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Additive process for patterned metallized conductive tracks on cotton with applications in smart textiles

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Abstract

The selective patterning of silver nanoparticles by a patent-pending process to act as a catalyst for metallization with electroless copper was explored on cotton, with a view towards application in the wearable technology sector. Whole area coverage or tracks serving as point-to-point connections were achieved by depositing the catalyst via spraying, or in a more controlled manner using a microdispenser, respectively. Optimization of the catalyst deposition is described, including substrate characterization via contact angle, FTIR and surface charge measurement. The effects of the copper plating bath temperature and dwell time in the plating bath are examined. With plating times as short as 10 minutes, samples of good conductivity (sheet resistance, R, = <10 Ω/sq) and consistency were produced. A higher or lower plating temperature (compared to supplier recommended conditions) increased or reduced the amount of copper deposited respectively. The technology was used to produce well-defined conductive tracks on cotton with widths between 1.5 and 4.0 mm.

Keywords: smart textiles; conductive tracks; cotton; additive

Introduction

Metallized textiles are well established for their use in electromagnetic interference (EMI) shielding and static dissipation (Gan, Wu, Liu, Shen, & Hu, 2008; Han, Kim, & Oh, 2001; Jagatheesan, Ramasamy, Das, & Basu, 2014; S. Q. Jiang & Guo, 2009; LessEMF ; Marchini, 1991), however the rapid development of wearable technology has opened up a range of other exciting potential applications, such as pressure sensing, heating textiles, integration of electronics into yarns, and as wearable antennas (Castano & Flatau, 2014; Cherenack & Van Pieterson, 2012; Dias, 2015; Stoppa & Chiolerio, 2014). Whether discussed under the term wearable technology, smart textiles, e-textiles, intelligent textiles or similar, wherever a point-to-point connection is required on a garment, patterned metal tracks could be used instead of traditional wiring technology. It can therefore be said that conductive textiles are a vital enabling technology within the wearables sector. Whilst for static dissipation and EMI shielding applications textiles of relatively low conductivity are suitable, and indeed preferable in the case of antistatic coverings (Chung, 2000; Marchini, 1991), textiles of higher electrical conductivity are desirable for smart textile applications.

To produce metal tracks of high electrical conductivity there are options such as knitting or weaving in conductive threads or metal wires. However, metal wires are limiting to the flexibility of the textile and can break during manufacturing and use (Cherenack et al., 2012; Stoppa et al., 2014). Also, the usual way to cut fabrics involves applying heat therefore this method does not suit materials with metal wires (integrated early in the manufacturing process) due to the high thermal conductivity of the metal (Cherenack et al., 2012). A process where the conductive aspect is integrated at the end of the textile treatment is therefore preferable. Conductive threads offer greater flexibility but are also at risk of snapping and can be prone to fraying. The threads can either consist of a non-conductive core wrapped with metal wire or metal plated; or it could be a metal fibre which has been very finely drawn to be processed as a conventional yarn. With wires and threads the user can be limited in design by the capability of the weaving or knitting machine (Berlin, Joswik, & Ivanovich, 2015), e.g. threads can only be knitted in two directions. Printing conductive inks is another option, although there are still challenges here regarding conductivity during stretching and direct fabric printability (Ghaffarzadeh, 2016). Typically the ink will be printed onto a polyurethane film and this will then be adhered to the textile (Rodie, 2016). Conductive inks also tend to have a high metal content and are therefore expensive, as well as requiring a sintering or curing step which adds additional time and cost to the process (Sigma Aldrich, Silver Nanoparticle Ink, 50 wt.%).

The process of electroless plating of non-conductive materials proceeds by sensitizing the surface of a substrate with a catalyst, in order to initiate metal deposition at these catalyst sites. Electroless plating as a means of metallizing textiles to make them electrically and thermally conductive was first reported by Thibodeaux & Baril, 1973. Since this publication, using electroless plating to achieve whole area coverage of textiles with metals such as copper, silver and nickel has been well explored by other researchers (R. H. Guo, Jiang, Yuen, Ng, & Lan, 2013; S. Q. Jiang et al., 2009; S. X. Jiang & Guo, 2011; S. X. Jiang, Guo, & Zheng, 2011; Muthu Kumar & Thilagavathi, 2014) and some work has also investigated patterning via this method (Sawhney, Agrawal, Patra, & Calvert, 2006). Using the electroless technique to metallize textiles offers significant benefits, such as the high conductivity of the resulting textile; the process can be carried out at any stage of a textile’s manufacturing (thread, roll, garment); the process is relatively low temperature; there is no need for a vacuum (as is required for sputter coating); and it is a relatively cheap and easy process if the right metals are chosen. As well as academic interest in the process, there is also significant commercial relevance, for example, to realize “soft circuits”.

To activate the substrate towards electroless plating, a palladium-tin colloid is used within the Printed Circuit Board (PCB) industry. Many researchers have followed a tin/palladium catalytic approach with textiles (Gan, Wu, Liu, Shen, & Hu, 2007; Gan et al., 2008; R. H. Guo, Jiang, Yuen, & Ng, 2009; R. H. Guo et al., 2013) as part of whole area coverage, however the cost of palladium is high and this method involves multiple processing steps such as scouring, etching and rinsing in addition to the sensitisation and activation stages. A cheaper option studied by some groups is to use tin (II) chloride with a silver nitrate activator so that silver (0) clusters are produced to act as an alternative catalyst to palladium (R. Guo, Jiang, Yuen, & Ng, 2009; Muthu Kumar & Thilagavathi, 2014). In addition, Sawhney et al. (2005, 2006) deposited just silver nitrate to initiate electroless silver plating, to form the connecting leads to piezoresistive strain sensors on nylon and cotton fabrics. Liu, Hu, & Yang (2016) reported the use of silver nitrate as a seed layer on cotton, which is followed by electroless copper plating. In this case the optimum electroless plating time required was reported to be between 90 and 120 minutes, which is longer than desired for a commercial operation.

Copper is one of the cheapest metal options for electroless plating and the chemistry is well established (Bindra & White, 1990; S. Q. Jiang & Guo, 2009)). A typical copper plating solution consists of the metal salt, reducing agent, complexing agent, buffer and stabilizer. In this current formulation a copper-EDTA complex (formed in solution from copper (II) chloride and the complexing reagent, ethylenediaminetetraacetic acid) is reduced by formaldehyde at the catalyst sites in a plating bath of pH >11. The reactions continue autocatalytically on the copper surface once the initial catalyst layer has been covered by plating. Aside from comparing the catalyst options, it was also noted from the literature that the majority of studies of electroless copper plating onto textiles use synthetics such as polyester/PET and nylon. Less attention has been paid to cotton. Cotton as a natural material is commonly used in healthcare applications and has favourable properties such as comfort, water absorbency, strength and resistance to heat (Swicofil). Opportunities for conductive textiles within healthcare include as connecting leads to assist sensor and electrode integration for monitoring physiological properties or a medical condition (Stoppa & Chiolerio, 2014).

In this paper electroless copper plating on cotton using an NPL patent-pending catalyst system (ASHAYER-SOLTANI & HUNT, C. P., Conductive Fibres,WO2014/128505 A1, 2014)) is described, which builds on our previously published work (Ashayer-Soltani, Hunt, & Thomas, 2015). The catalyst used is silver nanoparticles produced by *in situ* reduction of silver nitrate by sodium borohydride on the cotton surface. This work further characterizes the pre-treated cotton fabric using surface zeta potential measurements and water droplet contact angle measurements. It explores the optimum electroless copper plating conditions for the textile to achieve a high conductivity and, more importantly, describes how selective patterning of conductive tracks has been successfully accomplished.

Experimental

Formaldehyde (ACS reagent, 37 wt. % in H_2O), sodium hydroxide (reagent grade, ≥98 %, pellets), silver nitrate (99.9999 % trace metals basis), sodium borohydride (99.99 % trace metals basis) and poly(diallyldimethylammonium chloride) solution (PDADMAC, 20 wt. % in H_2O) were purchased from Sigma-Aldrich and used as bought. Nitric acid (trace analysis grade >68%) was purchased from Fisher Scientific. The electroless copper plating chemistry was purchased from A-Gas Electronic Materials. The copper plating bath consisted deionized (D.I) water (81.2 % by volume), Circuposit 3350 M-1 (15.0 % by volume), Circuposit 3350 A-1 (1.0 % by volume) and NaOH (2.3 % by volume of a 344 g/L solution (8.6 M)). These reagents were added in the listed order, with stirring, and heated to the plating temperature. At this point formaldehyde was added (1.0 % by volume, from a 37 wt. % in H_2O solution).

