TECHNICAL UNIVERSITY OF LIBEREC
Faculty of Textile Engineering

Surface Deposition of Metals on Textile Structures

Azam Ali, M.Sc.

SUMMARY OF THE THESIS

TECHNICAL UNIVERSITY OF LIBEREC
Faculty of Textile Engineering

Title of the thesis:	**Surface Deposition of Metals on Textile Structures**
Author:	**Azam Ali, M.Sc.**
Field of study:	**Textile Technics and materials Engineering**
Mode of study:	**full time**
Department:	**Department of Material Engineering**
Supervisor:	**prof. Ing. Jiří Militký, CSc.**

Committee for defence of the dissertation:

Chairman:	
prof. Ing. Jakub Wiener, Ph.D.	FT TUL, Department of Material Engineering
Vice-chairman:	
prof. Ing. Luboš Hes, DrSc., Dr.h.c.	FT TUL, Department of Textile Evaluation
prof. Dr. Ing. Miroslav Černík, CSc. (oponent)	CxI TUL, The Institute for Nanomaterials, Advanced Technologies and Innovation
doc. Ing. Vladimír Bajzík, Ph.D.	FT TUL, Department of Textile Evaluation
doc. Ing. Antonín Kuta, CSc.	University of Chemistry and Technology Prague, Department of Polymers
doc. RNDr. Miroslav Šulc, Ph.D.	FP TUL, Department of Physics
Ing. Michal Černý, Ph.D. (oponent)	University of Pardubice, Faculty of Chemical Technology
Ing. Miroslava Pechočiaková, Ph.D.	FT TUL, Department of Material Engineering
Ing. Blanka Tomková, Ph.D.	FT TUL, Department of Material Engineering

The dissertation is available at the Dean's Office FT TUL

Liberec, 2021

ABSTRACT

The present work deals with the development of electrically conductive, EMI shielded, multifunctional fabrics. At first, the conductive textiles were developed by in-situ deposition of copper particles. The scanning electron microscope, and X-ray diffraction techniques were employed to study the morphology of deposited copper particles. The utility of conductive fabrics was analysed for electromagnetic shielding effectivity over frequency range of 30 MHz to 1.5 GHz. The electromagnetic interference shielding was found to increase with increase in number of dips, which was attributed to increased reflection of EM waves due to dense, uniform, and percolated network of conductive copper particles on the surface. Furthermore, the role of deposited copper particles on antibacterial properties was examined against pathogenic bacteria such as Staphylococcus aureus and Escherichia coli. At the end, the durability of fabrics was examined against washing. The fabrics showed good retention of the copper particles, proved by scanning electron microscopic microstructures and small loss in the conductivity of the material after washing.

The objective of second part was to develop multifunctional plain-woven conductive fabrics with acceptable electrical conductivity by in-situ deposition of silver particles. The effect of silver nitrate concentration and number of dips was investigated for change in electrical conductivity, EMI shielding, and antimicrobial properties of coated fabrics. SEM analysis were employed to study the morphology of deposited silver particles. The EMI shielding was found to increase with increase in concentration of silver particles. Furthermore, silver particles were also deposited on stretchable knitted fabrics by adopting the same method of in-situ deposition. The purpose of this study deals with the development of stretchable conductive fabrics for possible applications in electrotherapy. The performance of silver-coated fabrics was evaluated based on number of properties such as electrical conductivity at normal and stretching state of fabrics, antibacterial, and durability. Furthermore, the conductive fabrics were subjected to various repeated extensions and change in electrical resistivity was examined to simulate the performance of electrodes under various movements of human body. With increase in extension till 80%, very small change in electrical resistivity was observed and after 90% extension, the electrical resistivity was found to increase significantly. The resistivity was found to remain constant for repeated extensions of over 100 cycles and also there was insignificant change in electrical resistivity when constant current was applied over prolonged time. The utility of silver-coated fabrics can be expected as flexible textile electrodes in transcutaneous electrical nerve stimulation electrotherapy applications.

The third part of study, proposed a simple way of surface metallization of cotton fabrics by electroless plating using a shorter route than is conventional. The fabric surface was activated by deposition of silver and copper nanoparticles, and then a thin layer of copper was coated using electroless plating. The performance of coated fabrics was compared in terms of electrical conductivity, electromagnetic interference (EMI) shielding, Joule heating and antibacterial properties. The samples prepared by electroless plating of copper showed greater performance for the fabric first deposited with silver particles than those first deposited with copper particles. Samples of copper electroless plating over silver had surface resistivity of 20 Ω, EMI shielding of 75.53 dB and Joule heating of 119 °C by using DC input varied from 5–10 V and at constant current 1 A (the experiment was carried out up to 10 watt). Moreover, samples with modified electroless plating showed better attachment of the metal layer and therefore longer durability

The objective of fourth part was to make electrically conductive multifunctional fabrics and their further use as electrodes for the development of triboelectric generator (TrEG). The conductive fabrics were made by the coating of thin copper layer and then electroplating of

silver layer. The surface structure, electrical conductivity and antibacterial properties of coated fabrics were examined to know their multifunctional properties. Later, the energy harvesting performance of conductive fabric electrodes was studied by combining with oppositely charged triboelectric materials such as silicon rubber and rabbit fur. The fabricated TrEG was found to produce 21 V and 3.5 μA current under the stretching action whereas 33 V and 6 μA current under the pressing action. Furthermore, its energy harvesting performance was investigated under the mechanical actions of human body, it generated about 10 V from elbow movements and about 40 V from foot movements.

Keywords: Conductive textiles, copper particles, silver particles, stretchable conductive fabrics, surface metallization, electromagnetic interference shielding, antibacterial properties, smart textiles, TENs electrodes, electrotherapy, electroless plating, metal coatings, sensors and actuators, copper plating, energy harvesting, triboelectric generator

ABSTRAKT

Tato disertační práce se zabývá vývojem elektricky vodivých, multifunkčních textilií chránících proti elektromagnetickému záření v širokém rozsahu frekvencí (EMI). V první části práce byly připraveny vodivé textilie pomocí in-situ povrchové depozice částic mědi. Pro studium morfologie nanesených částic mědi byl použit skenovací elektronový mikroskop a rentgenové difrakční techniky. Funkčnost vodivých tkanin byla analyzována hodnocením účinnosti elektromagnetického stínění v kmitočtovém rozsahu 30 MHz až 1,5 GHz. Bylo zjištěno, že stínění elektromagnetického rušení se zvyšuje se zvyšujícím se počtem dílčích nánosů, což přímo souvisí se zvýšeným odrazem elektromagnetického záření jako důsledek tvorby husté (za perkolačním prahem) rovnoměrnější povrchové vrstvy vodivých částic mědi. Dále byla zkoumán vliv povrchové vrstvy částic mědi na antibakteriální odolnost proti patogenním bakteriím, jako je Staphylococcus aureus a Escherichia coli. Textilie s povrchovou vrstvou částic mědi vykazovaly dobrou odolnost v praní, což bylo prokázáno jak mikroskopickým zkoumáním mikrostruktury, tak malou ztrátou elektrické vodivosti po praní.
Cílem druhé části disertační práce bylo vyvinout multifunkční tkané vodivé textilie v plátnové vazbě s přijatelnou elektrickou vodivostí pomocí in-situ nanášení částic stříbra. Byl zkoumán vliv koncentrace soli stříbra a počtu dílčích nánosů na změnu elektrické vodivosti, elektromagnetického stínění (EMI) a antimikrobiálních vlastností těchto multifunkčních tkanin. Pro studium morfologie uložených částic stříbra byla použita SEM analýza. Bylo zjištěno, že elektromagnetické stínění se zvyšuje se zvyšováním obsahu částic stříbra.
Stříbrné částice byly také nanášeny na elastické pleteniny pomocí stejného způsobu in-situ nanášení. Cílem byla příprava elastických (vratně deformovatelných) vodivých pletenin pro možné aplikace v elektroterapii. Výhodnost těchto pletenin byla hodnocena na základě řady vlastností, jako je elektrická vodivost v normálním a deformovaném stavu, antibakteriální schopnosti a trvanlivost. Do 80% ní tahové deformace byla pozorována velmi malá změna elektrické vodivosti. Po 90% ní tahové deformaci bylo zjištěno, že se elektrický odpor významně zvyšuje. Bylo simulováno chování vodivých pletenin (elektrod) při různých pohybech lidského těla pomocí změn elektrického odporu při opakovaných cyklech prodlužování a odlehčování. Bylo zjištěno, že elektrický odpor zůstává konstantní při více než 100 cyklech prodlužování a odlehčování. Dlouhodobé působení konstantního elektrického proudu nevýznamně změnilo elektrický odpor elastických vodivých pletenin. Tyto elastické vodivé pleteniny textilií bude možno použít jako flexibilní textilní elektrody v elektroterapii transkutánní elektrické stimulace nervů.
Třetí část disertační práce je zaměřena na návrh jednoduchého způsobu povrchového ukládání částic kovů na bavlněné tkaniny bez použití elektrického pole zkráceným. Povrch tkaniny byl aktivován nanesením nanočástic stříbra a mědi a následně byla vytvořena tenká vrstva částic mědi bez elektrickým pokovováním. Funkčnost povrchově pokovených tkanin byla hodnocena pomocí elektrické vodivosti, elektromagnetického stínění, teploty odporového ohřevu a bakteriální odolnosti. Textilie, kde byla provedena aktivace nanesením částic stříbra s následným bezproudovým pokovováním mědí, vykazovaly vyšší účinnost ve srovnání s textiliemi, kde byla provedena aktivace nanesením částic mědi s následným bezproudovým pokovováním mědí. Textilie aktivované nanesením částic stříbra s elektrolytickým pokovením mědi měly povrchový odpor 20 Ω, elektromagnetického stínění 75,53 dB a teplotu 119 ° C při ohřevu pomocí stejnosměrného napětí 10 V při konstantním proudu 1 A (10 wattů). Kromě toho tyto textilie vykazovaly delší trvanlivost efektů.
Cílem čtvrté části disertační práce bylo připravit elektricky vodivé multifunkční textilie využitelné jako elektrody pro triboelektrický generátor (TrEG). Vodivé textilie byly vyrobeny depozicí částic mědi a následnou galvanizací stříbrem. Pro posouzení multifunkčních vlastností byla zkoumána struktura povrchu, elektrická vodivost a antibakteriální vlastnosti. Byla

studována účinnost sběru energie vodivých textilních elektrod kombinací s opačně nabitými triboelektrickými materiály, jako je silikonový kaučuk a králičí kožešina. Bylo zjištěno, že takto připravený TrEG produkuje napětí 21 V a proud 3,5 μA při protažení. Při stlačení je produkováno napětí 33 V a proud 6 μA. Dále byla zkoumána energetická účinnost tohoto triboelektrického generátoru při mechanickém působení lidského těla. V důsledku pohybů loktů se generuje napětí asi 10 V a v důsledku pohybů nohou napětí asi 40 V.

Klíčová slova: Vodivé textilie, částice mědi, stříbra částice, elastomerní vodivé textilie, povrchová metalizace, stínění elektromagnetického rušení, antibakteriální vlastnosti, inteligentní textilie, elektrody TEN, elektroterapie, elektrolytické pokovování, kovové povlaky, senzory a akční členy, pokovování mědi, sběr energie, triboelektrický generátor.

Table of contents

List of Figures

List of Tables

1. Introduction

In recent years, research on functional textiles gained significant importance due to their utilization in different advanced materials [1]. A variety of functional textiles e.g. solar textiles (reflecting or absorbing), color-changing textiles, shape-memory textiles, waterproof and moisture permeable textiles, anti-bacterial textiles, UV protected textiles and electrically conductive textiles have been developed [1,2]. Among them, the electrically conductive textiles are becoming most dynamic and fast-growing sectors due to their novel applications in flexible and wearable electronics, sensors and actuators, electromagnetic interference (EMI) shielding, heat generators, etc. [3]. There are various approaches to render the textiles with electrical conductivity such as fabrics made by naturally conductive yarns and those specially treated to impart conductivity. The naturally conductive yarns can be spun directly from electrically conductive materials like metals [4, 5]. While special treatments like chemical coating, surface metallization (Cu, Al, Ni, Ag, etc.), deposition of conductive fillers (carbon black, carbon nanotubes, etc.), coating of conductive polymers (polyaniline, polypyrrole, polytiophene, etc.) can be attempted to impart electrical conductivity on textile surfaces [5, 6]. However, the conductive textiles made by blending of metal wires during yarn or fabric formation lead to deterioration of their comfort properties and were easily affected by washing and abrasion [7]. They cannot be widely used for personal protective clothing because of their prickliness, heavy weight, cost inefficiency, poor flexibility, and poor scratch resistance. The fabrics made by a coating of conductive polymers, inks, and chemical doping were found not durable to washing and were susceptible to cracking and rubbing [8-10]. Therefore, the textile surface metallization was investigated in detail in this research work as unique method to provide multifunctional properties such as electrical conductivity, EMI shielding, ohmic heating and anti-bacterial properties [10].

2. Purpose and the aim of the thesis

The main aim of thesis is to investigate preparation properties and selected applications of multifunctional textiles having required electrical conductivity, EMI shielding, ohmic heating capability, and anti-bacterial properties by different surface metallization methods. To develop the conductive fabrics for novel applications (electrotherapy, energy harvesting) a suitable amount of deposited metal is required. This thesis is focused on the metallization of two different kinds of fabrics i.e. 100 percent cotton woven fabric and knitted stretchable fabric composed up of nylon, spandex and cotton.

At first in-situ deposition of copper particles was done on plain woven cotton fabric and studied their electrical and functional properties.

In second step deposition of silver particles was done on cotton fabric and knitted fabric. The purpose of deposition the silver particles over knitted fabric was to find the suitable application in the field of electrotherapy for TENs machine.

Third step was to perform the electroless plating on previously copper and silver particles coated woven fabrics. Generally, electro less plating is performed after a number of steps (1) pre-treatment, (2) sensitization of the surface, (3) activation of the surface (4) copper plating. The aim was to eliminate the sensitization step by coating of copper or silver particles over the surface of fabric before electroless plating of any metals.

In fourth step, the cost effective and complete procedure to develop TrEG (Triboelectric generators) is described. we performed the silver plating on stretchable knitted fabrics composed up of nylon, spandex and cotton. Then the suitable application of plated fabrics in the field of energy harvesting was find.

3. Overview of the Current State of Problem

The metallization of textile is the process which adds to and enhance the functional properties of textile [11]. Metallized textiles have numerous advantages over fabrics made entirely of thin metal wires and polymers. The advantages over no metallized fabrics include resistance to sever weather conditions like sunlight, smog and soil, resistance to chemicals and lower the sorption of hydrophilic materials. Thick and dense coating of metal is done in the field of protective textile to enhance the anti-ballistic and anti-stabbing properties. On the other hand by thing metal coating we can achieve the flexible and light in weight fabrics as compared to fabrics produced by thin metal wires and metallic sheets [21, 22]. Another advantage is in the field of textile fashion designing to produce the bright, shining and decorative textiles [23, 20]. By using metallization, it is possible to reduce the static charge. The static charge usually produces on the surface of synthetic fabrics and polymer sheets. These charges cause the attraction of dust particles and significantly put the electronic chips and devices in risk of damage [21, 22]. Another significant advantage is in the field of smart textile. Where metal coated textiles are important due their novel property of electrical conductivity and electromagnetic shielding. Electrically conductive flexible textile materials are new approach for the production of fabric sensors which can be used for certain medical application like electromyography (EMG), electroencephalography (EEG) and electrocardiogram sensing. These textiles also use in bandages and surgical gowns due to antibacterial effect. Moreover, due to their novel property of flexibility they can be integrated into textiles to detect field effect transistors, health monitoring, sports action detectors. Metal coated textiles can be used as electrodes in energy harvesting devices and in the replacement of carbon based polymer electrodes etc. A number of techniques have been devoted to plating of copper using formaldehyde as reducing agents, however, this process may release hazardous gases during their operation [3]. In another research, the ultrasonic-assisted electroless silver plating of polyethylene terephthalate fabrics showed the SE of more than 32 dB at frequency ranging from 0.01 MHz to 18 GHz [15]. However, the plating of silver is costly than plating of copper. Therefore, further research is necessary to effectively modify the textile surface with controllable conductivity and high durability in safe conditions. Several papers have studied the electroless copper plating solutions using sodium hypophosphite as reducing agent due to its low pH, low cost, and relative safety features [3]. Those researches focused mainly on the effect of additives, on the properties of the deposits and the application of electroless copper plating to fabrication of printed circuit boards.

Research gaps were found after an extensive literature review shown above. According to the knowledge following research gaps were identified.

In-situ deposition of metal particles on woven and stretchable fabric for produce the flexible, stretchable sensors and electrodes (was here selected). Hence better replacement of coating the particles and nano/microwires of metals with binder [16]. Furthermore, searchability of fabric is also affected if binder is used to attach particles over the fabric surface.

Copper and silver particles coated fabrics should have good anti-bacterial properties and ohmic heating. Due to antibacterial effect, resistive heating, flexibility and searchability the fabrics will be better replacement for the carbon rubber-based hard electrodes (use in electrotherapy) [17].

Developed stretchable electrodes would be easily applied for long time over the skin of patient, and avoid from discomfort, redness, rashes and sweat, which were the frequent problems occur by self-adhesive carbon electrodes [12, 79].

In addition, fabric based electrodes can be washed and reused, while adhesive carbon based electrodes cannot use for more than three times [20]. Furthermore, it is compulsory and irritant to apply adhesive gel each time over the skin to attach the rubber electrodes.

