemical impedance measurement at 1 kHz for the different printed electrodes pairs (Design 1 and Design 2) using Ink 4 (blue) and Ink 3 (cyan).

The optimization of the sintering process has also been reported in detail. The required temperature to sinter the Cu films was settled at 300-400 °C. To avoid oxidation 3% hydrogen gas with 97% argon was flowed in the vacuum chamber with ~4 torr resultant chamber pressure. The resistivity for each ink was low enough to receive further consideration for printing flexible electrodes. Based on the resistivity measurement and fluid properties, Ink 3 and Ink 4 were considered for further investigation i.e., inkjet printing flexible electrodes pairs. The printed electrodes were analyzed with the EIS measurement using the PBS solution (pH 7.43). The best electrical impedance was obtained using Ink 4 Cu nanoparticle conductive ink with Design 2 (interdigitated electrode). Based on our experiments/investigation (viscosity, surface tension, particle size measurement, and pH value) and reported optimized inkjet printing parameters (waveforms, platen temperature, cartridge temperature, jetting frequency, jetting voltage, and meniscus set point), it is possible to use commercially available Cu ink (Ink 3) for printing flexible electronics using both legacy and newly commercialized samba G3L printheads. However, our modified/optimized Cu ink (Ink 4) showed excellent performance with lowest impedance (resistivity and EIS measurement) to receive significant consideration for flexible electronic device fabrication and its applications using both legacy and samba printheads (DMP 2850).

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