The cotton used in this work was Merz Cotton Natural (Jersey) from Whaley's, Bradford. The cotton samples were prepared as follows. Portions of size 240 x 110 mm were first immersed in a 400 mL aqueous solution of the cationic polymer PDADMAC (0.2 %) at a pH of 6.2. Samples were left in the polymer solution for 3 minutes, then removed and put through a roller to remove excess liquid and improve evenness of penetration of the polymer into the cotton. The samples were then dried in an oven at 65 °C.

Prior to electroless plating, the PDADMAC-coated cotton samples were then activated with a silver catalyst. The silver was applied according to one of three methods; (1) airbrush; (2) microdispenser; (3) inkjet printing.

(1) To obtain the whole area coated samples, the 240 x 110 mm portion of cotton was fixed in a PTFE frame to carry out a silver nanoparticle deposition. Sodium borohydride was sprayed first (4 mL, 1.639 mM, in 0.1 M NaOH, pH = 13) using the air brush system, followed by silver nitrate (1.4 mL, 25 mM, pH = 5.2). Silver nanoparticles were observed to form immediately on the cotton surface. A separate air brush was used for each reagent and the guns were connected to a compressed air line with a flow rate of 5 L min^{-1}. The samples were dried at 65 °C and a second and third reduction were carried out in the same way. Finally, a rinse in DI water (500 mL, 3 minutes) was performed, followed by drying and cutting to the size required for the experiments (40 x 40 mm). Ten samples were obtained from each portion.

(2) A microdispenser from Vermes Gmbh was used, model MDS 3010A suited to low viscosity media. Operating parameters were generally rise time 5 ms, fall time 1 ms, needle lift 60 %, delay time between 100 and 400 ms, number of passes for each layer between 2 and 10 lines of reducing agent followed by silver nitrate. There were 5 layers in total; reducing agent, silver, reducing agent, silver, reducing agent and the reagent concentrations were the

same as in method (1). The dispenser was controlled via an xy stage in order to print the tracks.

(3) For inkjet printing a Dimatix Materials Printer, DMP-2831, was used. The reducing agent (sodium borohydride, 1.639 mM) was applied initially to the surface and dried, followed by inkjet printing of the silver salt (12.5 mM stock solution, mixed in an 8:1 ratio with ethylene glycol).

Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out on a Perkin Elmer OES Optima 5300DV instrument. Each silver catalysed cotton sample was digested in nitric acid (35 %, 20 mL) at 70 °C for 60 min, filtered through Whatman 541 filter paper and made up to 100 mL with reverse osmosis (RO) water. For calibration, 1, 2, 3, 4 and 5 mg/L silver calibration standards were prepared. Samples were analysed at the silver wavelength of 328.068 nm.

SEM images were obtained on a Zeiss Supra Field Emission SEM or a LEO 1530 VP Field Emission SEM. Plain cotton and catalyst coated samples were sputter coated from a gold/palladium target, whereas copper plated samples did not require sputter coating. FTIR measurements were made on a NICOLET iS50 system (ThermoFisher Scientific) in 32 acquisition scans and with a resolution of 4 cm^{-1}. Electrical resistance measurements of the copper plated cotton were performed using a four-point probe device (comprising four parallel gold wires as electrodes, fixed in a rigid plastic block, with a separation distance of 12 mm) and a Keithley 2010 DMM. The device was held in place on the textile sample, and pressure applied, by using a weight of 500g. Resistance values (in Ω) were converted to sheet resistances (Ω/square) using the equation; R(Ω/sq) = (fabric width*measured resistance)/probe separation.

Contact angle measurements were made with water on a Kruss DSA (Drop Shape Analyzer) 100. Between 5 and 10 droplets were measured in each experiment at a room temperature of 22 °C. Surface zeta potential measurements were made using a SurPASS 3 instrument from Anton Paar.

Results and Discussion

Characterization and functionalization of cotton substrate

The advantages of using the cationic polymer PDADMAC as a linking molecule to aid attachment and uniformity of the silver catalyst have previously been reported (Ashayer-Soltani et al., 2015; Dubas, Kumlangdudsana, & Potiyaraj, 2006; Hyde, Rusa, & Hinestroza, 2005), where it was found that the polymer assists in creating a uniform charge layer for the silver particles to attach to. This methodology has been continued here and in each experiment PDADMAC was applied prior to catalyst application. Further work is reported here and in the following section to quantify and validate the functionality of the polymer and the catalyzation method used.

There will always be some variation between textile samples, and particularly for cotton as a natural product, due to their porous, rough, surfaces. However to ensure a valid study into the electroless plating of cotton samples, time was spent developing a consistent approach for sample preparation. The polymer was applied via immersion of the cotton into a solution of concentration of 0.2 % followed by feeding samples through a roller to improve penetration of the solution and to remove excess liquid. Contact angle measurements using water were taken before and after polymer application. The surface of the cotton used in this study is unusually hydrophobic, with a median and mean contact angle of 140°. The surface became more hydrophilic as the cationic polymer was applied, with the median contact angle dropping to 133° and the mean to 134°.

An effect was also noted in terms of time taken for droplet absorption, which occurred more quickly when the PDADMAC was applied. Surface charge measurements using an electrokinetic analyzer also allowed us to differentiate between plain cotton and that coated with polymer. The SurPASS 3 instrument was used, which is designed for zeta potential measurements on macroscopic solids via streaming potential measurements. The measurement is achieved by circulating an electrolyte over the sample in a measurement cell and analyzing the relative movement of charges at the solid/liquid interface. It is a useful system for validating the surface charge modifications introduced by different coatings, and can also potentially be used for studying *in situ* how the polymer is adsorbed onto textile surfaces. As Figure 1 shows, the surface charge is always more positive across the pH range 3-12 with a coating of 0.2 % polymer than on the plain cotton. A more positively charged surface allows for better silver nanoparticle attraction and adhesion and these measurements reinforce previous findings. The data is consistent with what we would expect for cotton, where the acidic hydroxyl functional groups dissociate in the aqueous environment and for the effect to be enhanced at a higher pH. This leaves a negatively charged surface from the residual $–O^-$, which exhibits a stable zeta potential of -25 mV in the pH region of 4 to 12. As anticipated, introduction of the cationic polymer onto the cotton shifts the zeta potential into a region of more positive charge.

[Figure 1]

ATR-FTIR was also used to study the cotton surface, and to check homogeneity of the polymer coating. From the spectrum of PDADMAC in water at its supplied concentration of 20% aq., one peak due to PDADMAC was observed, at 1474 cm^{-1}. This is attributed to the C-N bond within the pyrrolidine ring. FTIR of the cotton and cotton coated with PDADMAC was then carried out. At the relatively low working concentrations the polymer cannot be discerned from the background cotton signal. However at a much higher concentration of 10% a peak attributed to the C-N bond within the polymer is seen to grow in at ~1450 cm^{-1} (Figure 2). Several areas of the cotton were studied with FTIR to check for polymer coverage via this peak at 1450 cm^{-1} and each area looked the same.

[Figure 2]

Applying PDADMAC is favourable for improving wettability as noted through the contact angle measurements and from general observation in the laboratory. Also, as noted in our group’s previous SEM work (Ashayer-Soltani et al., 2015), a polymer coating improves uniformity of silver particle dispersion across the cotton. A balance is required though as the viscous PDADMAC causes an increase in rigidity of the cotton when used at high concentrations. Therefore in consideration of this surface characterization data and our previous work, an optimized working concentration of 0.2% polymer is recommended.