Formaldehyde based reducing agents have been reported in many studies to develop the copper and silver particles. Formaldehyde has severed disadvantages on health such as carcinogen and irritant to skin, so cannot use for electrotherapy or in other medical applications [21]. Some more studies are available for another famous reducing agent $NaBH_4$. Sodium borohydride is extra active agent and give fast reduction. $NaBH_4$ provide a lot of H^+ ions and fast nucleation of metal ions, which tends to the formation of clusters and uneven coating [22]. Moreover, the coat of $NaBH_4$ is too high than sodium hydrosulphite and reduction potential is almost the same. Hence, glucose and sodium hydrosulphite are safe to use and better replacement of formaldehyde and sodium borohydride [23].

Moreover, glucose and sodium hydrosulphite reducing agents provide low pH, low cost and relative safety. Low pH is attractive for better nucleation of metallic ions, which tends to produce small size metal particles and avoid from aggregation [24]. While in basic pH there is need of alkali and complexing agents, which cause Metal hydroxide/oxide ions and produce uneven coating with large size agglomerated particles.

In situ deposition of particles provide thin layer of coating and resultant fabric will be light in weight as compared to heavy metal coating techniques such as physical vapour deposition and chemical vapour deposition etc.

Furthermore, by dip-dry-reduction method, we are directly growing/reducing the particles over the fabric surface. Therefore, eliminated the problems of cluster and agglomeration which are more common in solution or sol-gel method [27].

Purpose for in-situ deposition is to provide the better base for further electroless/electroplating of metals. So, in this way we have eliminated a number of pre-treatments, activation and sensitization steps, which are normally required to proceed further metal plating. Whereas conductive inks, conductive polymers and carbon-based materials provide in inadequate base and are not suitable form hygienic point for the development of electrodes (use in medical applications).

Surface activation with nanoparticles is more stable and provide better base for further electroless plating. Because nanoparticles cover more surface area and also penetrate into the fabric structure properly, to provide the volume conductivity. Furthermore, we are using copper and silver nanoparticles. Who has positive redox potential than copper which is going to be deposit. Actually, if we do use any base particles which has negative redox potential than copper depositing. Then the host element will replace by copper. So, the base will not give the homogeneous ground and will cause for the thickness variation for copper plating, in turn, electrical resistivity will also affect [28].

Copper electroless deposition on nano copper and silver particles is also better regarding comfort properties (drape, thickness and stiffness).

After deposition of silver and copper particles the fabric is ready for copper electroless plating. This method of plating is focused on less cost and environmental friendly (palladium free, stannous free and formaldehyde free) copper plating over cotton fabric [28].

A lot of worked has been done for copper plating over, stannous, cobalt and lead. Which cannot be used for hygienic applications. As tin (Sn) is hazardous and irritant to skin and persons with existing skin disorders may be more susceptible to the effects of these agents[29].

In existing methods copper and silver particles base for the deposition of further copper plating also confirmed the antibacterial activity of developed fabrics. Fabrics can be used for environmental friendly applications like electrodes for (TENs) machine, west for military application where we need electromagnetic shielding and hygienic west in case of injury of sliders.

During electroless plating by conventional method we need to use hydrochloric acid with stannous chloride which in turn effect the strength of cotton fabric. Instead of it, we are performing the electroless plating in alkaline bath using sodium hydroxide. Therefore, a study is describing more favourable deposition of copper in alkaline pH [30].

For selection of proper reducing agent, it should have high standard reduction potential as compared to the metals (copper and silver) being reduced. For instance, the reduction potentials of some important reducing agents like hypophosphite (-1.57V), formaldehyde (-1.30 V) can be useful as they are higher compared to the reduction potentials of copper +0.34V and silver +0.80V [31]. The another important property of reducing agent is self catalytic reaction ability which can help in deposition of maximum copper on target metal (fabric coated with copper particles) [32].

Researchers have been using formaldehyde and hypophosphite as a reducing agent during electroplating, which has serious disadvantages. Formaldehyde has severed disadvantages when use for electroplating. It is carcinogenic, irritant to skin, give harmful vapor etc. While using hypophosphite is not proper for copper, because copper is not a good catalyst for the oxidation of hypophosphite. So, in result give not proper plating over copper. So to overcome these issues glyoxalic acid appeared as a best alternative, provide more stable, higher deposition with very less environmental pollution.

Electroless plating method by using glyoxalic acid is more environmentally friendly and not give off harmful vapours.

The main advantage of performing the electroless plating over already copper and silver particle coated fabric is to achieve very low electrical resistivity with high EMI shielding because silver and copper particles coated base is already conductive.

4. Method used, study materials

Two types of fabrics were used for metallization. One is plain-woven standard bleached cotton fabrics with weave structure (EPI × PPI = 28 × 23, warp and weft count = 23s Ne, GSM = 150 g m^{-2}) having thickness 0.35 mm were used. The second fabric is a special type of knitted textile mostly used for medical therapy. This knitted fabric is composed up of cotton-Nylon 66–Lycra (80:15:5) with areal density - GSM 110 g/m^2 and construction of WPC × CPC = 10 × 9 (26 Tex, 20 Denier, 70 Denier), having thickness about 0.85 mm.

The experimental part is composed up of four parts.

- First part, is the development of copper particles on plain woven cotton fabric.
- Second part, is the deposition of silver particles over plain woven cotton fabric and deposition of silver particles on stretchable knitted fabric (to develop the electrodes for TENs machine for electrotherapy.
- Third part is related to further copper electro-less plating on previous two developed (Cu particles coated woven fabrics and Ag particles coated woven fabrics) fabrics.
- Part fourth is the silver electroplating over knitted fabric (to develop the energy harvesting device).

4.1 Deposition of copper particles on textiles

These experiments are done to incorporate the copper particles over the plain woven cotton fabrics. Copper sulfate was used as the base material along with sodium hydrosulfite as reducing agent for in situ deposition of copper particles on cotton fabrics. At first, different concentrations of copper sulfate from 30 g/L, 20 g/L and 10 g/L were prepared by dissolution in distilled water. Then, the cotton fabric was dipped 10 times in the solution and dried at 100 °C for 3 minutes. This procedure of dipping and drying was continuously carried out up to 150 dips. The dwell time of fabric in solution was about 30 seconds against each dip. Subsequently, (after each 10 number of dips) the treated fabrics were transferred to the 30 g/L sodium hydrosulfite solution. Hence, we made 15 samples against each copper sulfate concentration. The concentration of sodium hydrosulfite was determined based on the concentration of copper sulfate. It should be always higher or at least equal to copper sulfate concentration. The reduction was continued for the duration of 20 minutes. The duration of reduction treatment was determined based on change in color of cotton. The cotton fibers changed their color from blue to blackish gray after 15 minutes of reaction with reducing agent. So, 20 minutes of reduction treatment was allowed to complete the reaction.

4.2 Deposition of silver particles on textiles

Silver particles were deposited on plain-woven cotton fabric and also on stretchable knitted fabric.

4.2.1 Silver particles on cotton woven fabric. The cotton fabric was treated with 10 wt % aqueous NaOH solution at room temperature for 10 min and rinsed with distilled water. At first, different concentrations of silver nitrate ($AgNO_3$) from 51 g/L, 34 g/L and 17 g/L were prepared by dissolution in distilled water. Then, the aqua ammonia (28 wt %) was added dropwise into aqueous solutions of $AgNO_3$ and stirred continuously until a transparent solution of $[Ag(NH_3)_2]^+$ was obtained. Cotton fabric was dipped in this solution for 30 seconds and dried at 100 °C for 3 minutes. The dip and dry process was repeated a number of times to deposit the maximum concentration of $[Ag(NH_3)_2]^+$ on the fabric. This procedure of dipping and drying was continuously carried out up to 150 dips. Subsequently, the treated fabrics were transferred to 18 g/L glucose stock solution. The reaction was allowed to proceed for 15 minutes. Finally, the fabrics were rinsed with water and dried in air.

4.2.2 Silver particles on blended knitted fabric. Pre-treatment of fabric via local oxidation was carried out by dipping fabric into 1 % (w/w) $KMnO_4$ and 10 g/l sodium chloride (NaCl) for 25 min in an ultrasonic bath. This treatment was done to enhance the carbonyl groups on the nylon 66 fibers. The fabric was rinsed thoroughly with distilled water and dried at 60 °C. The fabric was then treated with 12 wt % aqueous NaOH solution at room temperature for 10 min and rinsed with distilled water. Meanwhile, three different concentrated solutions (170 g/L, 85 g/L and 42.5 g/L) of silver nitrate ($AgNO_3$) were prepared and the aqua ammonia (28 wt %) was added dropwise to get the transparent solution of $(Ag(NH_3)_2)^+$. Later, alkali treated fabrics were dipped in each solution for 10 minutes and dried at 90 °C for 10 minutes. The dipping and drying process was repeated for 10 times to deposit the maximum concentration of $(Ag(NH_3)_2)^+$and Ag^+ ions on the fabrics. Towards the end, the dipped fabrics were immersed into 54 g/L glucose stock solution, and the reaction was allowed to progress for 15 min. The silver coated fabrics were then rinsed with distilled water, dried in air and post cured at 100 °C in the oven for 10 minutes.

4.3 Electroless plating of copper over previously coated fabrics

Based on previous experiments, the surface activation of fabric was carried out using 10 g/L of copper sulphate for deposition of copper particles and 17 g/L of silver nitrate for deposition of silver particles. Then, the copper and silver particles coated fabric samples were immersed in the electroless copper plating bath at room temperature for different intervals of

time. The bath composed of 30 g/L $CuSO_4$-$5H_2O$, 20 g/L glyoxylic acid as reducing agent (50% aqueous solution), EDTA as complexing agent and 12 g/L sodium hydroxide. The concentration of EDTA was adjusted according to the concentration of copper sulphate in the ratio of 1:1 to avoid the formation of complexes with substrate metal (Ag or Cu). After plating the fabric was cleaned with deionized water and dried in oven at 85°C.

4.4 Plating of silver over stretchable fabrics for the development of TrNG

Cotton-Nylon–spandex (80:15:5) stretch fabrics were used as a substrate to produce the conductive fabrics. The conductive fabrics were made by the deposition of copper nanoparticles followed by silver electroplating. At first, the fabrics were treated with 15 wt % aqueous NaOH solution at room temperature for 10 min and rinsed with distilled water. Then 10 g/L of copper sulphate was prepared by dissolution in distilled water, blue colour was appeared. The alkali treated fabric was dip and dry several times in solution at 60°C, with a time interval of 30 minutes. The treated fabric was then transferred to the 30 g/L sodium hydrosulphite solution. The reduction was continued for the duration of 20 minutes. It is necessary, fabric should be conductive and act as a catalyst to locate conductive material on it. The purpose of silver electroplating was to produce compact layer of metal on substrate. Copper nanoparticles covered fabric was used as a substrate. To perform the electroplating, 5 gram of Silver nitrate ($AgNO_3$) was dissolved in 1 liter of distilled water. Electrolytic power source was rated at 10V/1Amp. A constant current was maintained throughout the complete electroplating. Anode was connected with silver rod acting as source of silver metal while cathode was connected with conductive fabric (Cu-NPs coated) to deposit the silver metal. It was made sure that solution continuously circulate the electroplating bath. For fabrication of triboelectric generator, the rabbit fur and silicon rubber were employed as two triboelectric layers due to their high stretch ability, softness and different electron affinities. Rabbit fur is positive dielectric while the silicon rubber is negative dielectric. The developed TrEG was designed to generate the energy under both stretching and pressing modes.

4.5 Surface morphology testing

Scanning electron microscope (SEM) was used to observe the surface structure of coatings. An accelerated voltage of 10 kV was applied by Tescan VEGA III TS5130 SEM apparatus. EDX analysis was performed to measure the elemental percentage by weight. XRD analysis was performed with a diffractometer equipped with a conventional X-ray tube Cu Ka1 radiation (5 1.5406 A˚) power condition (40 kV/30 mA). The XRD pattern was measured in the 2θ range 10–80° with the step size of 0.02°.

4.6 Electrical conductivity testing

Electrical resistivity was measured for all the conductive fabric samples. For that purpose, ASTM D257-07 concentric electrode method was applied. The constant pressure of 2.3 kPa was maintained at 20°C with the relative humidity RH=55±5%. The apparatus was consisting of two circular electrodes. The final measurement was considered after taking the average of three measurements. The DC power source was used to apply the constant 100 V. The voltage potential followed by change in current with resistance was measured. Following equation was applied to measure the resistivity ρs [Ω].

$$\rho_s = R_s \left(\frac{\pi D_0}{g}\right) \quad (1)$$

Where R_S [Ω] is the resistance reading, D_0 is $(D_2 - D_1)/2$, D_1 is the outer diameter of the center electrode [mm], D_2 is the inner diameter of the outer ring electrode [mm], g is the distance between D_1 and D_2 [mm].

4.7 Electromagnetic shielding testing

It was measured by coaxial transmission line method using insertion loss principle according to standard ASTM D4935-10 over frequency range of 30 MHz to 1.5 GHz. The measurement set-up consisted of a sample holder with its input and output connected to the network analyzer. A shielding effectiveness test fixture (Electro-Metrics, Inc., model EM-2107A) was used to hold the sample. The network analyzer (Rohde & Schwarz ZN3) was used to generate and receive the electromagnetic signals. The ratio between transmitted to incident power of the electromagnetic waves was calculated to express the effectiveness of EMI shielding (*SE*) in dB as depicted in Equation 2.

$$SE\ (dB) = 10\ log \frac{P_t}{P_i} \quad (2)$$

Where, P_t and P_i is power density (W/m^2) measured in presence of sample (transmitted), and without the sample (incident) respectively.

4.8 Antibacterial testing

The zone of inhibition test (AATCC 147) was conducted to confirm the antibacterial property of metal coated fabrics [35]. The zone of inhibition is a clear area of interrupted growth underneath and along sides of the test material and indicates the bioactivity of specimen. It is a qualitative test for the bacteriostatic activity by the diffusion of antibacterial agent through agar. The bacterial strains of Gram-negative Escherichia coli (CCM 3954) and Gram-positive Staphylococcus aureus (CCM 3953) used in this study were obtained from the Czech Collection of Microorganisms, Masaryk University Brno, Czech Republic. Bacterial suspensions were always prepared fresh by growing a single colony overnight at 37 °C in a nutrient broth. All agar plates were freshly prepared before the antibacterial tests.

4.9 Durability testing

The washing durability of metal coated fabrics was studied to have an idea of their activity in service. It was examined according to ISO 105-C01 by vigorously stirring the metal coated fabrics in 5 g/L standard detergent with the liquor ratio of 50:1. Sample was rinsed at 40 °C with stirring speed of 800 rpm for 30 minutes. After washing, all samples were dried and conditioned in a standard atmosphere (65 % humidity; 25 °C) for 24 hours before testing. Later, the performance was verified based on measurement of electrical conductivity and SEM observation of metal particles on the fabric surface.

5. Summary of the results achieved

5.1 Deposition of copper particles on textiles

5.1.1 Electrical conductivity

The effect of copper sulfate concentration and number of dips was investigated for electrical resistivity of copper-coated plain-woven textiles. The development of electrical conductivity was verified by flow of electric current. It is clear from Figure 1 that the higher concentration of copper sulfate solution resulted in higher electrical resistivity of coated fabric samples. This behavior can be attributed to the formation of big sized copper particles at higher concentration of copper sulfate solution. Surprisingly, lower concentration 10 g/L of copper sulfate produced more conductive fabrics due to formation of percolated network by creation of continuous connectivity between the small sized copper particles. This can be further justified from SEM images shown in Figure 2 (a, b), where formation of more percolated network of smaller particles can be found in case of 10 g/L than 20 g/L copper sulfate concentration. Therefore, the action of agitation or ultrasonication for disrupting the nucleation of copper particles is good topic for further research in order to obtain more percolated network at higher copper sulfate concentration. Furthermore, the electrical resistivity was found to reduce with increase in number of dips for all concentrations of copper sulfate solution. This

indicated more dense and uniform deposits of copper particles at higher number of dips. This can be further justified from SEM images shown in Figure 3. As lower concentration of copper sulfate provided acceptable results for electrical conductivity, so in further sections, detailed discussion is made on samples coated with 10 g/L of copper sulfate.

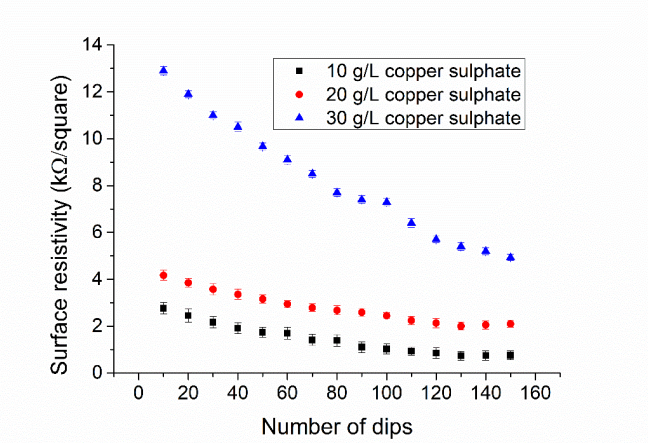
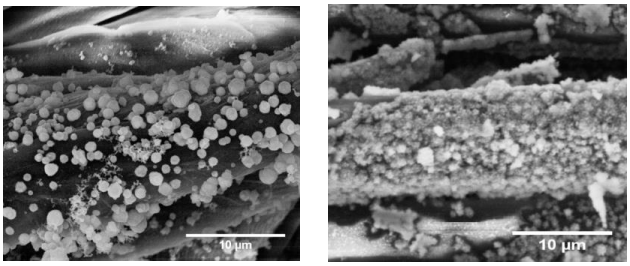


Figure 1: Effect of copper sulphate concentration and dipping on electrical resistivity.