Catalyzation of cotton substrate with silver

The silver catalyst can be applied in different ways. Sequential application of a reducing agent and then a silver salt has been found to be a fast and reliable method with limited generation of metal nanoparticle waste solution. It also removes the need for any stabilization of nanoparticles in solution, which is generally required to prevent aggregation (Virkutyte & Varma, 2011) using immersion techniques. Instead the reagents react on the cotton surface to produce the nanoparticles *in situ*, which is visually apparent by an immediate colour change on the cotton. In this section catalyst deposition using method (1), an air brush system, is explored. Sodium borohydride (pH stabilized to prevent rapid decomposition in water) is first sprayed onto the cotton followed by silver nitrate. Using method (1) is appropriate to achieve the large area coverage of catalyst that was desired, although it is acknowledged that this method is not ideal for reproducibility. The size of sample and volumes of reducing agent and silver nitrate were kept constant between samples. The buildup of silver after one, two and three spray depositions, and its resulting effect on copper plating, was monitored through weight gain of the cotton (Table 1) and SEM (Figure 3). It was found that to achieve a suitable catalyst coating on the textile and the most uniform copper plating, three spray treatments of catalyst should be carried out. From SEM it was seen that the catalytic silver particles are clearly visible across the cotton fibers relative to the bare sample image (Figure 4.). After the three spray applications they exist sometimes as well dispersed particles and in some areas as larger clusters. The silver particle size is generally <50 nm.

[Table 1]

[Figure 3]

[Figure 4]

The amount of silver catalyst applied after this sequential spray method was quantified using ICP-OES. From this, a comparison could be made between samples to compare reproducibility of the method. Catalyzed cotton with PDADMAC linker was analyzed, with five samples analyzed per experiment and a repeat carried out. The silver was desorbed from the cotton using a nitric acid digest. The results for the mass of silver (µg per cm^2) per sample are shown in Table 2. From the standard deviation it is seen that there is some variation across the data within a batch, which is attributed to error in the spraying method. However the mean catalyst loading between different batches of the same type of sample is similar, between 46 and 48 µg cm^{-2}.

[Table 2]

Using a spray deposition also provides the opportunity to sensitize, plate and therefore make conductive only one side of the cotton (Figure 5).

[Figure 5]

This is possible since the liquid loading during the spray process can be controlled such that there is limited penetration of catalyst into the textile. This may be a key benefit of this process to potential applications within wearable technology, for example, if having a metal coating in contact with the skin is a concern.

This method of producing a silver catalyst active towards electroless plating is also beneficial as a relatively quick and cheap process, with low waste generation. It can be produced without the use of a vacuum, high temperature or lengthy curing operations meaning overall processing times can be much shorter than conventional print and cure options. It also removes any requirement to separately deposit onto another material (e.g. polyurethane film) for adherence to the textile i.e. direct deposition on the substrate.

Optimizing copper plating bath parameters for cotton

With the parameters for cationic polymer and catalyst application established, work moved on to electroless plating of the activated cotton samples. Copper plating of the silver-catalyzed cotton can be achieved according to the supplier data sheet, which specifies immersion for 25 minutes at 45 °C. However changing conditions of the electroless bath (time, temperature, reagent concentrations, catalyst choice) will affect the reactions taking place. Finding the cheapest and most efficient conditions, that offer optimal plating quality with consistent conductivity, is critical to achieving a viable process on a commercial scale. The temperature of the plating bath is known to affect the rate of electroless metal deposition, with higher operating temperatures achieving increased plating rate (Ashassi-Sorkhabi, Dolati, Parvini-Ahmadi, & Manzoori, 2002; Gan et al., 2008; Hanna, Hamid, & Aal, 2004). Its influence on copper plating on cotton was investigated to see if there was scope for improvement over the PCB industry recommended method. Batches of five samples were studied in each experiment. The plating bath was operated initially according to the supplier data sheet, i.e. for 25 minutes at 45 °C. The bath was then run at the higher and lower temperatures of 50 °C and 40 °C which resulted in increased/decreased copper weight gain respectively, compared to the plating at 45 °C (Figure 6). The effect of temperature with respect to the copper plating process can be understood as a faster/slower reaction initiation at the higher/lower temperatures.

[Figure 6]

Conductivity was highest within the samples plated at 50 °C, with all samples measuring a sheet resistance of <0.1 Ω/sq. However the additional copper on the surface was obvious by touch and resulted in rougher, more rigid, cotton samples which is undesirable for wearable applications. The samples from 40 °C were comparable to those plated at 45 °C in terms of textile handle and drape, measured sheet resistance (R ranged from 0.3-1 Ω/sq across both temperature batches) and inspection via SEM which showed similar deposits. Therefore a lower plating bath temperature is feasible.

Experiments studying weight gain, conductivity and deposit uniformity on cotton samples after 5, 10, 15, 20 and 25 minutes in the copper plating bath were then carried out. For this experiment the temperature was fixed at 45 °C and batches of five samples were studied in each experiment. The weight gain of samples with time is plotted in Figure 7(a). A positive correlation between the time spent in the electroless copper bath and the sample weight gain was observed. The build-up of copper with increasing time in the plating bath is known to be due to the autocatalytic effect of the plating reaction on the copper surface. The copper deposition is lowest at 5 minutes, as would be expected. The weight gain continues to increase linearly and there is no plateau in the copper build-up. This is in contrast to what is typically observed with electroless copper plating, where a plateau is usually observed. It is possible that the larger surface area of the textile is a dominating factor here, allowing the plating chemistry reactions to continue for longer. Perhaps if the plating was allowed to continue past the 25 minutes time point then a plateau would become apparent.

[Figure 7]

The sheet resistances of the samples in each batch were plotted against plating time (Figure 7b) and an overall trend is observed. Catalysed cotton samples plated for only 5 minutes produced samples of very high resistance (varying between 500 Ω/sq and MΩ/sq) and are not plotted. Increasing the plating time to 10 minutes produced samples of significantly lower sheet resistance (~5 Ω/sq) and better stability (judged by how stable the multimeter reading is over time). There were then consistently low sheet resistances observed for the batches at 15, 20 and 25 minutes, with values typically ≤ 2 Ω/sq. Low resistance tracks are favourable for wearable electronics as there will be less voltage drop across the track and consequently a lower power loss. To an extent, the drop in sheet resistance over time is a reflection of the increased mass of copper introduced onto the cotton surface. However we have also recognised during our work that uniformity of plated deposit is critical too. The effect of increasing plating time could be followed from SEM imaging (Figure 8), with an improved uniformity visible with plating time.

[Figure 8]

Cross section analysis of the samples was also carried out with SEM (Figure 9a and b). After 25 minutes of copper plating at 45 °C the thickness of the copper layer was on average 3 µm, although a broad range of deposit thicknesses over the samples were measured (Fig. 9c).

[Figure 9]

One contributing factor to this variation could be uneven catalyst deposits due to the spraying technique, causing uneven electroless plating. There may also be an issue with penetration of chemistry through the sample as only one side was sprayed with catalyst. However, in summary, it was found that reproducible electroless copper plating to generate highly conductive samples could be achieved on cotton catalysed using method 1 deposition. Lower plating bath temperatures and shorter plating times are feasible, which is very encouraging when considering any commercial scale up viability.

Selective patterning of catalyst by microdispensing or ink jet printing

A significant requirement for this process is the ability to selectively apply the metal coating to textiles, in tracks or more complex designs. By printing or applying one catalyst reactant then the other, tracks of silver catalyst can be deposited which will form the template for electroless copper plating. Once copper plated, they serve as highly conductive connecting traces across the cotton. One way to achieve this effect is via a contactless microdispensing system (Figure 10b and c). User-controlled parameters, such as the valve open time and the distance of the needle lift, the volume and speed of liquid deposition can be dictated. This is very valuable when working with absorbent substrates such as textiles. Once the operating parameters have been optimised, fine tracks can be produced by printing the reducing agent solution followed by silver nitrate. For example, Figure 10(a) shows an SEM image of a copper-plated track across cotton, with 1.5 mm width. It was found that dispensing wider tracks decreases the electrical resistance from end to end, improving their applicability to wearable devices. For example, Figure 10 (d) shows a track of 2.5 mm width, 50 mm length and a resistance along the track from end-to-end of 20 Ω (1 Ω/sq) measured with a 2-probe multimeter.

[Figure 10]

Inkjet printing was also explored as a catalyst deposition method. Sodium borohydride was applied to the cotton first and silver nitrate was then printed on top to form the silver catalyst. In this case tracks of 4 mm were printed around the fingers of a glove (Figure 11) and after copper plating they formed highly conductive tracks. For example, the track along the middle finger is 240 mm in length and measures a resistance from end-to-end of ~30 Ω (0.5 Ω/sq). The resolution of the tracks achievable from inkjet printing is greater than that of the microdispenser, although the microdispenser offers other advantages such as dispensing from a higher point and having greater deposition rates.

[Figure 11]

These reactive printing methods have been recognised (Bidoki et al., 2005; Bidoki, Nouri, & Heidari, 2010; Li, Sutton, Burgess, Graham, & Calvert, 2009) as being simpler, cheaper and more environmentally friendly compared to typical silver nanoparticle print processes, where usually high-loading metal inks are used. It allows us to deposit catalyst in a more controlled way and produce more complex conductive patterns, without the need for any sintering or curing.

Conclusions

The process of copper electroless plating onto cotton, initiated by a nanosilver seed layer, has been explored as whole area coverage and selectively depositing as tracks. This process could offer exciting opportunities as a key enabling technology within the wearables and smart textiles sector. Research focused on the repeatability of the process to best compare results between different samples. Contact angle, surface charge and IR spectroscopy measurements were completed for the cotton and cotton coated with a cationic polymer linker. The ability of the polymer to alter the surface chemistry of the cotton was quantified and a spray method for applying the catalyst layer was optimized. A detailed analysis of the effects of the copper plating time and temperature on the properties of the metallized cotton was undertaken. It was found that uniform plating to obtain sheet resistance <10 Ω/sq across the samples was possible after just 10 minutes at 45 °C. Higher conductivities and weight gains were subsequently observed with 15, 20 and 25 minutes plating.

To improve on the control of catalyst deposition and to achieve selective, patterned, metallisation of textiles we have produced samples via a microdispenser and inkjet printing. This reactive chemistry approach produced uniform tracks between 1.5 mm and 4.0 mm wide on cotton. Tracks > 2 mm width are preferable for forming high conductivity, stable connecting leads. This process can directly be applied to the cotton, is relatively quick, cheap and easy to carry out and can fit broadly into a number of sectors. It can be used wherever a point-to-point connection across a textile is desired and has the potential to be a key enabling technology within smart textile and wearable technology sectors.

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List of figure captions

Figure 1

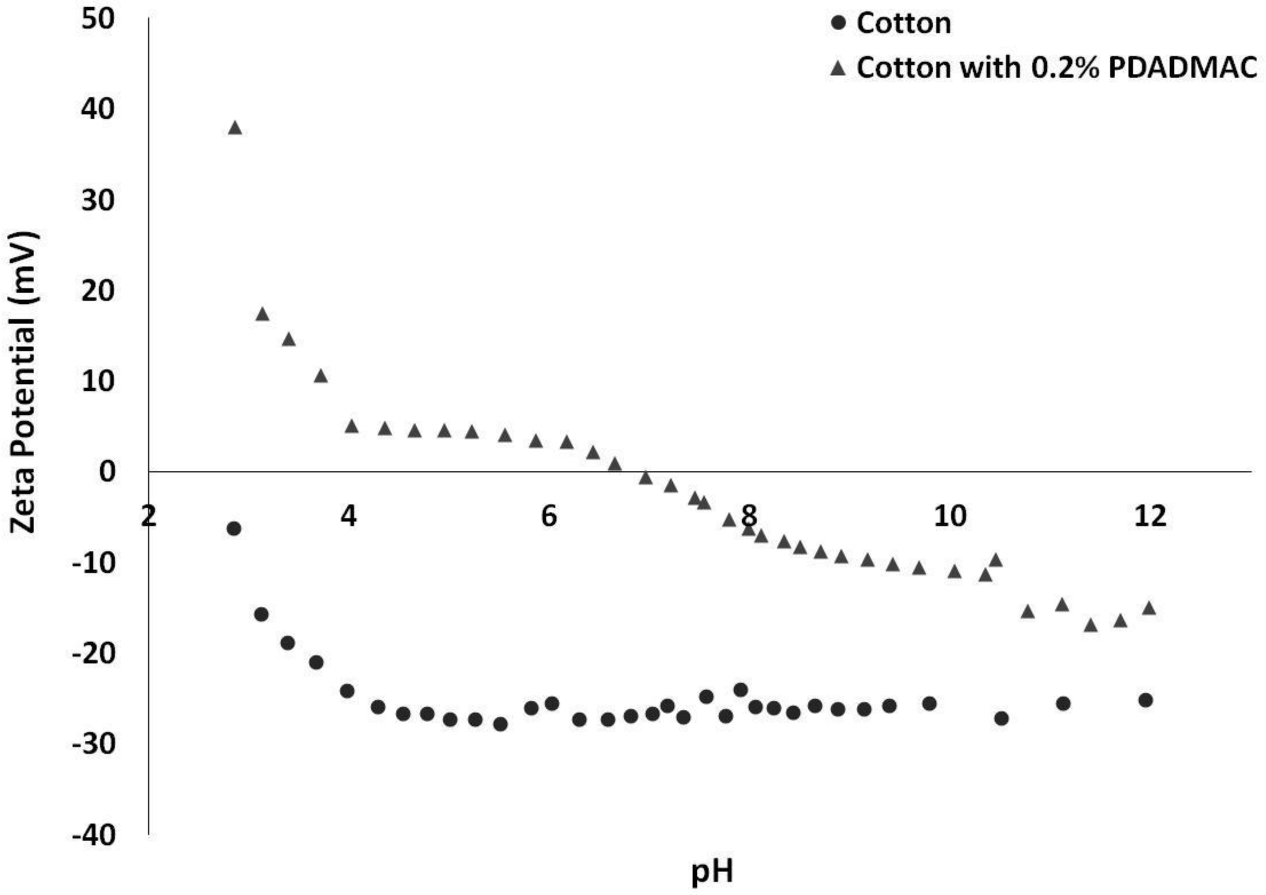

● Cotton
▲ Cotton with 0.2% PDADMAC
Zeta Potential (mV)
50
40
30
20
10
0
-10
-20
-30
-40
2
4
6
8
10
12
pH