(a) 20 g/L *(b) 10 g/L*

Figure 2: SEM image of copper coated fabrics for different copper sulfate concentration.

5.1.2 SEM analysis

The scanning electron microscopy was employed to observe the deposition of copper on fabric surface. The SEM micrographs with inset images at a higher magnification shown in Figure 3 revealed the nano/micrometer scale of copper particles deposited on fabric surface. With increase in number of dips, the deposition of copper was found more uniform and denser. This further indicated the higher tendency of formation of percolated network of copper particles when number of dips increased. Table 1 shows the elemental composition of copper coated fabrics determined by EDX analysis. It clearly showed the increase in contents of copper with higher number of dips.

Table 1: Elemental composition of copper coated cotton fabrics of 10 g/L copper sulfate.

Wt. %	C	O	Si	Ca	Cu	Total
50 dips	53.06	38.83	2.33	0.94	4.84	100.00
100 dips	52.48	38.24	2.58	1.25	5.45	100.00
150 dips	52.84	37.63	2.63	0.83	6.08	100.00

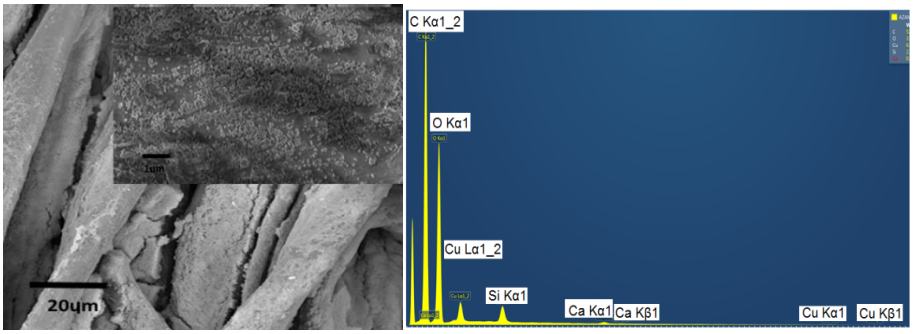


Figure 3: SEM image with EDX spectra for copper coated cotton fabrics at 150 dips.

5.1.3 XRD analysis

The XRD analysis was carried out to know the phase composition of deposited copper particles. The XRD spectra of the cotton fibers dipped and dried in the copper solution prior to reduction treatment are not given because it will only show the peaks of cotton due to absence of crystal structure of copper. The XRD analysis was performed on copper coated cotton fibers after reduction step. Figure 4 shows the XRD patterns of samples for the 2θ range of 10 to 80 degrees with a step of 0.02 degree. The phase purity of the prepared copper particles can be clearly seen from perfect indexing of all the diffraction peaks to the copper structure. The diffraction peaks appeared at 2θ of 43.3 º, 50.5 º, and 74.2 º represented (1 1 1), (2 0 0) and (2 2 0) planes of copper, respectively [3]. The crystalline nature of copper particles was confirmed from the sharp peak, whereas the broadening of the peaks indicated the formation of nanoscale copper particles [36].

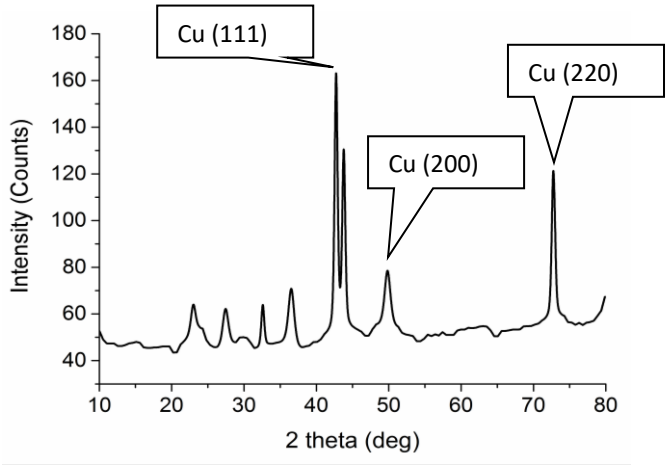


Figure 4: XRD patterns for copper coated cotton fabrics.

5.1.4 Mechanism

The mechanism of attachment of copper on cotton fabric surface can be explained from the schematic diagram shown in Figure 5. The dissolution of $CuSO_4$ in water resulted into Cu^{+2} and SO_4^{-2} ions. Subsequently, copper (II) ions adsorbed on the surface of cotton fibers based on heterogeneity (voids or pores) of the cellulose phases in the fabric [37].

Due to enrichment of anionic cotton substrate, further uptake of copper ions continued. This resulted in formation of ionic bond between the copper (II) and negative groups available on cotton surface. In similar way, sodium hydrosulphite $Na_2S_2O_4$ dissolved in water to give reducing agent dithionite ion ($S_2O_4^{2-}$). Later, when cotton fabric was dipped in aqueous $Na_2S_2O_4$ solution, the redox reaction occurred between oxidizing Cu^{+2} ions and reducing $S_2O_4^{-2}$ ions. This ultimately reduced Cu^{2+} to Cu^{+}, and possibly to copper metal. Moreover, the presence of few sulphur ions produced insoluble and conductive copper sulphide layer [38].

The sulphur was not detected in EDX analysis given in Table 1 because it was present in small quantity and a few spots. The color of cotton changed from white to blue after treatment with copper sulfate solution, and then from blue to dark brown after treatment with reducing agent sodium hydrosulfite.

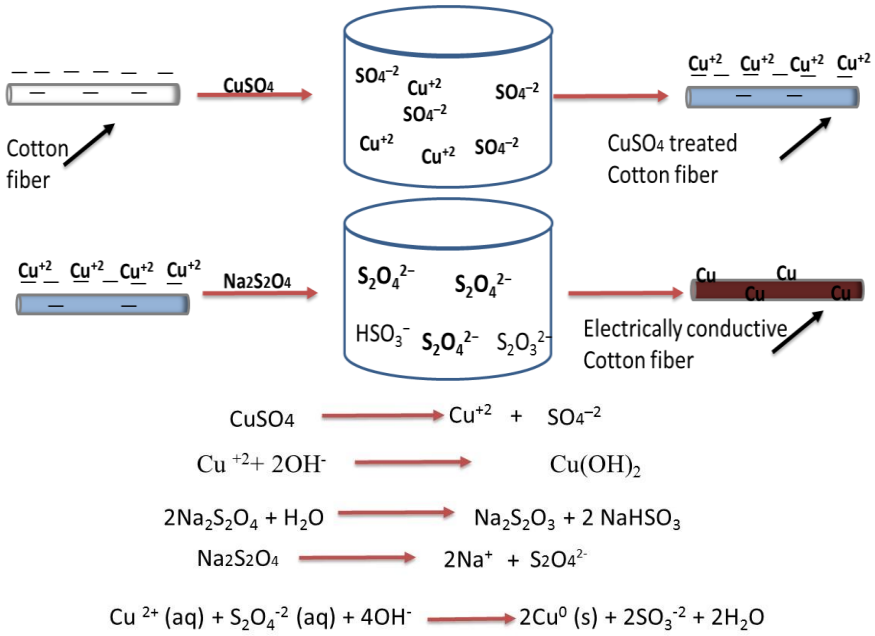


Figure 5: Mechanism of copper deposition on cotton fabrics.

5.1.5 Electromagnetic shielding of copper particles coated fabric

Figure 34 shows the results of shielding effectiveness for the cotton fabric samples coated from 10 g/L of copper sulphate solution after 50, 100 and 150 dips. The number of dips showed significant effect on shielding effectiveness. The samples showed increase in shielding effectiveness with more number of dips in copper sulphate solution. The sample produced from 50 dips revealed the lowest electromagnetic shielding effectiveness of about 6 dB in frequency range of 600 MHz–1.5 GHz. On the other hand, the sample produced from 100 and 150 dips exhibited the maximum shielding ability of 10 dB and 13 dB, respectively. This behavior was attributed to increased reflection of EM waves due to formation of dense, uniform and percolated network of conductive copper particles with higher number of dips [39]. This can be further explained by SEM images shown in Figure 6, where dense network of copper particles can be found for more number of dips.

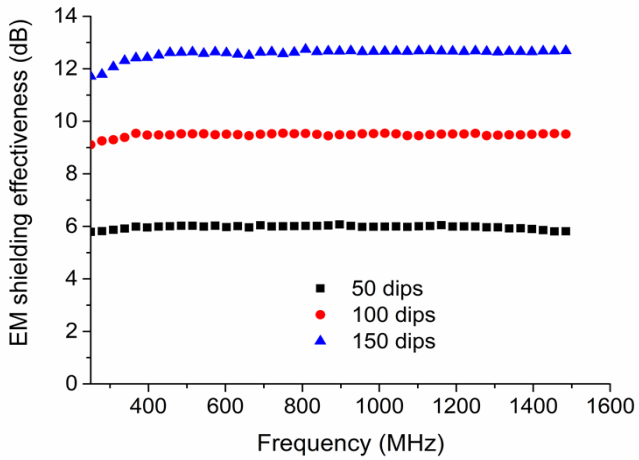


Figure 6: Shielding effectiveness of copper coated cotton fabrics.

5.1.6 Antibacterial properties

The anti-bacterial property is important because EMI shielding fabrics are excellent media for microorganism growth, particularly when used in hospitals or working environments with unhealthy indoor air quality [40]. The anti-bacterial properties are studied in this work to find suitable applications of coated fabrics as personal protective clothing in hospitals. The antibacterial activity of copper coated fabrics was tested against Gram-negative Escherichia coli and Gram-positive Staphylococcus aureus. The test was repeated three times and the average value of zone of inhibition presented in Figure 7. The virgin cotton fabric without copper coating showed no antibacterial activity. However, the zone of inhibitions was evidenced against both type of bacteria Staphylococcus aureus and Escherichia coli after the copper coating. Furthermore, Staphylococcus aureus depicted the highest sensitivity as compared to Escherichia coli. The zone of inhibitions for Staphylococcus aureus increased from 9.5 to 15.5 mm, while for Escherichia coli it increased from 7.5 to 12 mm with increasing number of dips as shown in Figure 8. The antibacterial property of coated fabrics can be attributed to the combination of chemical and physical interactions of bacteria with copper particles[123,124].

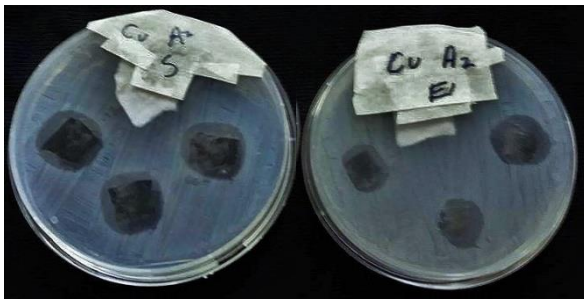


Figure 7: Zone of inhibition for copper coated cotton fabrics.

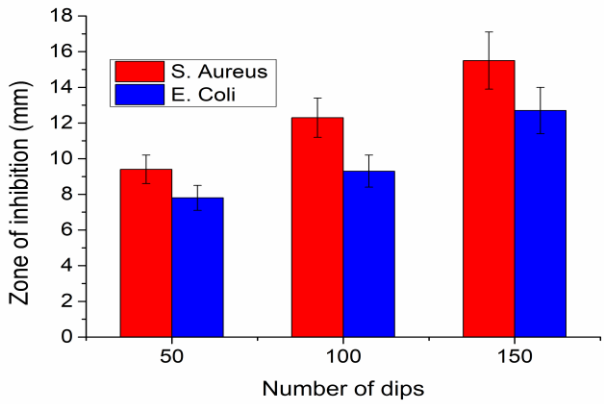


Figure 8: Values of inhibition zone against different number of dips.

5.1.7 Durability

When the intake of copper exceeds the range of biological tolerance, it can cause adverse effects, including hemolysis, gastrointestinal distress, liver and kidney damage in humans [43]. Therefore, the removal of copper particles and their durability was verified against washing. The electrical resistivity of samples was measured before and after washing as shown in Figure 9. There was no significant difference in change in conductivity of fabrics before and after washing. Therefore, similar EMI shielding properties can be expected for the fabrics after washing. Furthermore, no significant increase in the resistivity of the fabrics was found before and after washing. This indicated efficient working of firmly fix the copper particles on cotton fabric surface without deterioration of electrical conductivity. The SEM

images shown in Figure 10 also confirmed the presence of copper particles on fabric surface after washing. This indicated strong attachment of copper particles with fabric surface and therefore reduced toxicity in routine applications.

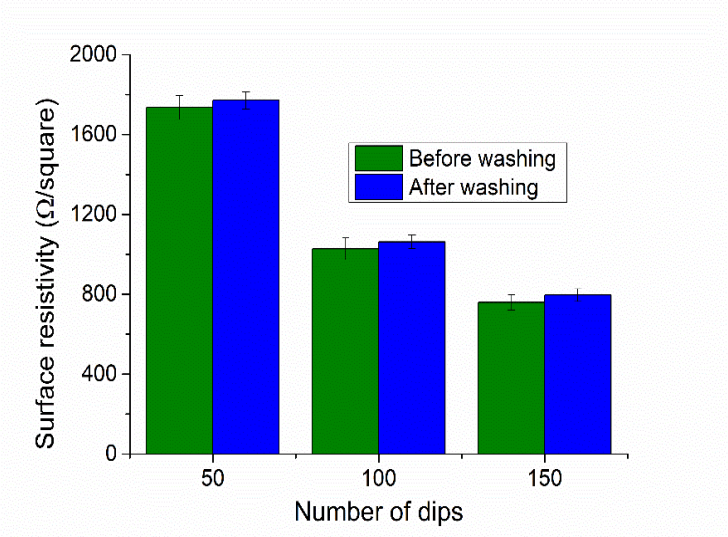
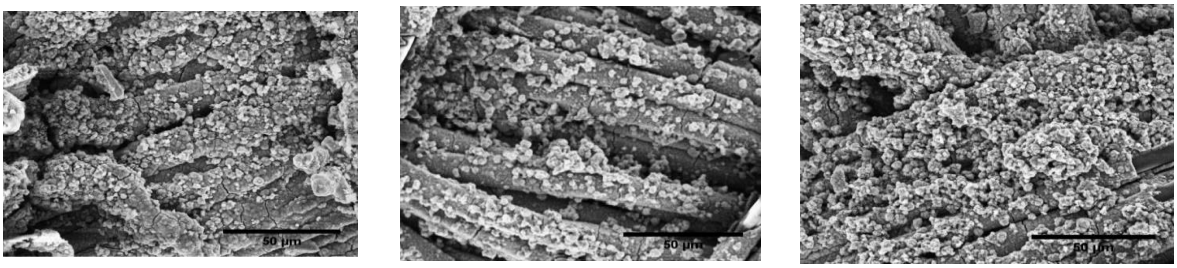


Figure 9: The electrical resistivity of samples before and after washing.



(a) 50 dips (b) 100 dips (c) 150 dips

Figure 10: SEM image of copper coated cotton fabrics after washing.

5.1.8 Oxidation of copper-coated fabrics

Copper coated textile was suitable because of low cost and electrical properties. The electrical properties of copper are almost near to silver. But the universal problem regarding oxidation make the use of copper limited in some area of applications. The copper particles especially in range from nano to micro are most susceptible to oxidation and gets greenish-black (it is not colour of CuO but mixture of carbonate and hydroxide). That is why developed copper particles coated conductive fabrics were put in standard atmosphere (65% RH, 20 ± 2 °C) for a number of days. It was observed that up to 50 days the electrical resistivity remains almost the same. After 50 days the process of oxidation become expedite and we observed the reduction in electrical conductivity over time as shown in Figure 11. So, the developed electrodes from these fabrics were not remain suitable for the use in transcutaneous electrical nerve stimulation (TENs) device. Therefore, further research was aimed at coating of silver particles. Moreover, electroless copper plating was performed to enhance the ageing properties of copper coated textile.

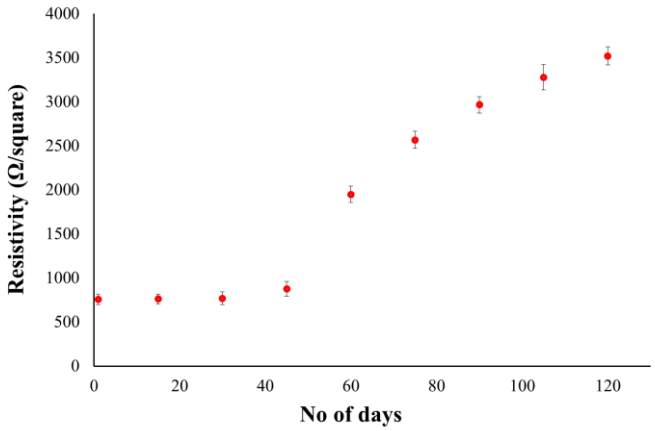


Figure 11: Reduction in electrical resistivity due to oxidation with the passage of days.

5.2 Deposition of silver particles on textiles

The results are composed up of two sections. At first, results are described for silver particles coated woven fabrics. Secondly, results for silver particles coated stretchable fabric electrodes.