Figure 2

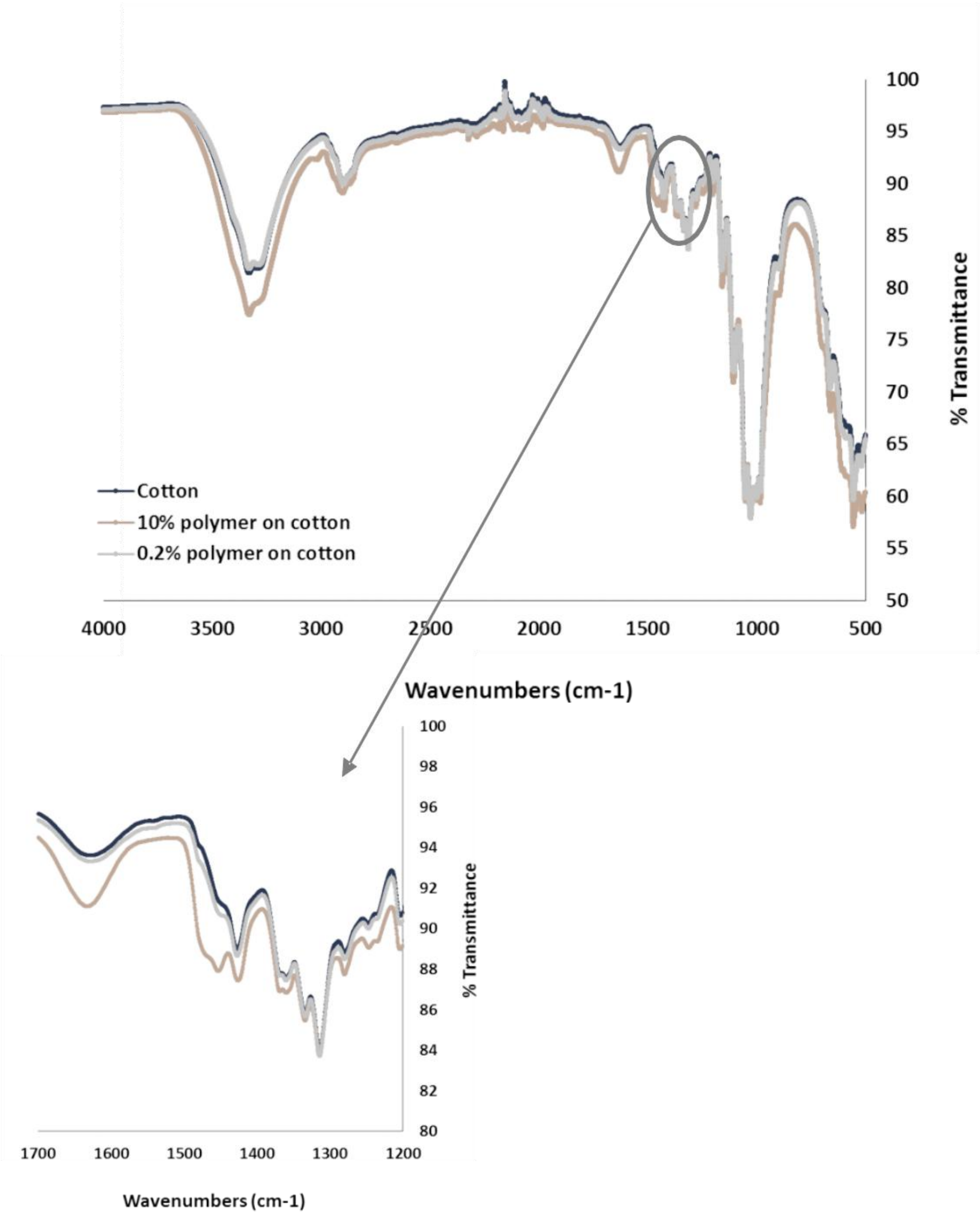
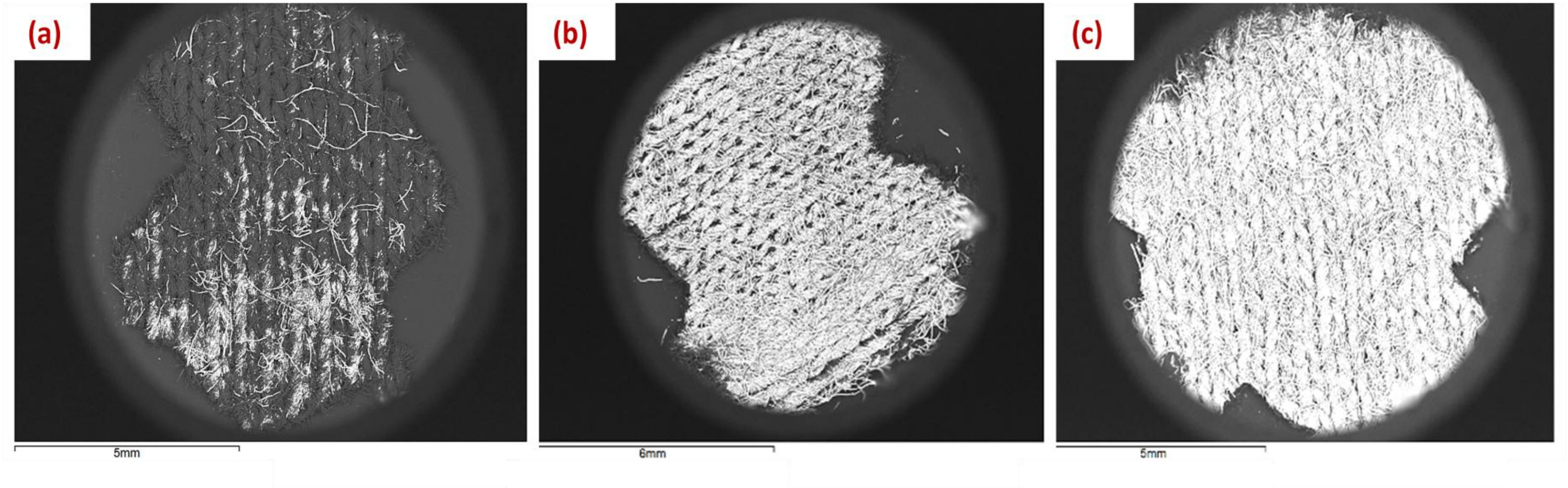

100
95
90
85
80
75
70
65
60
55
50
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
Cotton
10% polymer on cotton
0.2% polymer on cotton
100
98
96
94
92
90
88
86
84
82
80
% Transmittance
1700
1600
1500
1400
1300
1200
Wavenumbers (cm-1)

Figure 3



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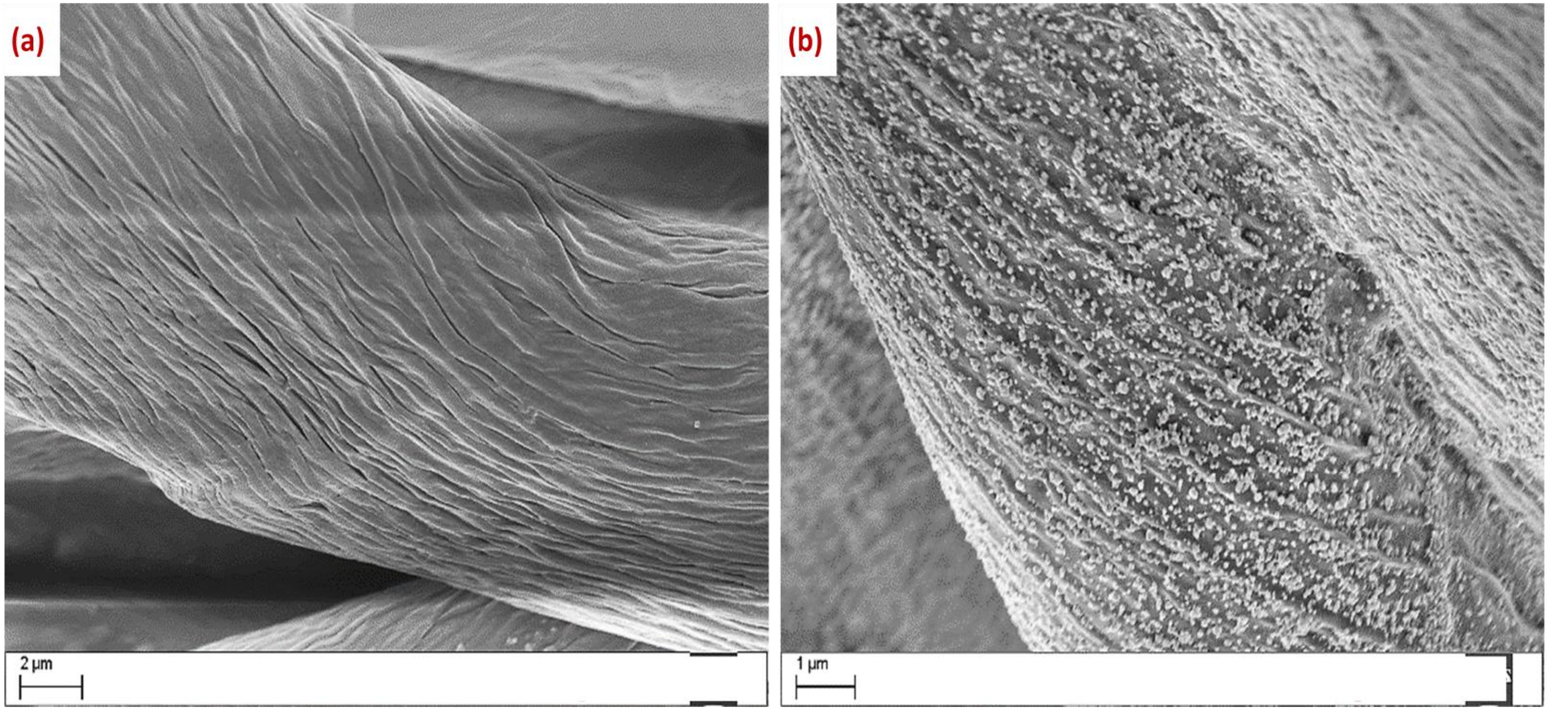
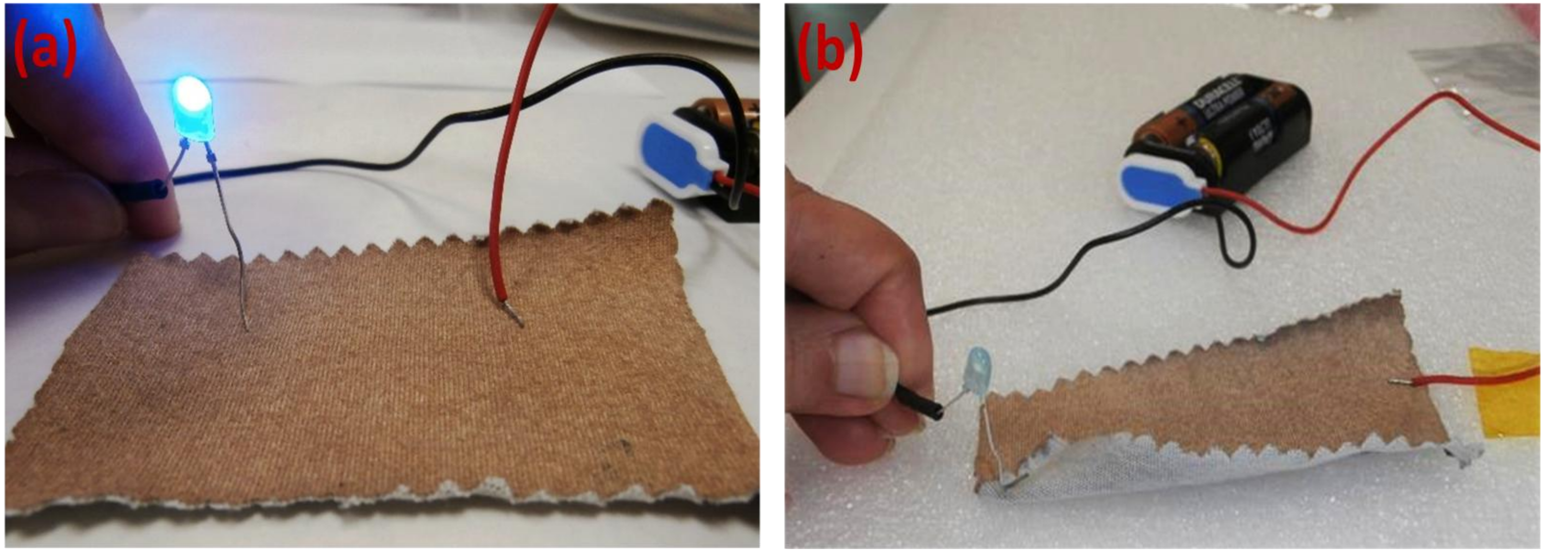


Figure 5



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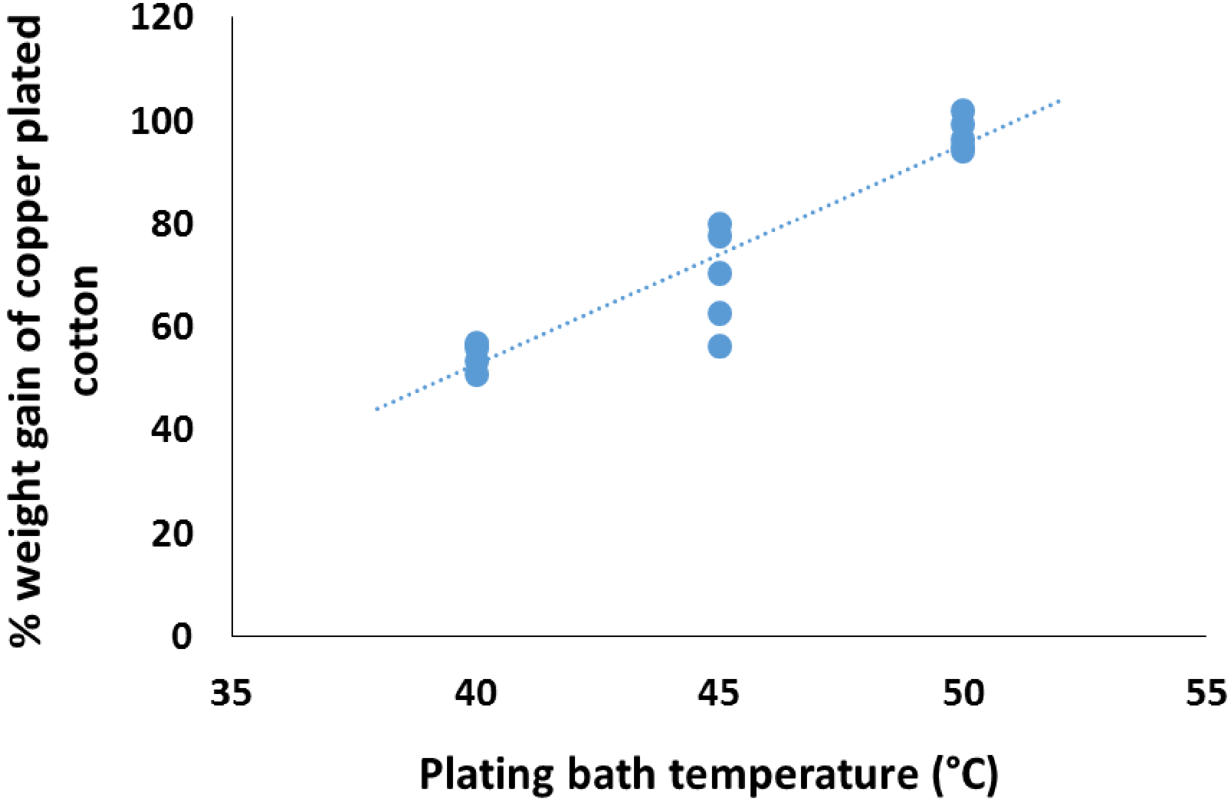

% weight gain of copper plated cotton
0
20
40
60
80
100
120
35
40
45
50
55
Plating bath temperature (°C)