5.2.1 Silver particles coated woven fabric

5.2.1.1 Electrical conductivity

The untreated cotton fabric is electrically insulating material. However, the silver coated cotton fabrics were supposed to be electrically conductive. The conductivity of the fabrics was expected to increase with increasing deposition of the nanoparticles. This hypothesis was confirmed by the electrical conductivity tests performed on the developed conductive fabric samples. It is clear from Figure 12 that the higher concentration of silver nitrate solution caused to increase electrical resistivity of coated fabric samples. This behaviour can be attributed to the formation of big sized silver particles at higher concentration of silver nitrate solution. The lower concentration (i.e. 17 g/L) of silver nitrate produced more conductive fabrics due to formation of percolated network by creation of continuous connectivity between the small sized silver particles. Furthermore, the electrical resistivity was found to reduce with increase in number of dips for all concentrations of silver nitrate solution. This indicated more dense and uniform deposits of silver particles at higher number of dips. This behavior can be further justified from SEM images shown in Figure 13. As lower concentration of silver nitrate provided acceptable results for electrical conductivity, so in further sections, detailed discussion is made on samples coated with 17 g/L of silver nitrate.

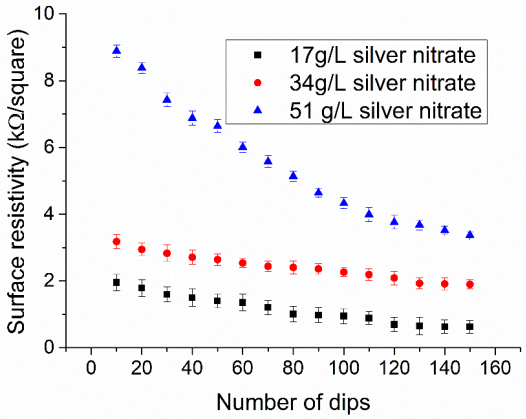


Figure 12: Effect of silver nitrate concentration and dipping on electrical resistivity.

5.2.1.2 SEM analysis of silver particles coated textile

The scanning electron microscopy was employed to observe the deposition of silver particles on fabric surface. The SEM images shown in Figure 13 depict the nanometer scale of silver particles deposited on fabric surface. With increase in number of dips, the deposition of silver was found more uniform and denser. This further indicated the higher tendency of formation of percolated network of silver particles when number of dips increased. The elemental compositions of silver coated fabrics determined by EDX analysis are shown in Table 2. It clearly showed the increase in contents of silver with higher number of dips.

Table 2: Elemental composition of silver coated cotton fabrics of 17 g/L silver nitrate.

Wt. %	C	K	Cl	Ag	Total
50 dips	61.01	36.60	-	2.39	100.00
100 dips	51.46	43.07	0.28	5.19	100.00
150 dips	51.74	37.59	-	10.67	100.00

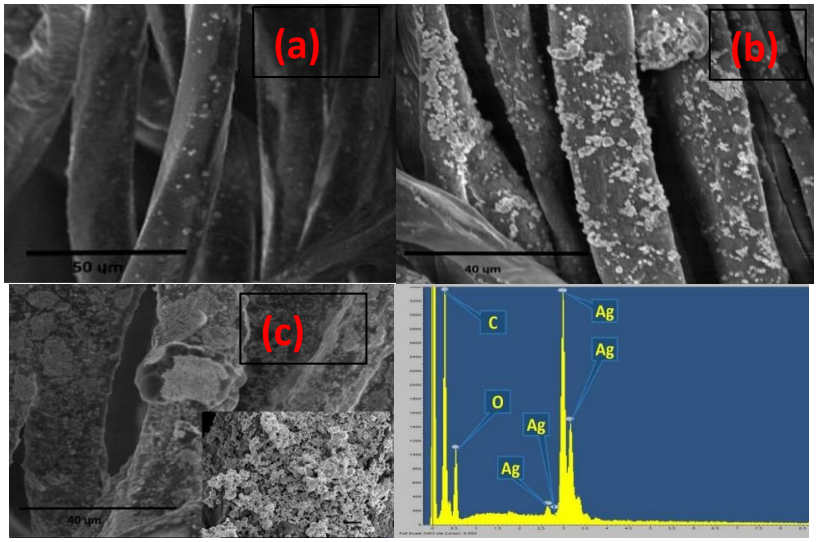
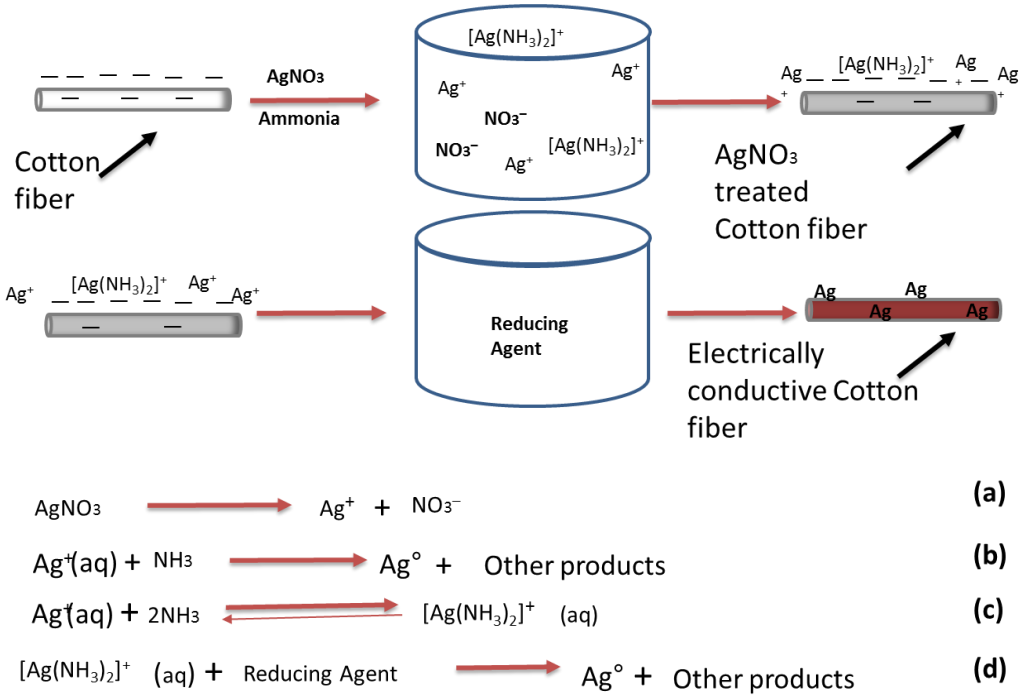


Figure 13: SEM image with EDS spectra for silver coated fabric (a) 50 (b) 100 (c) 150 dips.

5.2.1.3 Mechanism

The mechanism of attachment of silver on cotton fabric surface can be explained from the schematic diagram shown in Figure 14. The dissolution of $AgNO_3$ in water resulted into Ag^+ and NO_3^- ions (see 14 (a). Subsequently, the cotton fibers absorbed the silver ions to some extent based on heterogeneity of the cellulose phases in the fabric [37]. Ammonia also forms the complex ion $[Ag(NH_3)_2]^+$ with Ag+ through the equilibrium reaction (see 14 (c)) and this ion could also act as the oxidizing agent to form Ag°(see 14 (d)). Due to enrichment of anionic cotton substrate, further uptake of silver ions and complex ion $[Ag(NH_3)_2]^+$ resulted in formation of a strong ionic bond between the Ag^+ and negative groups available on cotton surface. In similar way, the reducing agents could be any organic substance which further reduces the silver ions and complex ion $[Ag(NH_3)_2]^+$ into Ag° means possibly to silver metal (see 14 (d)). Each reaction is governed by its rate constant. It is further assumed that Ag° atoms are produced first and then they combine to form nanoparticles [44].



$AgNO_3 \rightarrow Ag^+ + NO_3^-$ **(a)**

$Ag^+(aq) + NH_3 \rightarrow Ag^\circ +$ Other products **(b)**

$Ag^+(aq) + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ (aq)$ **(c)**

$[Ag(NH_3)_2]^+ (aq) +$ Reducing Agent $\rightarrow Ag^\circ +$ Other products **(d)**

Figure 14: Mechanism of silver particle deposition on cotton fabrics.

5.2.1.4 Electromagnetic shielding

Figure 43 shows the results of shielding effectiveness for the fabric samples coated with 17 g/L solution of silver nitrate after 50, 100 and 150 dips. The electromagnetic shielding effectiveness was found to increase with increase in number of dips. This behaviour was attributed to higher electrical conductivity behaviour of samples prepared from more number of dips due to uniform and dense packing of silver particles on the fabric surface. This can be further explained by SEM images shown in Figure 15, where dense network of silver particles can be found for more number of dips.

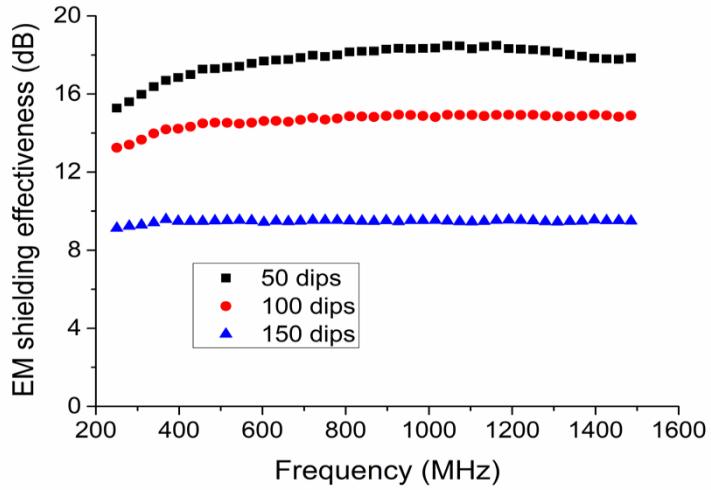


Figure 15: EMI shielding effectiveness of silver coated cotton fabrics.

5.2.1.5 Antimicrobial properties

The antimicrobial activity of silver coated fabrics was tested against gram-negative *E.coli* and Gram-positive *S. aureus*. Figure 16 shows the zones of inhibition around fabric samples after 24 h of incubation in dark at 37 °C. The untreated fabric samples without silver

coating showed no antimicrobial activity, however, the zone of inhibitions was evidenced against both type of bacteria *S. aureus* and *E. coli* after the silver coating.

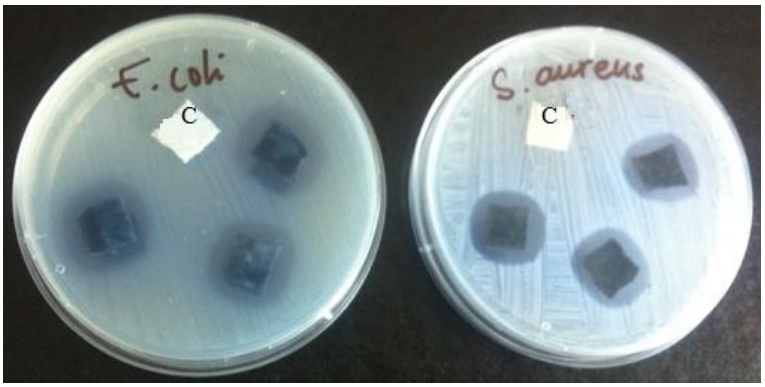


Figure 16: Antimicrobial property of silver coated cotton fabrics.

5.2.1.6 Durability

The durability of conductive fabrics under washing has been a critical challenge. To investigate these properties (fabric samples coated from 17 g/L solution of silver nitrate after 50, 100 and 150 dips) were selected. These three samples were selected because they provided satisfactory results regarding electrical conductivity. The electrical resistivity of samples was measured before and after washing as shown in Figure 17. It is evident that there is only a slight change in the resistivity of these samples after washing. It means nanoparticles are attached firmly on the surface of fabrics without losing any conductivity. This was also verified by the SEM picture (Figure 18), which showed the presence of silver particles on fibre surface after washing.

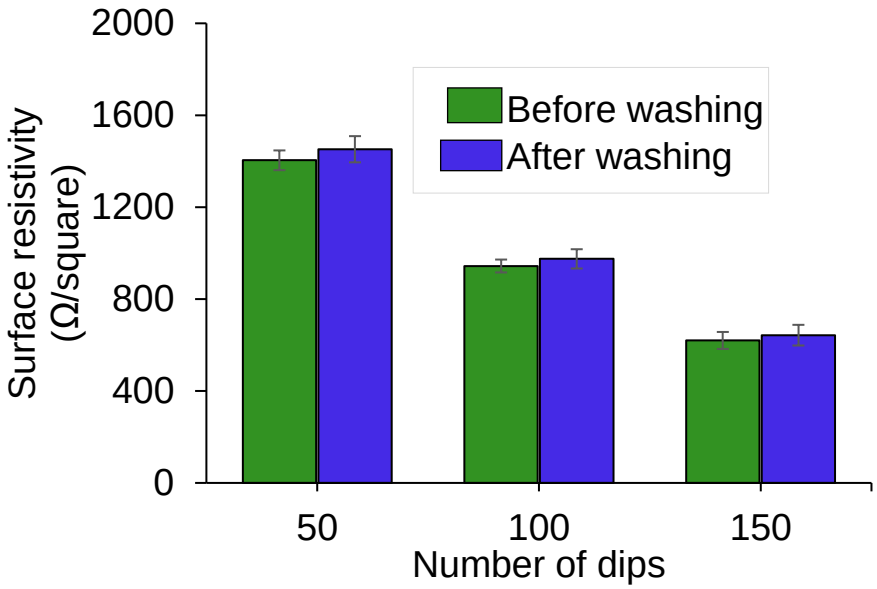


Figure 17: Electrical resistivity before and after washing.

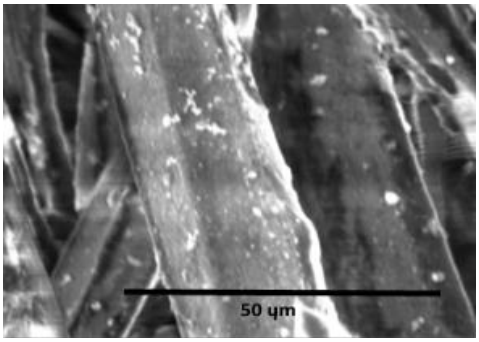


Figure 18: SEM image of silver coated cotton fabric after washing.

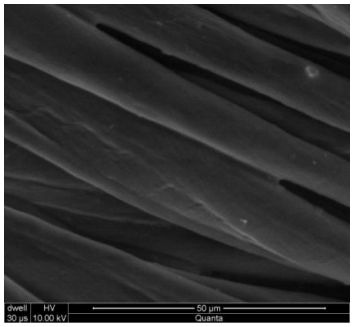
5.2.2 Silver particles coated knitted fabric

5.2.2.1 SEM analysis

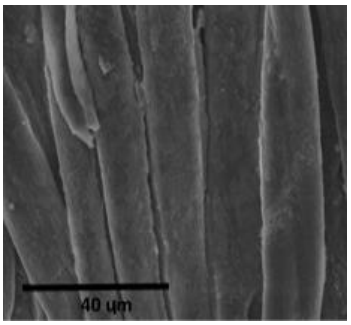
It can be seen from Figure 19 that the deposited silver particles on knitted fabrics are in nanometer scale. The coating of silver particles was found to become more uniform and dense with decrease in the concentration of $AgNO_3$. The silver particles covered maximum surface area at 42.5g/L $AgNO_3$ concentration compared to 85 g/L or 170 g/L of concentrations. This further indicated the higher tendency of formation of percolated network of silver particles as $AgNO_3$ concentration decreased. The elemental composition for silver coated fabrics is shown in Table 3. The increase in contents of silver can be observed at lower concentration of $AgNO_3$. The thickness of fabric was increased to 0.93 mm from 0.85 mm after the deposition of silver particles.

Table 3: Elemental composition of silver coated knitted fabrics.

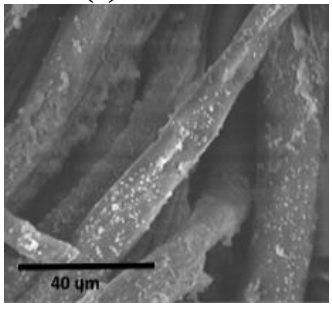
Silver nitrate concentration (g/L)	**Weight (%)**		
	C	**O**	**Ag**
170	61.01	36.59	2.4
85	51.65	36.59	11.76
42.5	42.06	42.88	15.06



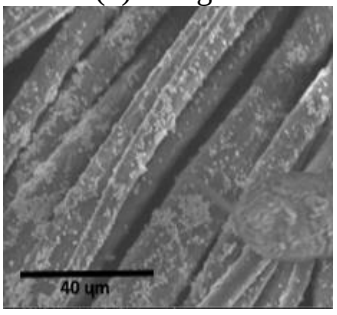
(a) Uncoated



(b) 170 g/L



(c) 85 g/L



(d) 42.5 g/L

Figure 19: SEM images of silver coated fabrics at different silver nitrate concentrations.

5.2.2.2 XRD analysis

It was carried out to know the phase composition of deposited silver particles. Figure 20 shows the XRD patterns of samples for the 2θ range of 20 to 80 degrees with a step of 0.02 degree. The phase purity of the prepared silver particles can be clearly seen from perfect indexing of all the diffraction peaks to the silver structure. Compared to the untreated cotton fabric, four new peaks at 2θ values of 38.1, 44.3, 64.5 and 77.5 were detected for silver coated fabrics, which were respectively attributed to the diffraction peaks of the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of silver with cubic structure reported in the International Center for Diffraction Data (JCPDS data number 04-0783 card) [45]. Furthermore, no characteristic peaks were observed for other impurities such as AgO.