Figure 7

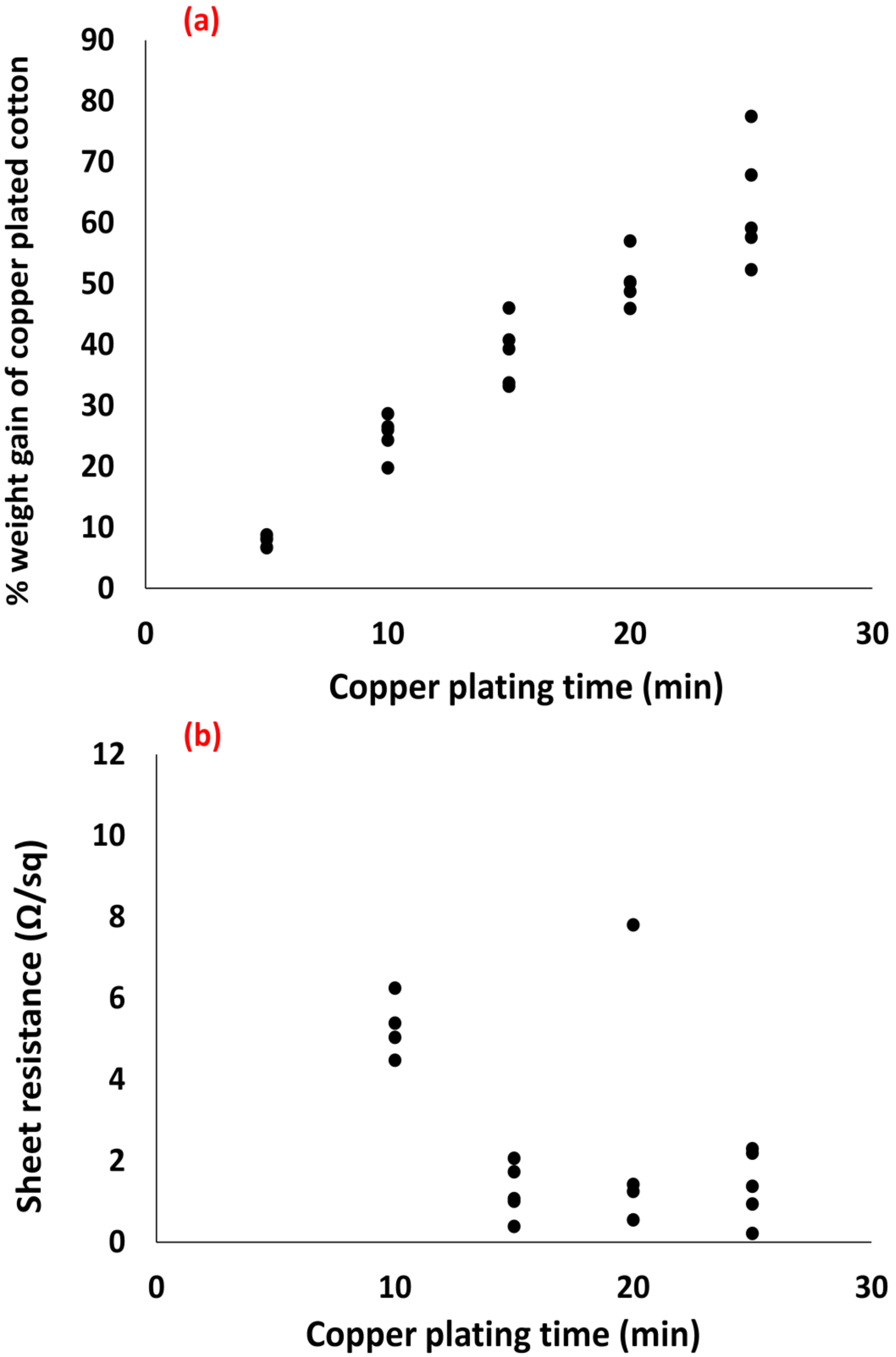

(a)
% weight gain of copper plated cotton
0
10
20
30
40
50
60
70
80
90
0
10
20
30
Copper plating time (min)
(b)
Sheet resistance (Ω/sq)
0
2
4
6
8
10
12
0
10
20
30
Copper plating time (min)

Figure 8

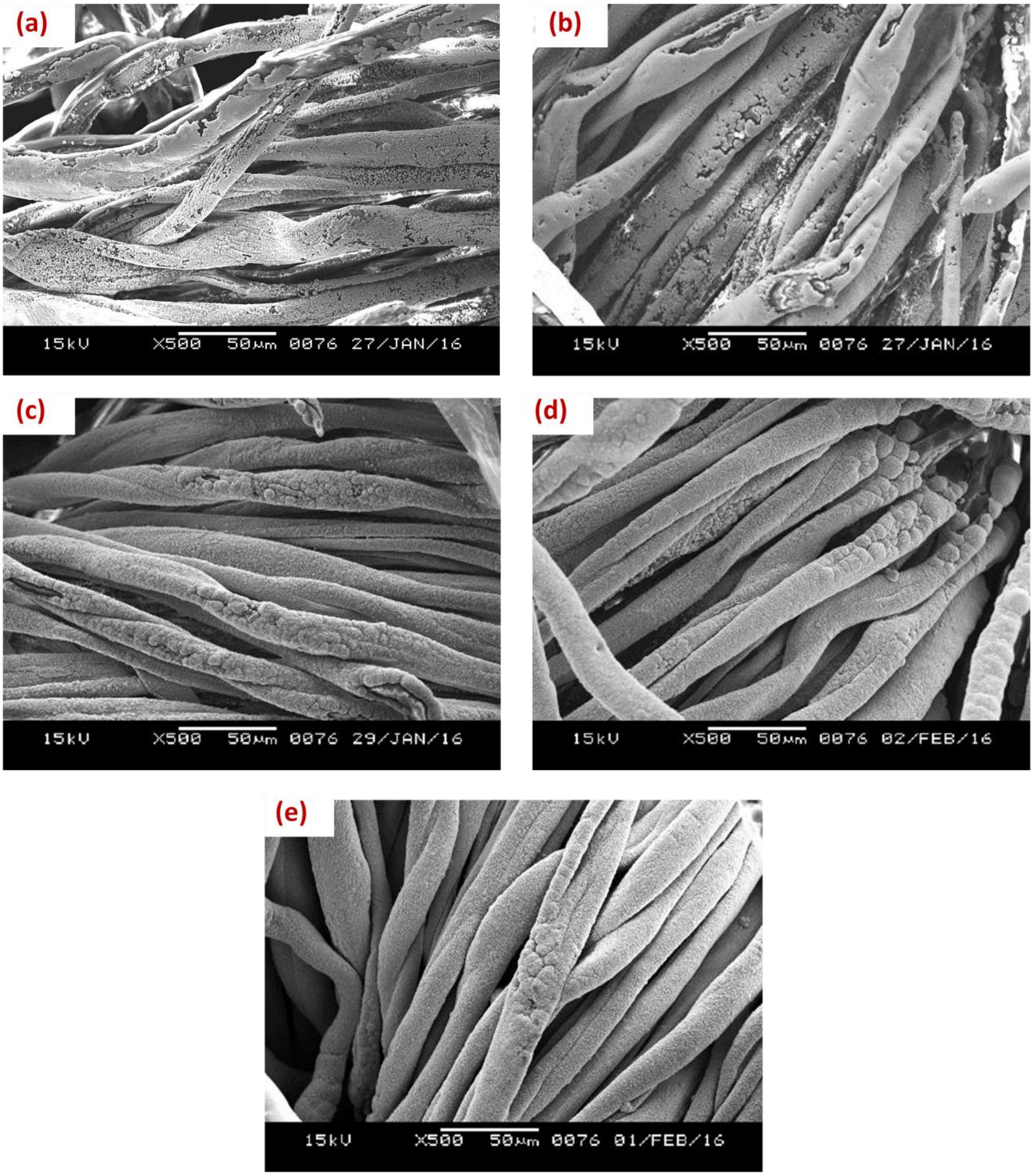

(a)
15kV X500 50µm 0076 27/JAN/16
(b)
15kV X500 50µm 0076 27/JAN/16
(c)
15kV X500 50µm 0076 29/JAN/16
(d)
15kV X500 50µm 0076 02/FEB/16
(e)
15kV X500 50µm 0076 01/FEB/16