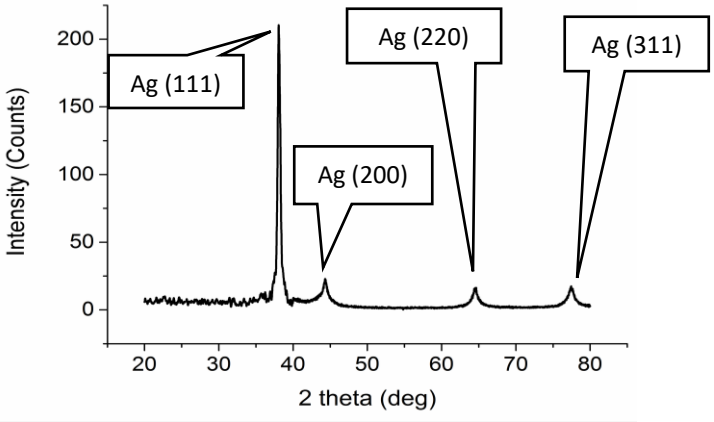


Figure 20: XRD patterns for silver coated fabric.

5.2.2.3 Electrical conductivity

The electrical resistance is related to the electrically conductive channels paths. More electrically conductive channels (particles, fillers, conductive fibres etc.) mean lower electrical resistance [46]. In present work, the effect of different concentrations of silver nitrate on electrical conductivity of coated fabrics was studied. From Figure 49, the resistivity was found to increase with increase in the concentration of silver nitrate. This behaviour can further be justified from regression analysis (i.e., equation of line) between two parameters. The relationship between concentration of silver nitrate and volume resistivity is positive, as explained by the equation of line and higher R^2 (0.988) value. The fabrics exhibited higher electrically conductivity at lower silver nitrate concentration due to uniform and dense deposition of silver particles which enabled the formation of more conductive paths. Furthermore, the formation of percolated network at 42.5 g/L silver nitrate concentration was in agreement with previous discussion on Figure 47 of SEM microstructures of coated fabrics. The development of electrical conductivity was later verified by flow of electric current as shown in Figure 22. The straight line in Figure 21 is regression line obtained by minimizing of standard least squares criterion (sum of squared deviation of points from regression line). All parameters (slope and intercept) were statistically significant.

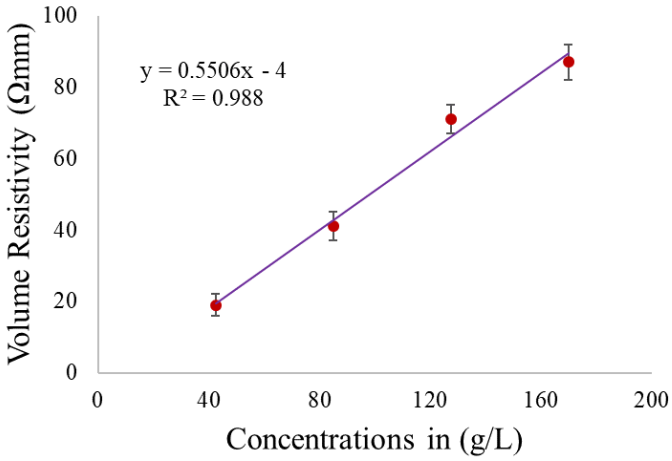


Figure 21: Effect of silver nitrate concentration on volume resistivity.

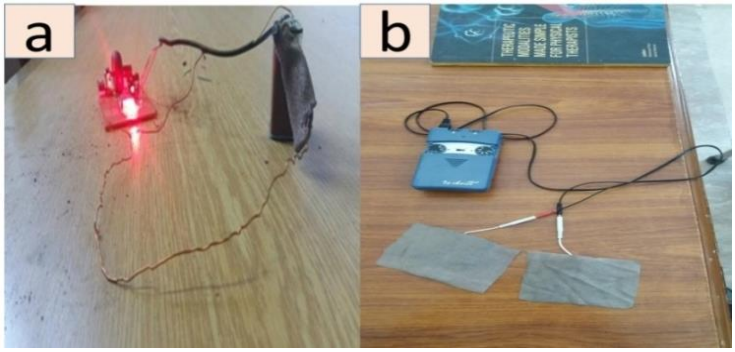


Figure 22: Flow of electricity in (a) silver coated fabrics (b) fabric electrodes with TENS.

In order to simulate the performance of electrodes under various movements of human body, the conductive fabrics made from 42.5 g/L silver nitrate were subjected to various extensions and change in resistivity was examined. Figure 23 shows the electrical volume resistivity of silver coated fabrics as a function of different extensions ranging from 0 to 100 %. At 0% stretch (i.e., when the fabric was unstretched), the volume resistivity was 19 Ω mm. The volume resistivity was found to gradually increase with increase in extension, reaching 164 Ω mm at 70% stretch and 478 Ω mm at 80% stretch. The change in volume resistivity was so small that it was considered a constant value in the stretch range of 0–80%. Nevertheless, the volume resistivity was found to increase sharply beyond the 80% extension, where it reached to 2167 Ω mm at 90% stretch and then to 4340 Ω mm at 100% stretch. This behavior can be attributed to the rupture of conductive network due to increasing of mean interparticle distance at higher extensions. This behavior of stretching can further elaborate by a recent study, researchers developed a stretchable electrically conductive fabric by coating of silver nanowires on cellulosic fabric. Initial electrical resistivity of fabric was around 0.0047 Ω. The resistivity was also measured as a function of stretching where maximum resistivity was measured about 0.0274 Ω at 200% stretching and then sharply to the highest value of 112.1649 Ω at 210% [7]. In another similar study, nylon/ spandex (95/5) electrically conductive knitted fabrics were used as a electrodes for TENs device. The fabrics were firstly coated with, poly-pyrrole, then for surface catalyzation, fabrics were dipped into a catalyzation solution containing $SnCl_2$, $PdCl_2$ and HCl. After that, furthermore plating was performed. It was noticed that there was insignificant decrease in electrical conductivity even up to 80|% stretch. However, due to low electrical conductivity the developed electrodes were not efficient for TENs device as compared to conventional electrodes [47].

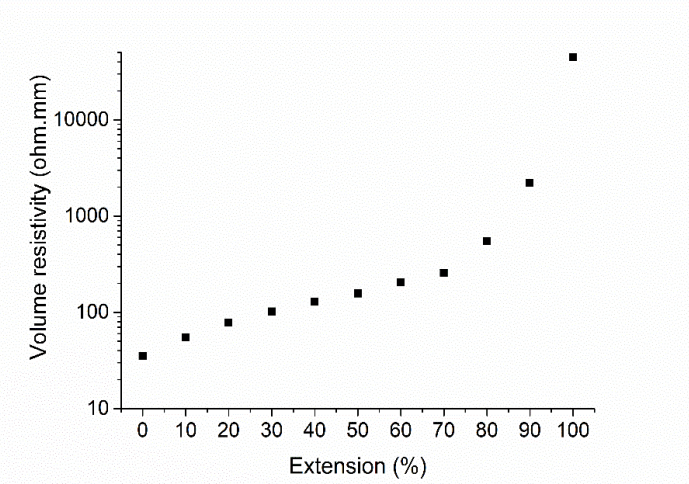


Figure 23: Effect of extensions on volume resistivity of silver coated knitted fabric.

From previous discussions, the electrical resistivity of coated fabrics was found to change with increase of extensions. Therefore, further investigation on multiple usages of developed textile electrodes was studied under repeated stretching and relaxing tests. Figure 24 showed the effect of repeated 50% and 100% extensions on change in volume resistivity of coated fabrics. For 50% extension, the volume resistivity of coated fabrics did not change significantly under different cycles of stretching. However, at 100 % extension, the coated fabrics showed significant change in volume resistivity with increase of stretching cycles. This behavior can be attributed to the damage of percolated networks of silver particles due to formation of cracks under repeated excessive extension.

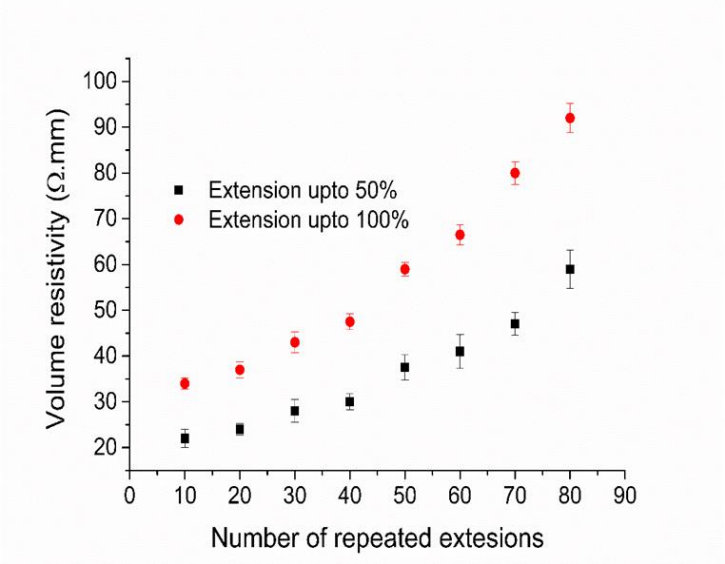


Figure 24: Change in resistivity with number of repeated extensions.

For electrotherapy applications over prolonged duration, the change in volume resistivity of coated fabrics was investigated with increase in time when constant current of 20 mA was applied. From Figure 25, it can be seen that the volume resistivity of coated fabrics remained unchanged with time over 13 min when the same current was applied. Therefore, consistent performance of developed electrodes can be expected for efficient electrotherapy operations over prolonged durations.

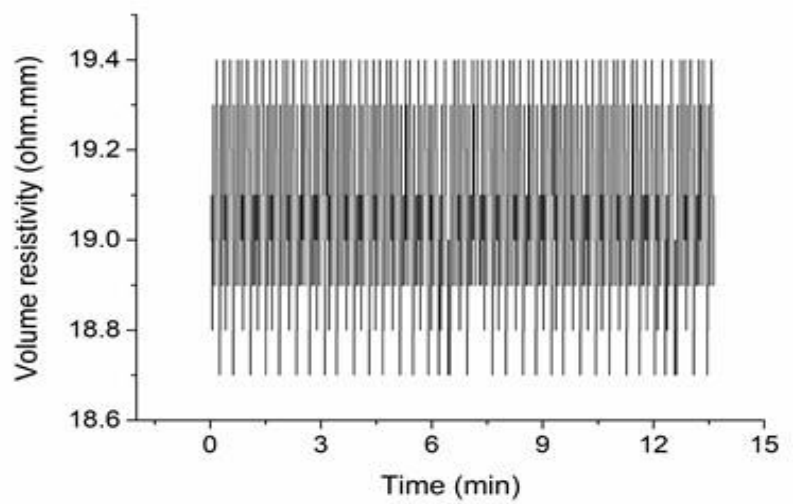


Figure 25: Change in resistivity over prolonged duration with constant current of 20 mA.

5.2.2.5 Antibacterial properties

The antibacterial activity of silver coated fabrics was tested against gram-negative *E.coli* and Gram-positive *S. aureus*. Figure 26 shows the zones of inhibition around fabric samples after 24 h of incubation in dark at 37 °C. It is clear that fabric sample without silver coating showed no antibacterial activity. However, the zone of inhibitions was evidenced against both type of bacteria Staphylococcus aureus and Escherichia coli after the silver coating. Further, Staphylococcus aureus depicted the highest sensitivity as compared to Escherichia coli. The zone of inhibitions for Staphylococcus aureus increased from 8.4 to 13.2 mm while for Escherichia coli it increased from 6.2 to 10.7 mm. The antibacterial property of coated fabrics can be attributed to the combination of chemical and physical interactions of bacteria with particles. The silver particles incorporated into the cell and leads to further massive oxidative stress for antibacterial performance. However, the low efficiency of the antibacterial property in present work was related to low oxidative stress of larger size silver particles as compared to silver particles of below 100 nm in literature.

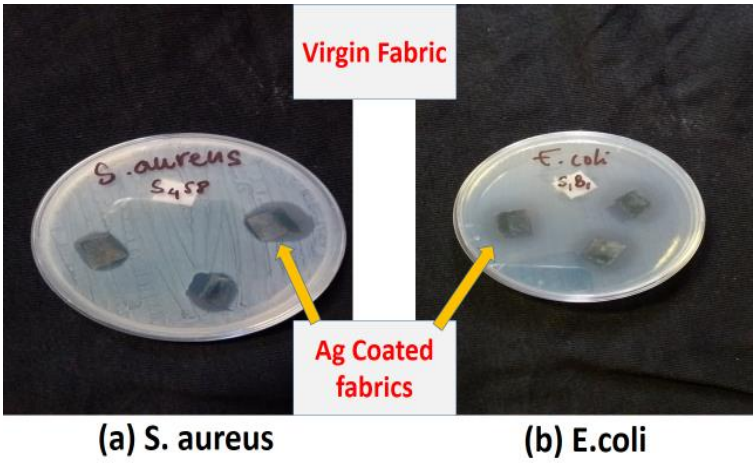


Figure 26: Antibacterial properties of silver coated fabrics.

5.2.2.6 Durability of silver particles coated knitted fabric

The silver particles were attached to fabrics through a combination of both physical and chemical interactions. Further, the additional silver particles filled the spaces between fibers and stacked together to form the electrically conductive networks. Therefore, the durability of coated fabrics was studied to determine the chances of silver particles removal from the surface. At first, an adhesion test was performed with transparent tape. However, no visible particles

were observed on the tape, which indicated strong bonding of silver particles with the fabric surface. In another test, the coated fabrics were washed according to method ISO 105-C01 standard and then change in electrical conductivity was measured (see Figure 27). From the results, the electrical resistivity of washed fabrics was found to increase in small percentage, which confirmed strong attachment of silver particles with fabric surface. Later, it was also verified from the SEM images shown in Figure 28, which depicted the presence of silver particles on fabric surface after the washing.

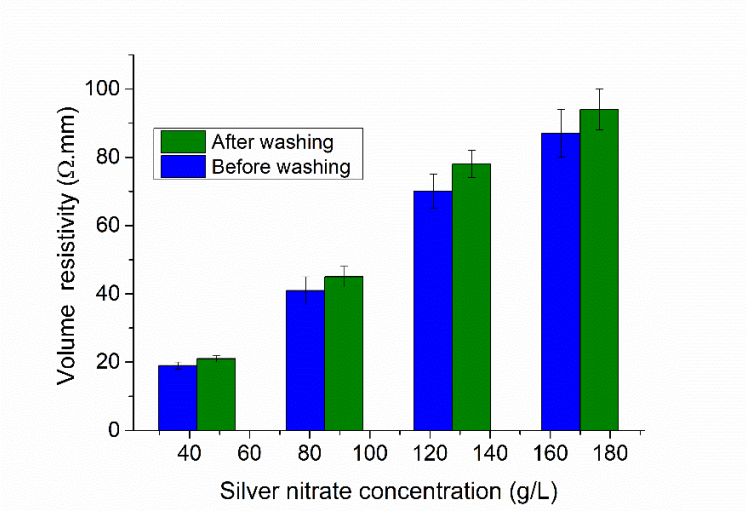


Figure 27: Electrical conductivity of silver coated fabrics before and after washing.

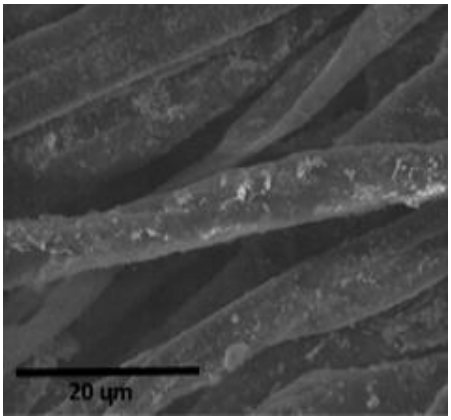


Figure 28: SEM image of silver coated fabric after washing.

5.3 Electroless plating of copper over previously coated fabrics

The results are composed up of two sections. At first results are described for the electroless plated fabrics woven fabrics. Secondly, the results of triboelectric generators made from plated knitted fabrics.

5.3.1 Electroless plated fabrics

Based on previous experiments discussed in part 1 and part 2, the surface activation of fabric was carried out using 10 g/L of copper sulphate for deposition of copper particles and 17 g/L of silver nitrate for deposition of silver particles. Then, the copper and silver particles coated fabric samples were immersed in the electroless copper plating bath at room temperature for different intervals of time

5.3.2 Electrical conductivity

The results of electrical resistivity before and after electroless plating are shown in Table 4. It is clear that there is significant decrease in electrical resistivity after electroless plating. Compared to values of electrical conductivity reported in part 1 and part 2, the higher values of electrical conductivity in this work were attributed to more dense deposition of metal particles during electroless plating. The previous layer of deposited copper or silver particles was uniformly penetrated across the thickness of fabric and it allowed even coating of deposition of metal during subsequent electroless plating.

Table 4: Electrical resistivity results before and after copper plating on woven fabrics.

Fabric samples	**Electrical resistivity (Ω/square)**	
	Before plating	**After plating**
Copper plating over copper particles coated woven fabric	759 ± 42	20 ± 2
Copper plating over silver particles coated woven fabric	620 ± 37	27 ± 1

5.3.4 EMI shielding

Before electroless plating, the EMI shielding values of copper and silver particles coated fabric were about 12.65 dB and 18 dB respectively (as reported in part 1 and part 2). After performing the electrolesss copper plating, the same fabrics showed higher values of EMI shielding. The EMI shielding for fabrics of copper plated over silver and copper plated over copper fabric was noticed about 75.53 dB and 66.41 dB, respectively. This behavior was attributed to their higher electrical conductivity values and therefore increased reflection of electromagnetic waves.