Figure 9

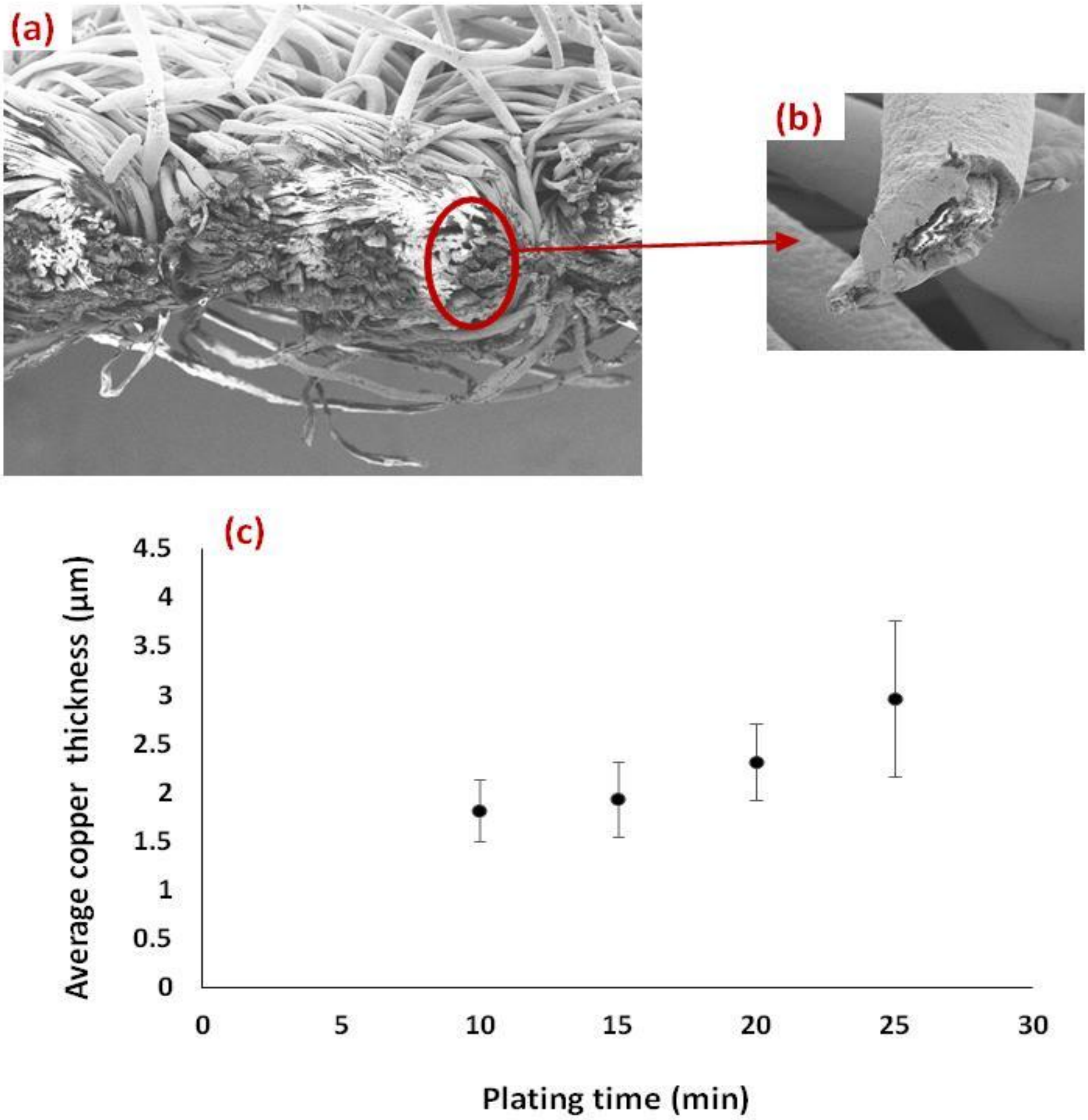

(a)
(b)
(c)
Average copper thickness (µm)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
5
10
15
20
25
30
Plating time (min)

Figure 10

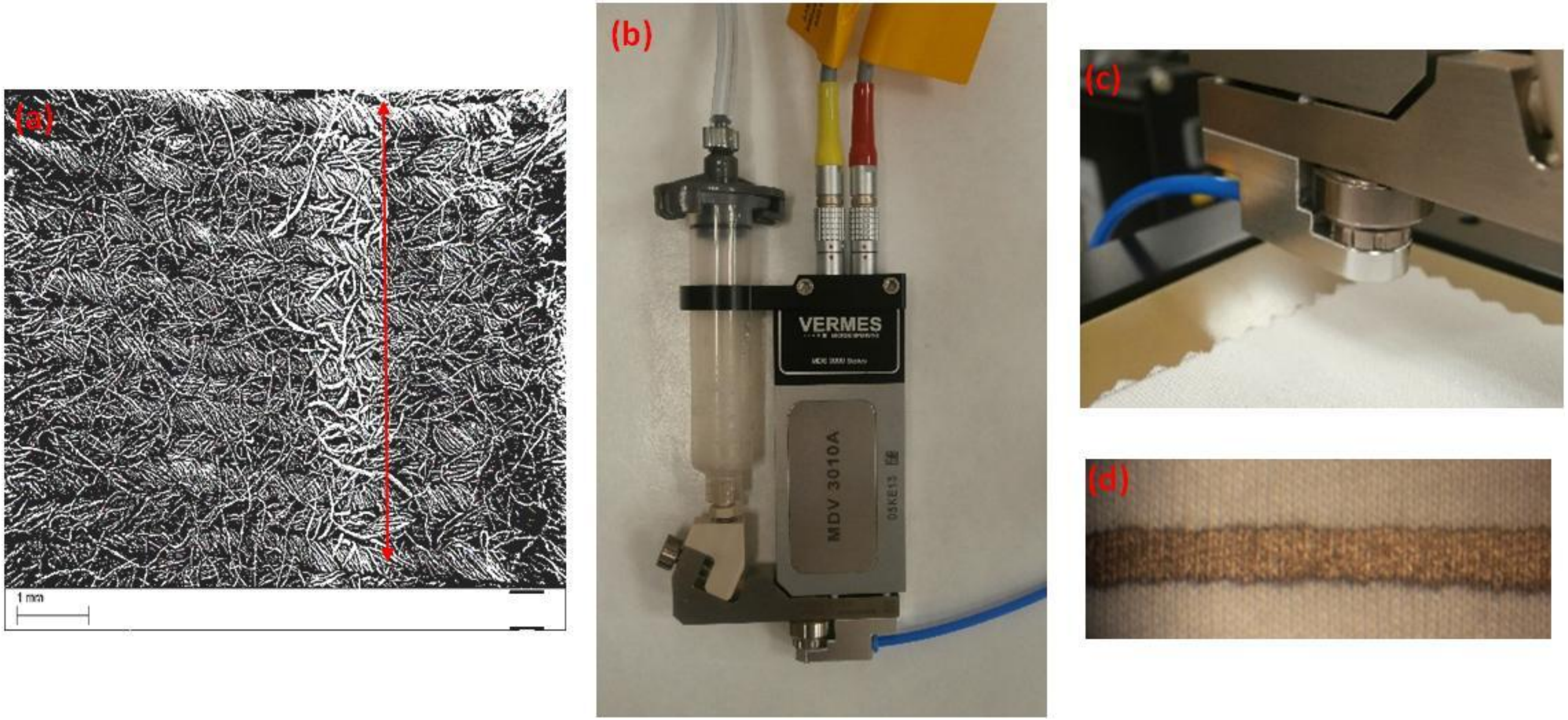
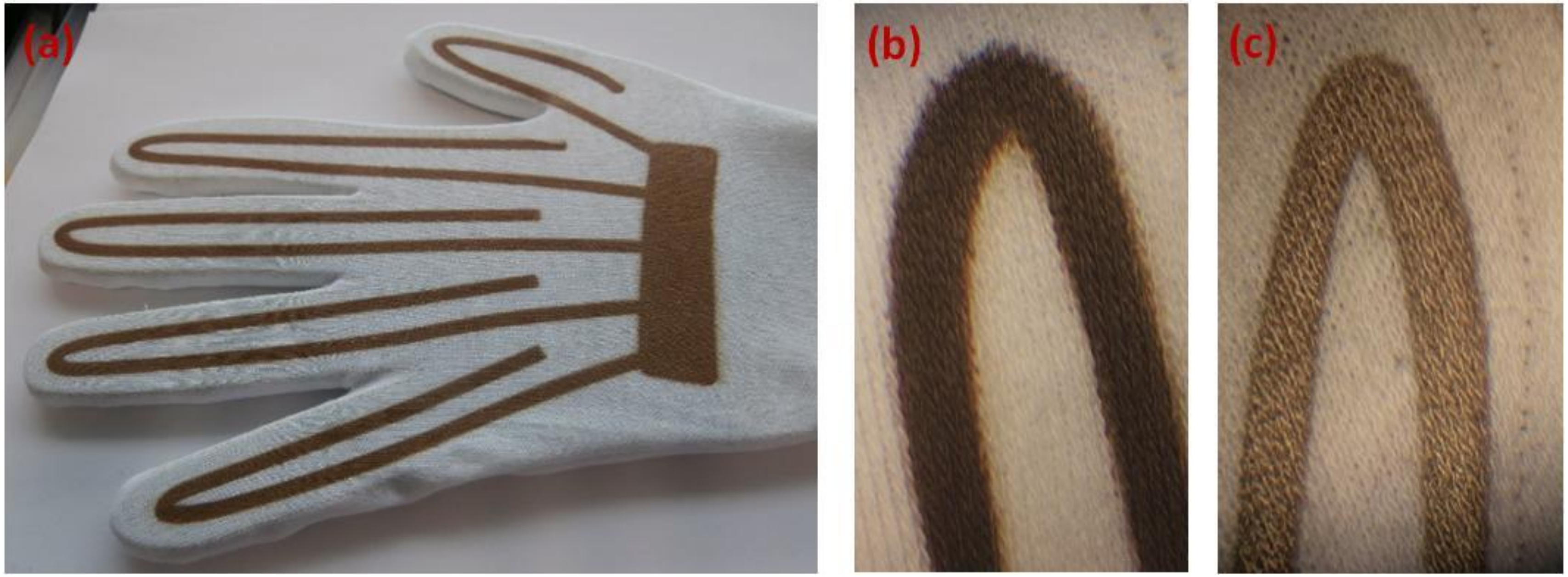


Figure 11



List of table captions

Table 1

	One silver coating	Two silver coatings	Three silver coatings
% weight gain of sample after copper plating	4.8	37.4	60.6

Table 2

Concentration of polymer applied	**Batch no.**	**Mean Ag mass from batch of five samples (μg cm^{-2})**
0.2 %	1	47.9 ± σ 2.67
0.2 %	2	46.1 ± σ 3.78