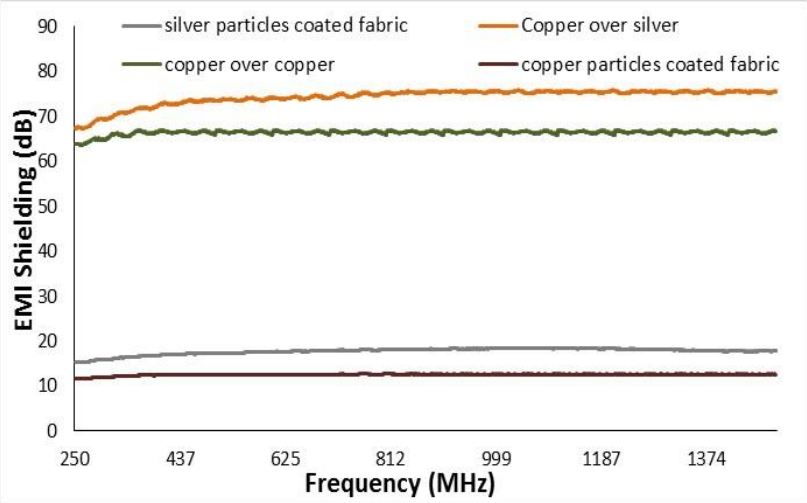


Figure 29: Electromagnetic shielding effectiveness of conductive fabrics.

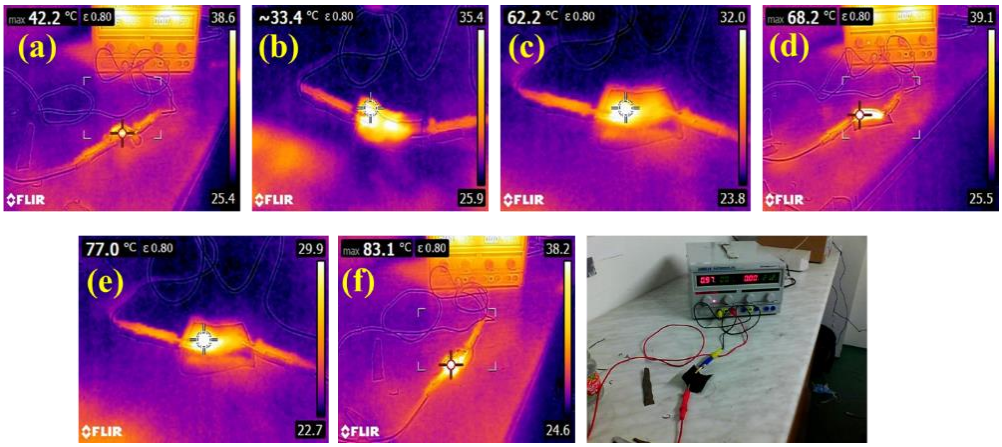
5.3.5 Heating performance

The heating performances of the Cu-NPs coated cotton fabric, Ag-NPs coated cotton fabric and electroless plated cotton fabric was investigated. Joule heating of conductive fabrics was measured by applying the voltage at the ends of fabric. The variation in surface temperature of fabrics were recorded (see Figure 29). Firstly, we applied fix voltage of 5 V with 0.9 to 1 A of current for 1 minute at the ends of eact fabric and recorded increase in temperature was studied.

The maximum temperature observed for Ag-NPs (17 g/L) coated fabric and Cu-NPs (10 g/L) coated fabric was about 42.2 °C and 33.4°C respectively (see Figure 29 (a), (b)). While the

temperature for copper plating over Ag-NPs coated fabric and copper plating over Cu-NPs coated fabric was recorded about 62.2°C and 68.2°C see Figure 30 (c), (d)). In second step the temperature was measured as a function of time up to 10 minutes with constant applied voltage of 5 V with 0.9 to 1 A of current. The maximum temperature (83 °C for copper plating over Ag-NPs coated fabric and 77°C for copper plating over Cu-NPs coated fabric) were obtained when the applied voltage was 5 V for 10 minutes, as shown in Figure 30 (e), (f)). The temperature on the fabric surface increased up to 83 °C and 77 °C within 1 min, then it slowly increased. In order to study the further stability of the surface heating of conductive fabric, the temperature was measured as a function of voltages with varying voltages from 5 to 10 V and current was maintained at 1 A. Hence the outcome (of different voltages DC input varied from 5–10 V and at constant current 1 A) was calculated in watt for plated fabric samples (copper plating over Ag-NPs coated fabric and copper plating over Cu-NPs coated fabric) and the steady state surface temperature was noted Figure 30 (g). The experiment was carried out up to 10 watt and the measured surface temperature was stable throughout the duration of the experiment with a homogenous temperature distribution of 119 °C and 112 °C for (copper plating over Ag-NPs coated fabric and copper plating over Cu-NPs coated fabric).

In a similar study cotton fabric were functionalized with carbon nanotubes (CNT), and completely loses the heating power of the conductive fabric after 220 s. While in the present study the stability of the conductive fabric is retained even after 60 min. In another study, Hamdani and co-workers tested the voltage effect on their functionalized conductive fabric made from silver coated polymeric yarn and reached a maximum surface temperature of 107 °C with 80 mm terminal separation and at 9 volt [48]. During the heating mechanism of conductive fabric system, the migration of charge carriers gets accelerated due to the applied electric potential. The heat is released once these charge carriers get collided in-elastically with phonons and defects present on the conductive materials. Since, the number of charge carriers get increased with increasing voltage, the surface temperature also starts increasing [49].



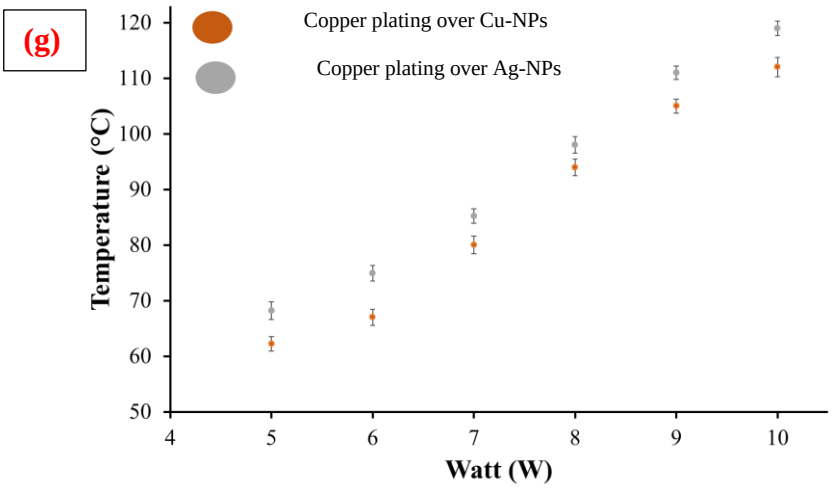


Figure 30: Surface temperature of copper plated fabrics samples: step one at 5 V and 1 min for (a) Cu-NPs coated fabric, (b) Ag-NPs coated fabric (c) electroless copper plating for Cu-NPs coated woven cotton fabric, (d) electroless plating for Ag-NPs coated woven.

5.3.6 Mechanism of electroless plating of copper

Figure 31 explain the mechanism of electroless plating of copper on cotton fabrics activated with deposition of silver and copper particles. The reactions during the electroless plating stage can be controlled by different parameters such as concentration of metal salt, concentration of reducing agent, concentration of complexing agent, temperature and pH [50].With increase in concentration of copper sulphate, the deposition rate of copper can be increased due to increased mass transfer of copper ions to the electrode surface and therefore accelerated rate of electron transfer. However, on further increase in concentration of Cu^{2+} ions, the deposition rate can reduce significantly due to poor stability of solution bath. This can be attributed to less effect of complexing agent, and therefore adverse reactions in solution followed by electrolyte decomposition. At very high concentration of metal salt, the copper plating may result in rough surface [51]. For selection of proper reducing agent, it should have high standard reduction potential as compared to the metals (copper and silver) being reduced. For instance, the reduction potentials of some important reducing agents like hypophosphite (-1.57V), formaldehyde (-1.30 V) can be useful as they are higher compared to the reduction potentials of copper +0.34V and silver +0.80V [31]. The another important property of reducing agent is self catalytic reaction ability which can help in deposition of maximum copper on target metal (fabric coated with copper particles) [32]. This is important to provide anodic oxidation to the substrate metal in order to avoid the replacement of copper particles by electroless plated copper. The reducing agent formaldehyde is well known to show anoidic oxidation, but the use of formaldehyde is banned due to its toxicity. Therefore, the reducing agent glyoxylic acid (OCHCOOH) was used in present work as a potential alternative to formaldehyde. When copper sulphate is dissolved in water, it results in acidic pH due to formation of H^{+} ions in solution.

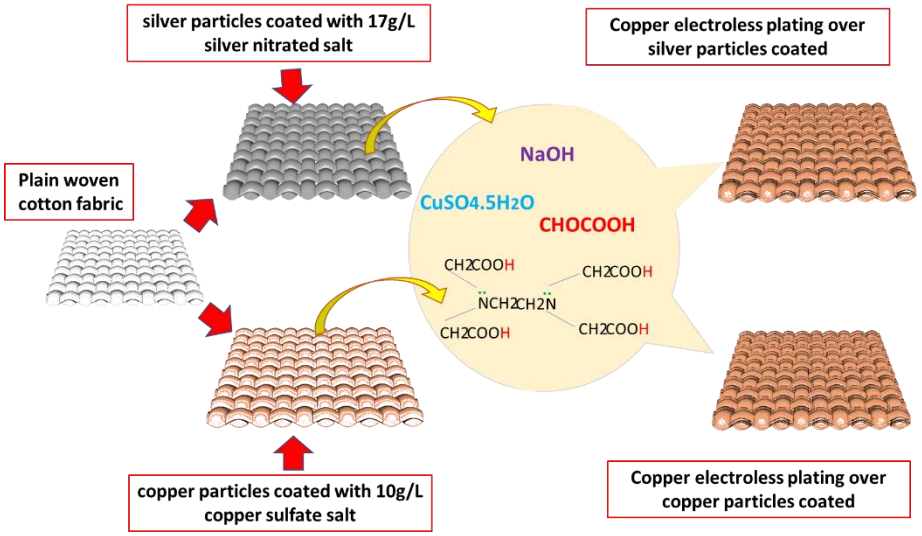


Figure 31: Schematic of copper electroless plating over silver and copper particle coated fabrics.

The complexing agent EDTA was used to maintain pH and to avoid the spontaneous reaction between reducing agent and metal salt by formation of complex on free coordination sites available on metal salt $(Cu(EDTA))^{-2}$. The possibility of forming copper hydride or copper hydroxide in solution is increased when complexing agent not used in bath [24]. The concentration of complexing agent is important as it decides the rate of reaction. The bath stability is achieved further with the help of complexing agent. If the concentration of EDTA is less than Cu ion concentration, $Cu(OH)_2$ precipitates in the bath even without the presence of a reducing agent. At higher amount of EDTA, there are higher chances of forming Cu_2O. The concentration of complexing agent should be decided in such a way, that there should be sufficient amount of free metal ions available for reduction purpose [110,111]. If a complexing agent provide low stability constant then it yield a large amount of metal ions as compared to the metal complex and therefore causes the rate of plating to be lower. The amount of complexig agent during equilibrium with free and complex ions in water can be seen from reaction given in Equation 3.

$$M^{+z} + mL^{n-1} \rightarrow M\ L^{z-mn} \tag{3}$$

The stability constant can be estimated from Equation (10).

$$Stability\ constant = \frac{[M\ L^{z-mn}]}{M^{+Z}+[mL^{n-1}]} \tag{4}$$

Where *M* metal ion, *m* is number of complexing agent or Ligand or coordination number, *L* is Ligand, L^{n-1} is complete complexing agent, *z-mn* is oxidation number.

During the deposition process either proton or hydroxyl ions are generated, which in turn changes the pH of solution. For instance, the reaction (5) reaction (6) show that oxidation of reducing agent can produce H^+ and therefore lower the pH [30]. The most suitable pH was found above 11. Furthermore, in a previous study it was observed that when EDTA and copper ions concentration were identical in solution, the $Cu(OH)_2$ still precipitated with increasing the OH^-. Therefore, the pH played important role in controlling the bath stability role during electroless plating [52]. When there are dust particles in electroless plating bath, it may result in spontaneous reduction reactions with the metal nuclei. The stabilizer can be added into the bath to prevent this problem. The stabilizer acts as an inhibitor by adsorbing on the nuclei and

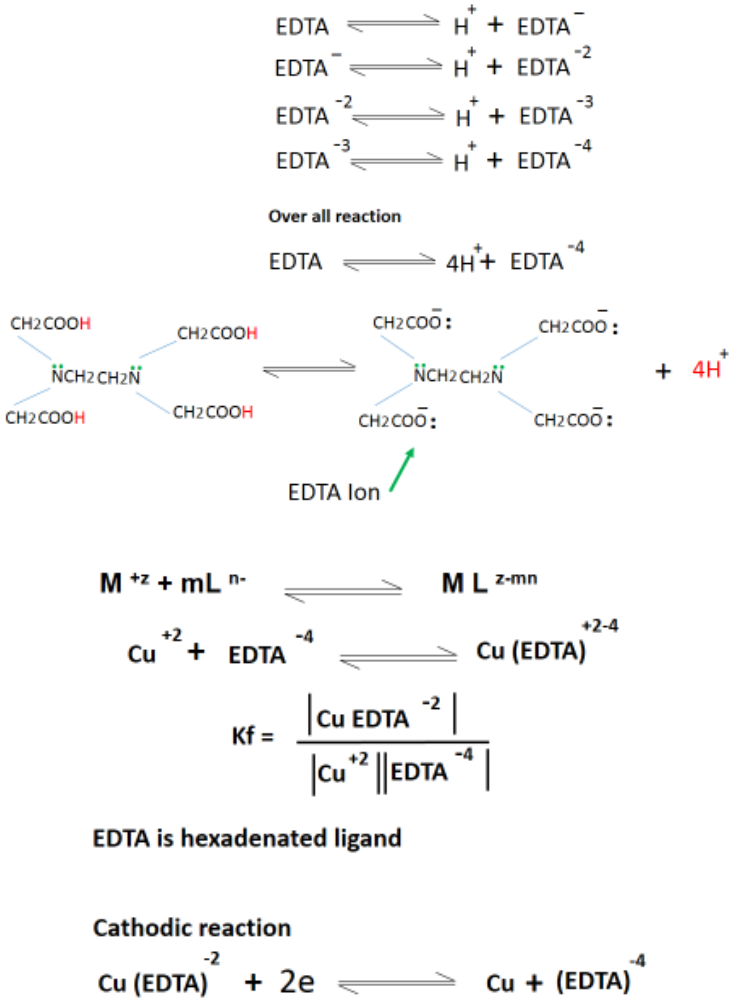
shields them from spontaneous reduction reactions in the solution. Therefore, 40 ppm of 2,2' bipyridyl was added to the Cu-EDTA solution to act as stabilizer [53].

The composition of electroless plating bath can not be decided easily as they can lead to a more complex electrochemical reaction pathway [54]. During the electroless plating system, the knowledge of mixed potential theory (cathodic and anodic half reactions) can be beneficial. Here, reducing agent oxidation is concerned to the anodic reactions (see reaction (5)) whereas metal reduction is concerned to the cathodic reactions (see reaction (6)). The choice of reducing agent is important as it provides the anodic oxidation. In a study Yu *et al* reported the anodic oxidation of glyoxylic acid on Cu [54].

Anodic reactions

$$2OCHCOOH + 4OH^- = 2HC_2O_4^- + 2H_2O + H_2 + 2e \quad (5)$$

Cathodic reaction



The oxidation of glyoxylic acid is important because it enhances the reduction of cupric-ion through intermediates. The theory of autocatalysis addressed that the reduction of cupric ions can refresh the electroless Cu surface, thus providing more catalytic sites which in turn can accelerate the glyoxylic acid oxidation [34] (see Figure 31 and reaction (8)).

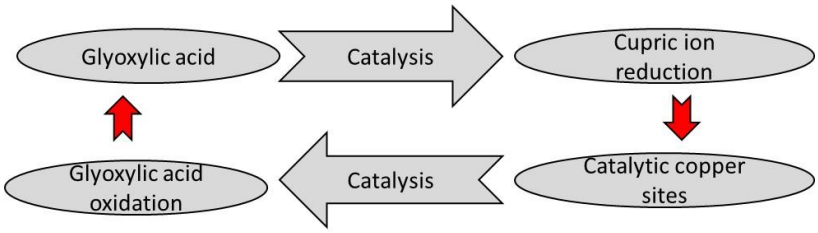


Figure 32: Autocatalysis mechanism involved during electroless plating of copper.

Overall reaction:

$$Cu(EDTA)^{-2} + 2CHOCOOH + 4OH^- = Cu + 2HC_2O_4^- + 2H_2O + H_2\uparrow + EDTA^{4-}$$

Some possible side reactions:

$$2Cu^{+2} + CHOCOOH + 5OH^- = Cu_2O\downarrow + HC_2O_4^- + 3H_2O \quad (8)$$

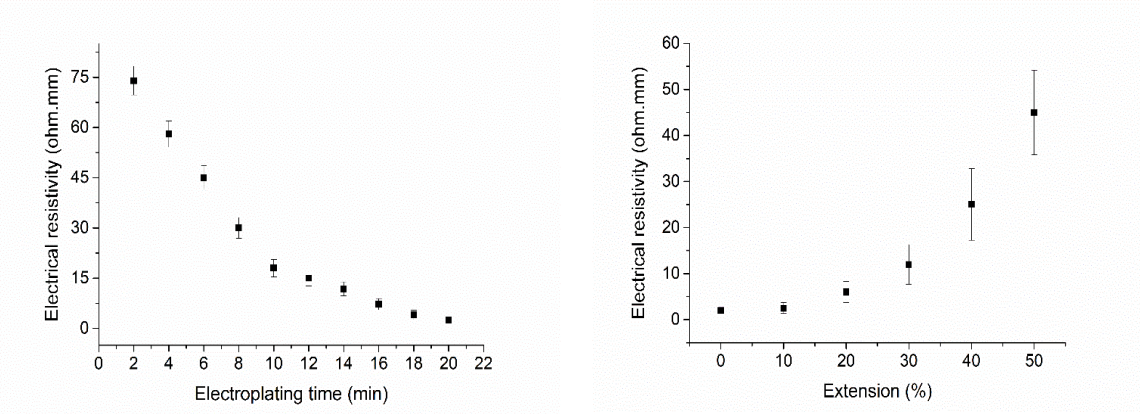
$$2CHOCOOH + 2OH^- = C_2O_4^{2-} + 2HOCH_2COOH + H_2O$$

$$Cu_2O + H_2O = Cu\downarrow + Cu^{+2} + 2OH^-$$

5.4. Triboelectric generators

5.4.1 Electrical conductivity of silver electroplated fabrics

The electrical volume resistivity of silver electroplated knitted fabrics was reported around 2 Ω mm. This behaviour can be attributed to the formation of uniform and dense network of silver metal particles over the surface of fabric, which enabled the formation of more conductive paths. In order to simulate the performance of electrodes under various movements of human body (i.e. stretching on elbow), the electrical conductivity of silver-plated fabrics was also examined at different stretch levels ranging from 0 to 50 %. From Figure 33 (b), it can be seen that the resistivity values of silver-plated fabric without stretching was 2 Ω mm, however it increased to 45 Ω mm at 50 % stretch. Nevertheless, this change in electrical resistivity was very low and can be considered as constant value for successful operation of TrEG during the human activity.



(a) Electroplating time (b) Extension level

Figure 33: Electrical resistivity of silver electroplated fabrics.

The explanation on reduction in electrical conductivity of coated fabrics at higher extension can be given from the micro photos of stretch areas shown in Figure 34. The grid structure of fabrics showed no ruptures in coating at lower extension levels. However, the frame work of coating gradually started to break with increase of extension due to stretching of yarns in knitted loop structures. In present work, the 50 % extension was found as limiting stretching limit to prevent further reduction in electrical conductivity of coated fabrics

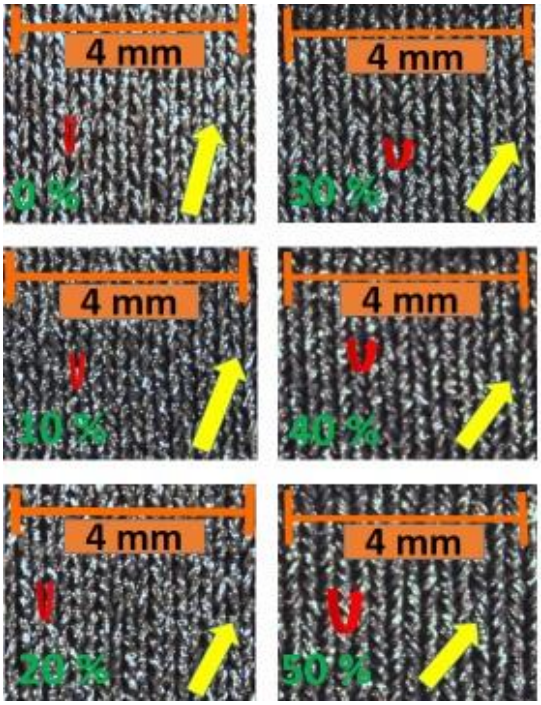
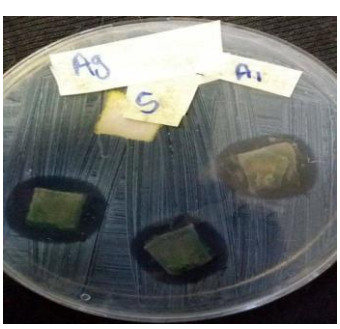


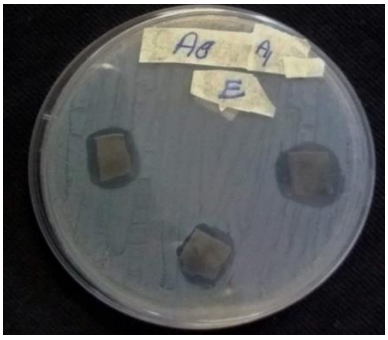
Figure 34: Photographs of silver electroplated fabrics at different stretch levels.

5.4.2 Antibacterial properties of silver electroplated fabrics

The antibacterial property of conductive fabric electrodes is extremely important as triboelectric generators are excellent media for microorganism growth due to prolonged contact with human skin or unhealthy indoor air quality. The antibacterial activity of silver-plated conductive fabrics was examined against Gram-negative Escherichia coli and Gram-positive Staphylococcus aureus. The fabric samples were kept for 24 h of incubation in dark at 37 °C and the zone of inhibition was observed. It can be clearly seen from Figure 35 that the zone of inhibition was absent in case of uncoated virgin fabric samples (i.e. no antibacterial property), whereas the zone of inhibitions was evidenced against both type of bacteria Staphylococcus aureus and Escherichia coli after the silver electroplating. The zone of inhibitions of 17.3 mm and 12.5 mm were found in case of Staphylococcus aureus and Escherichia coli, respectively. This indicated higher sensitivity towards Staphylococcus aureus as compared to Escherichia coli. The combination of chemical and physical interactions of bacteria with silver particles resulted into the antibacterial property of coated fabrics. The action started with the incorporation of silver particles into the cell via endocytotic mechanisms, and then release of ionic species within the cells due to dissolution of particles [55]. Therefore, the antibacterial performance originated from the massive oxidative stress due to high intracellular concentration gained within the cell. These results suggested that the developed TrEG can be in contact with elbow or foot for longer time with additional benefits of antibacterial performance.



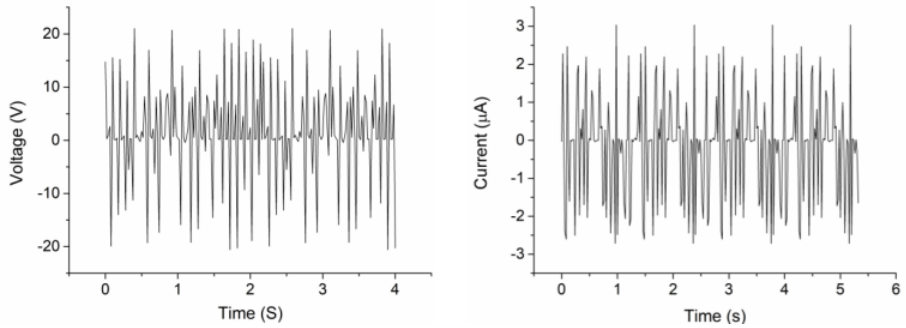
(a) Staphylococcus aureus



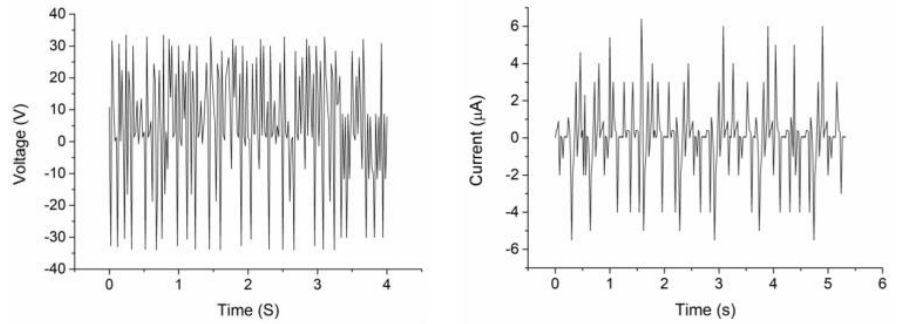
(b) Escherichia coli

Figure 35: Antibacterial properties of silver electroplated fabrics.

The performance of developed triboelectric generator was investigated under both stretching and pressing actions. When the two triboelectric layers were brought into contact, the AC current was produced and it was measured in terms of open circuit voltage *VOC* and short circuit current *ISC* using KEITHLEY TEKTRONIX 2450-SM, Source Meter SMU device. It can be seen from Figure 36 (a) that TrEG produced 21V and 3.5 μA current under the stretching state. However, when the pressing action was applied, it produced voltage of 33 V and current about 6 μA (see Figure 36 (b)). The different performance during stretching and pressing can be attributed to the difference in friction, vertical contact separation and mechanical deformation of triboelectric layers.



(a) Stretching action

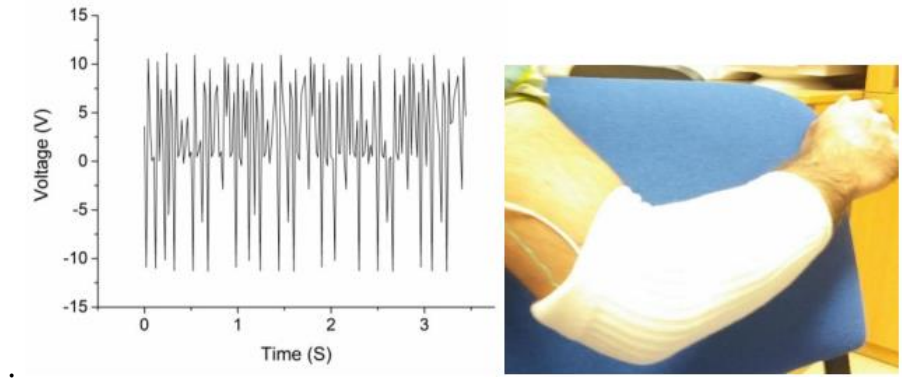


(b) Pressing action

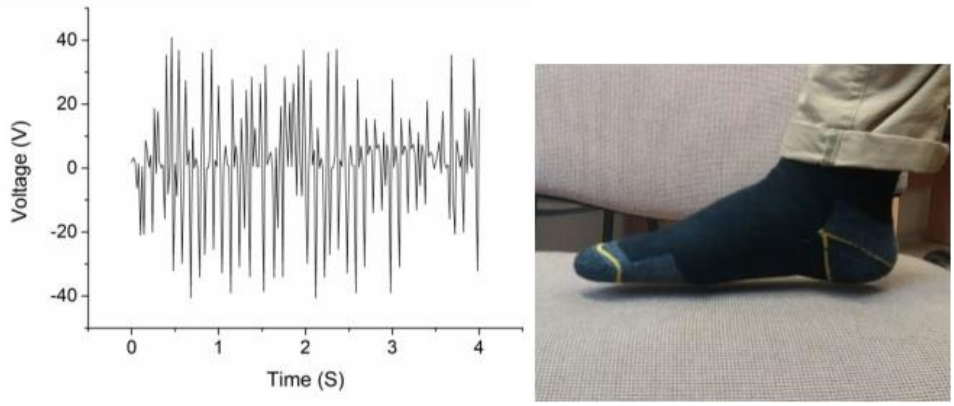
Figure 36: Performance of TrEG under different mechanical movements.

Furthermore, the utility of TrEG was investigated to harvest the energy from different daily human activities based on stretching and pressing motions. As major sources to create mechanical energy from human body are movements of elbow and foot, therefore TrEG was

attached to those human body parts. The TrEG was found to generate about 10 V from elbow movements due to stretching (Figure 37 a), whereas it generated about 40 V from foot movements due to pressing motion (Figure 37 b).



(a) Stretching action from elbow



(b) Pressing action from foot

Figure 37: Output of voltage during human activities.

Figure 38 shows the power generation mechanism of TrEG based on the coupling of triboelectrification and electrostatic induction. At the beginning when there is no rubbing action, no charge is transferred between the rabbit fur and silicone rubber (Figure 38 (a)). After the frictional contact between the rabbit fur and silicone rubber by rubbing, the TrEG get activated. This leads to the development of positive charge on the rabbit fur and negative charge on the silicone rubber. Subsequently, the electrons move from rabbit fur to silicon rubber through the silver-plated conductive fabric electrodes as shown in Figure 38 (b). Furthermore, when the external forces are removed, there is separation of rabbit fur and silicon rubber. This causes the flow of electrons from silicone rubber to rabbit fur via conductive fabric electrodes (Figure 38 (c)). In this way, the kinetic energy of stretching, pressing, and rubbing actions can be converted into electric energy by development of charges on the dielectric materials.

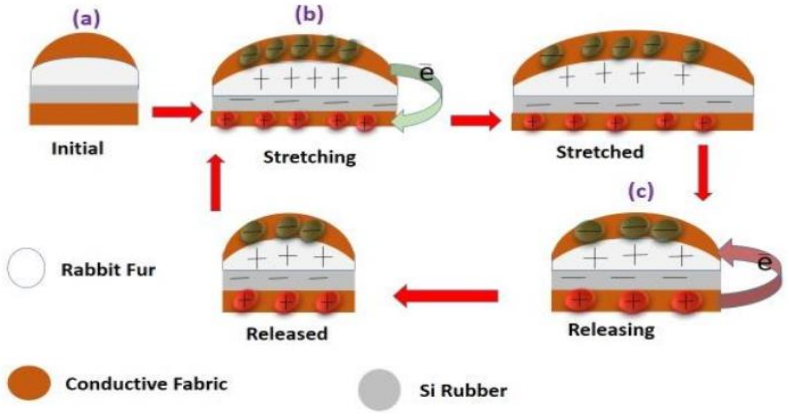


Figure 38: Illustration of the working mechanism of TrEG.

6. Evaluation of results and new findings

The part 1 of thesis was focused on the development of electrically conductive, multifunctional and durable cotton fabrics by in-situ deposition of copper particles. The copper particles were incorporated into the structure of cotton by sequential dipping in copper sulphate and then sodium hydrosulphite solutions. The amount of deposition of copper particles was controlled by several numbers of dips (i.e. 10 to 150) in copper sulphate. The concentration of copper sulphate was decided at 10 g/L based on acceptable level of achieved electrical conductivity. Further, the morphology of coated fabrics and copper particles was studied from SEM and XRD techniques. The utility of conductive fabrics was analysed for electromagnetic shielding ability over frequency range of 30 MHz to 1.5 GHz by coaxial transmission line method. The EMI shielding was found to increase with increase in number of dips, which was attributed to increased reflection of EM waves due to dense, uniform and percolated network of conductive copper particles on the surface. The sample produced from 50 dips revealed the lowest electromagnetic shielding effectiveness of about 6 dB in frequency range of 600 MHz–1.5 GHz. On the other hand, the sample produced from 100 and 150 dips exhibited the maximum shielding ability of 10 dB and 13 dB, respectively. For multifunctional behaviour, the copper coated cotton fabrics were further examined for antibacterial properties against pathogenic bacteria such as Staphylococcus aureus and Escherichia coli. The zone of inhibitions for Staphylococcus aureus increased from 9.5 to 15.5 mm, while for Escherichia coli it increased from 7.5 to 12 mm with increasing number of dips. Towards the end, the durability of coated fabrics was examined against washing. The fabrics showed good retention of the copper particles, proved by SEM microstructures and small loss in the conductivity of the material after washing.

The part 2 of thesis was focused on the development of electrically conductive fabrics by in-situ deposition of silver particles on the surface of cotton fabrics by sequential dipping in silver nitrate and then glucose stock solutions. The effect of silver nitrate concentration on electrical conductivity was investigated, and 17 g/L found to provide acceptable level of electrical conductivity values. Further, the amount of deposition of silver particles was controlled by several numbers of dips (i.e. 10 to 150) in silver nitrate solution. The higher number of dips produced dense network of silver particles, and therefore resulted in higher electrical conductivity. Later, the utility of conductive fabrics was analyzed for electromagnetic shielding ability over frequency range of 30 MHz to 1.5 GHz by coaxial transmission line method. The samples produced from higher number of dips provided higher EMI shielding due to increased reflection of EM waves. Moreover, the coated fabrics also showed promising behavior towards antimicrobial properties. Towards the end, the durability of coated fabrics was examined against washing after application of binder on the fabric. The fabrics showed

good retention of the silver particles, proved by SEM microstructures and small loss in the conductivity of the material after washing.

Furthermore, second section of part 2 was focused on the utility of silver coated stretchable fabrics as electrodes of TENS machine in electrotherapy applications. The sequential dipping in silver nitrate and then glucose stock solutions was employed for in-situ deposition of silver particles onto knitted fabric. The effect of silver nitrate concentration on performance of coated fabrics was investigated with respect to improvement of electrical conductivity, physiological comfort, and antibacterial properties. The dense and uniform deposition of silver particles was observed at lower (i.e. 42.5 g/L) concentration of silver nitrate and therefore resulted in higher electrical conductivity. Moreover, the coated knitted fabrics were subjected to repeated extension and change in electrical resistivity was examined. In the stretch range of 0–80 %, very small change in electrical resistance was observed, and then it changed significantly beyond 90 % of stretch. Moreover, the electrical resistivity of coated fabrics was found constant after repeated extension of several cycles and also when constant current was applied for prolonged time. Additionally, the coated fabrics also showed promising behavior towards antimicrobial properties. When the durability of coated fabrics was examined against washing, the fabrics showed good retention of the silver particles and small loss in the conductivity of the material.

The work in part 3 reported the significance of copper and silver coated woven fabrics (described in part 1 and part 2) for further deposition of metals during the electroless plating. The more even deposition of metals during electroless plating was obtained and thus fewer variations in electrical conductivity (surface and volume) across the substrate.

In part 4, silver plating was performed over knitted fabric. Plated fabric electrodes were used for the fabrication of TrEG self-powered device applications. The uniform and dense layer of metal was deposited on the fabrics. Then, the silicon rubber and rabbit fur were used as triboelectric materials in combination with plated conductive fabric electrodes and their energy performance was investigated under the mechanical stretching and pressing actions of human body movements (i.e. elbow and foot).

In this way, the presented research work described the various methods for surface metallization of fabrics. We produced more porous, less stiff and flexible conductive fabrics having extraordinary electrical conductivity and EMI shielding with antibacterial properties. The developed samples achieved interconnected network of conductive particles with thin and uniform metal deposition. Moreover, the step for further electroless plating over the particles coated fabrics enhanced the rubbing, washing and electrical properties. The procedure of electroless plating was short routed (reduced a number of steps) free from hazardous fumes, less costly and simple. The promising applications of developed fabrics are EMI shielding, strain sensors and as electrodes for electrotherapy and energy harvesting.

FUTURE WORK

- Investigation of electrical properties under different aging conditions (temperature, humidity, etc).
- Enhancement in electrical properties with different combinations of metal coating (in situ deposition, electroless plating, electroplating)
- Metallization of wool, glass and aramid fibers for different functional properties.
- Study of different triboelectric materials for energy harvesting
- Prevention of copper oxidation and improvement in durability of performance (by using capping agents, gums, binders, semiconductors, and alloys)
- Impact of thickness of metal coating on EMI shielding effectiveness, hardness and against anti-stabbing effect

7. References

[1] A. Ali, V. Baheti, J. Militky, Z. Khan, V. Tunakova, and S. Naeem, "Copper coated multifunctional cotton fabrics," *J. Ind. Text.*, vol. 48, pp. 448–464, Sep. 2017.

[2] A. Ali, V. Baheti, J. Militky, and Z. Khan, "Utility of silver-coated fabrics as electrodes in electrotherapy applications," *J. Appl. Polym. Sci.*, vol. 135, p. 46357, 2018.

[3] X. Gan, Y. Wu, L. Liu, B. Shen, and W. Hu, "Electroless plating of Cu-Ni-P alloy on PET fabrics and effect of plating parameters on the properties of conductive fabrics," *J. Alloys Compd.*, vol. 455, no. 1–2, pp. 308–313, 2008.

[4] F. Ko *et al.*, "Electrospinning of Continuous Carbon Nanotube-Filled Nanofiber Yarns," *Adv. Mater.*, vol. 15, no. 14, pp. 1161–1165, 2003.

[5] X. Liu, H. Chang, Y. Li, W. T. S. Huck, and Z. Zheng, "Polyelectrolyte-Bridged Metal / Cotton Hierarchical Structures for Highly Durable Conductive Yarns," *Appl. Mater. Interfaces*, pp. 529–535, 2010.

[6] K. Coessens, V.; Pintauer, T.; Matyjaszewski, "Funtional Polymers by Atom Transfer Radical Polymerization," *Prog. Polym. Sci.*, vol. 26, pp. 337–377, 2001.

[7] H. W. Cui, K. Suganuma, and H. Uchida, "Highly stretchable, electrically conductive textiles fabricated from silver nanowires and cupro fabrics using a simple dipping-drying method," *Nano Res.*, vol. 8, no. 5, pp. 1604–1614, 2015.

[8] T. Yamashita, T.; Khumpuang, S.; Miyake, K.; Itoh, "Characterization of contact structure for woven electronic textile using conductive polymer micro-cantilever array," *Electron. Commun. Japan*, vol. 97, pp. 48–53, 2014.

[9] et al Molina J, del Rı´ o AI, Bonastre J, "Electrochemical polymerisation of aniline on conducting textiles of polyester covered with polypyrrole/AQSA," *Eur Polym J*, vol. 45, pp. 1302–1315, 2009.

[10] F. J, "Wearable electronics and clothing from Philips and Levi," *Tech. Text. Int.*, vol. 10, pp. 22–4, 2001.

[11] K. Bertuleit, "Silver Coated Polyamide a Conductive Fabric," *J. Coat. Fabr.*, vol. 20, pp. 211–215, 1991.

[12] W. C. Smith, *Smart Textile Coatings and Laminates*. Woodhead Publishing, UK and CRC Press, Boca Raton, FL, 2010.

[13] B. J. and K. M. P. Rytlewski, "Laser-assited electroless metallization of polymer materials: A critical review," *Rev. Adhes. Adhes.*, vol. 4, pp. 334–365, 2016.

[14] S. Q. Jiang, E. Newton, C. W. M. Yuen, and C. W. Kan, "Chemical Silver Plating on Cotton and Polyester Fabrics and its Application on Fabric Design," *Text. Res. J.*, vol. 76, no. 1, pp. 57–65, 2006.

[15] Y. Lu, S. Jiang, and Y. Huang, "Ultrasonic-assisted electroless deposition of Ag on PET fabric with low silver content for EMI shielding," *Surf. Coatings Technol.*, vol. 204, no. 16–17, pp. 2829–2833, 2010.

[16] Z. Adamczyk, L. Szyk-Warszyńska, M. Zembala, and M. Lehocký, "In situ studies of particle deposition on non-transparent substrates," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 235, no. 1–3, pp. 65–72, 2004.

[17] A. Keller, T. and Kuhn, "Electrodes for transcutaneous (surface) electrical stimulation," *J. Autom. Control*, vol. 18, no. 2, pp. 35–45, 2008.

[18] K. W. Oh, H. J. Park, and S. H. Kim, "Stretchable conductive fabric for electrotherapy," *J. Appl. Polym. Sci.*, vol. 88, no. 5, pp. 1225–1229, 2003.

[19] J. Johnson, MI, Ashton, CH, Bousfield, DR, Thompson, "Analgesic effects of different pulse patterns of transcutaneous electrical nerve stimulation on cold-induced pain in normal subjects," *J. Psychosom. Res.*, vol. 35, pp. 313–321, 1991.

[20] A. Corazza, M, Maranini, C, Bacilieri, S, Virgili, "Accelerated allergic contact dermatitis to a transcutaneous electrical nerve stimulation device," *Dermatology*, vol. 199, p. 281, 1999.
[21] A. and G. E. R. Brenner, "Nickel plating on steel by chemical reduction," *J. Res. Nat. Bur. Std*, vol. 37, pp. 31–34, 1946.
[22] A. Ali, V. Baheti, J. Militky, Z. Khan, and S. Q. Z. Gilani, "Comparative Performance of Copper and Silver Coated Stretchable Fabrics," *Fibers Polym.*, vol. 19, no. 3, 2018.
[23] P. E. and O. M, "M. Smart fabric, or washable computing," in *In: First IEEE international symposium on wearable computers*, 1997, pp. 167–168.
[24] H. H. and T. Kobayashib, "Electroless Copper Deposition Process Using Glyoxylic Acid as a Reducing Agent," *J. Electrochem. Soc.*, vol. 141, pp. 730–733, 1994.
[25] Z. B. Xie Haowen, "Effects of preparation technology on the structure and amorphous forming region for electroless Ni-P alloys," *J. Mater. Process. Tech*, vol. 124, pp. 1–8, 2002.
[26] J.-W. H. Kwang-Lung Lin∗, "Effect of thiourea and lead acetate on the deposition of electroless nickel," *Mater. Chem. Phys.*, vol. 76, pp. 204–211, 2002.
[27] R. Hasan, "Production of Antimicrobial Textiles by Using Copper Oxide Nanoparticles," *Int. J. Contemp. Res. Rev.*, vol. 9, no. 08, pp. 20195–20202, 2018.
[28] K. McNaughton, TG & Horch, "Metallized polymer fibers as leadwires and intrafascicular microelectrodes," *J. Neurosci. Methods*, vol. 70, pp. 103–110, 1996.
[29] J. Mackison, F. W., R. S. Stricoff, and L. J. Partridge, *NIOSH/OSHA - Occupational Health Guidelines for Chemical Hazards.* Washington, DC: U.S: Government Printing Office, 1981.
[30] D. Barker, "Electroless deposition of metals," *Trans. Inst. Met. Finish.*, vol. 71, no. pt 3, pp. 121–124, 1993.
[31] Y. Huang, K. Shi, Z. Liao, Y. Wang, L. Wang, and F. Zhu, "Studies of electroless Ni-Co-P ternary alloy on glass fibers," *Mater. Lett.*, vol. 61, no. 8–9, pp. 1742–1746, 2007.
[32] and S. S. Zenglin Wang, Osamu Yaegashi, Hiroyuki Sakaue, Takayuki Takahagi, "Suppression of native oxide growth in sputtered TaN films and its application to Cu electroless plating," *J. Appl. Phys.*, vol. 94, p. 4697, 2003.
[33] and R. A. Lu Yu, Lian Guo, Robert Preisser, "Autocatalysis during Electroless Copper Deposition using Glyoxylic Acid as Reducing Agent," *J. Electrochem. Soc.*, vol. 12, p. 160, 2013.
[34] L. Yu, L. Guo, R. Preisser, and R. Akolkar, "Autocatalysis during Electroless Copper Deposition using Glyoxylic Acid as Reducing Agent," *J. Electrochem. Soc.*, vol. 160, no. 12, pp. D3004–D3008, 2013.
[35] "AATCC Test Method 147. Antibacterial activity assessment of textile materials: parallel streak method. In: AATCC technical manual. North Carolina, USA: American Association of Textile Chemists and Colorists, 2011."
[36] Y. Zhao, Z. Cai, X. Fu, B. Song, and H. Zhu, "Electrochemical deposition and characterization of copper crystals on polyaniline/poly(ethylene terephthalate) conductive textiles," *Synth. Met.*, vol. 175, pp. 1–8, 2013.
[37] J. M. Sheffield, A., and Doyle, "Uptake of Copper(II) by Wool," *Wool, Text. Res. J*, vol. 75, pp. 203–207, 2002.
[38] 3 S. Baseri, 1 A. Zadhoush, 1 M. Morshed, 1 M. Amirnasr, 2 M. Azarnasab1, "Synthesis and Optimization of Copper Sulfide-Coated Electrically Conducting Poly(acrylonitrile) Fibers," *J. Appl. Polym. Sci.*, vol. 104, pp. 2579–2586, 2007.
[39] S. Naeem, V. Baheti, V. Tunakova, J. Militky, D. Karthik, and B. Tomkova, "Development of porous and electrically conductive activated carbon web for effective

EMI shielding applications," *Carbon N. Y.*, vol. 111, pp. 439–447, 2017.
[40] Z. Yu *et al.*, "Antibacterial properties and electrical characteristics of multifunctional metal composite fabrics," *J. Ind. Text.*, no. 100, 2015.
[41] J. Gabbay, G. Borkow, J. Mishal, E. Magen, R. Zatcoff, and Y. Shemer-Avni, "Copper oxide impregnated textiles with potent biocidal activities," *J. Ind. Text.*, vol. 35, no. 4, pp. 323–335, 2006.
[42] G. Irene *et al.*, "Copper-coated textiles: Armor against MDR nosocomial pathogens," *Diagn. Microbiol. Infect. Dis.*, vol. 85, no. 2, pp. 205–209, 2016.
[43] N. Lewinski, V. Colvin, and R. Drezek, "reviews Cytotoxicity of Nanoparticles," *Small*, vol. 4, no. 1, pp. 26–49, 2008.
[44] T. Suwatthanarak, B. Than-ardna, and D. Danwanichakul, "Synthesis of silver nanoparticles in skim natural rubber latex at room temperature," *Mater. Lett.*, vol. 168, pp. 31–35, 2016.
[45] M. E. Y. M. Shateri-Khalilabad, "Fabricating multifunctional silver nanoparticles-coated cotton fabric," *Arab. J. Chem.*, vol. 10, p. 1016, 2017.
[46] H. W. Cui, Q. Fan, and D. S. Li, "Novel flexible electrically conductive adhesives from functional epoxy, flexibilizers, micro-silver flakes and nano-silver spheres for electronic packaging," *Polym. Int.*, vol. 62, no. 11, pp. 1644–1651, 2013.
[47] S. H. Kim, K. W. Oh, and J. H. Bahk, "Nylon / Spandex for Electrotherapeutic Pad Electrode," *J. Appl. Polym. Sci.*, vol. 91, pp. 4064–4071, 2004.
[48] S. T. A. Hamdani, P. Potluri, and A. Fernando, "Thermo-mechanical behavior of textile heating fabric based on silver coated polymeric yarn," *Materials (Basel).*, vol. 6, no. 3, pp. 1072–1089, 2013.
[49] L. R. Pahalagedara, I. W. Siriwardane, N. D. Tissera, R. N. Wijesena, and K. M. N. de Silva, "Carbon black functionalized stretchable conductive fabrics for wearable heating applications," *RSC Adv.*, vol. 7, no. 31, pp. 19174–19180, 2017.
[50] B. Glenn O. Mallory Juan, *Electroless Plating*, 1st ed. William Andrew, 1990.
[51] and Z. H. Y. D.H. Cheng, W.Y. Xu, Z.Y. Zhang, "Electroless Copper Plating Using Hypophosphite as Reducing Agent," *Met. Finish.*, vol. 95, no. 1, pp. 34–37, 1997.
[52] F. Inoue *et al.*, "Glyoxylic Acid as Reducing Agent for Electroless Copper Deposition on Cobalt Liner," *ECS Trans.*, vol. 64, no. 40, pp. 63–75, 2015.
[53] W. . Cheonga, "The effect of stabilizer on the bath stability of elecroless Ni-deposition and the deposit," *Appl. Surf. Sci.*, vol. 229, p. 282, 2004.
[54] I. Ohno, "Electrochemistry of electroless plating," *Mater. Chem.*, vol. 146, p. 33, 1991.
[55] A. Ali, V. Baheti, J. Militky, and Z. Khan, "Utility of silver-coated fabrics as electrodes in electrotherapy applications," *J. Appl. Polym. Sci.*, vol. 135, no. 23, 2018.

8. List of Publications

8.1 Publications in Impact Factor Journals

[1] **Azam Ali**, Nhung. H.A Nguyen, Vijay Baheti, Munir Ashraf, Jiri Militky, Tariq Mansoor and S. Ahmad, "Electrical conductivity and physiological comfort of silver coated cotton fabrics," **Journal of textile institute.** vol. 109, pp. 1–9, 2017. *[Impact factor = 1.1]*

[2] **Azam Ali,** Vijay Baheti, Jiri Militky, Muhammad Zaman Khan, Veronika Tunakova, and Salman Naeem, "Copper coated multifunctional cotton fabrics," **Journal of industrial textile.** vol. 48, pp. 448–464, 2017. *[Impact factor = 1.884]*

[3] **Azam Ali**, Vijay Baheti, Jiri Militky, Muhammad Zaman Khan, "Utility of silver-coated fabrics as electrodes in electrotherapy applications," **Journal of applied polymer science**. vol. 135, pp. 46357, 2018. *[Impact factor = 2.188]*

[4] **Azam Ali**, Vijay Baheti, Jiri Militky, Muhammad Zaman Khan, Sayed Qamer Zia Gilani, "Comparative Performance of Copper and Silver Coated Stretchable Fabrics" **Fibers and Polymers**. vol. 19, 2018. *[Impact factor = 1.43]*

[5] **Azam Ali**, Vijay Baheti, Jiri Militky, Muhammad Usman Javaid, "Enhancement in ageing and functional properties of copper-coated fabrics by subsequent electroplating," **Applied physics A**, vol. 124, pp. 651, 2018. *[Impact factor = 1.784]*

[6] **Azam Ali,** Vijay Baheti and Jiri Militky, "Energy Harvesting Performance of Silver Electroplated Fabrics" **Journal of materials chemistry and physics of solids**, Vol. 231, pp. 33-40. 2019. *[Impact factor = 2.781]*

[7] **Azam Ali**, Vijay Baheti, Jiri Militky, Muhammad Zaman Khan, "Copper electroless plating of cotton fabrics after surface activation with deposition of silver and copper nanoparticles, copper and stannous chloride" **Journal of Physics and chemistry of solids**, Vol. 137, 2020. *[Impact factor = 2.048]*

[8] **Azam Ali**, Vijay Baheti, Jiri Militky, Muhammad Zaman Khan, and Guocheng Zhu, "Metal Coating on Ultrafine Polyester Non-woven Fabrics and Their Ageing Properties" **Fibers and Polymers**, Vol.20, pp.1347-1359, 2019. *[Impact factor = 1.43]*

[9] **Azam Ali**, Vijay Baheti, Jiri Militky, Muhammad Zaman Khan, "Development of electrically conductive composites based on recycled resources" **Journal of Textile Institute**, DOI: 10.1080/00405000.2019.1644121 *[Impact factor = 1.1]*

[10] **Azam Ali**, Khubab Shaker, Yasir Nawab, Jiri Militky, and Vijay Baheti, "Hydrophobic treatment of natural fibers and their composites — A review," **Journal of industrial textile**. vol. 47, pp. 253–283, 2016. *[Impact factor = 1.884]*

[11] **Azam Ali**, K. Shaker, Y. Nawab and M. Ashrif, "Impact of hydrophobic treatment of jute on moisture regain and mechanical properties of composite material," **Journal of Reinforced Plastics and Composites.** vol. 34, pp. 2059–2068, 2015. *[Impact factor = 1.18]*

[12] Hafz Faisal Siddique, Adnan Ahmed Mazari, Antonin Havelka, Tariq Mansoor, **Azam Ali,** Musaddaq Azeem1, "Development of V-Shaped Compression Socks on Conventional Socks Knitting Machine," **Autex Research Journal** J. 2018. *[Impact factor = 0.75]*

[13] Tariq Mansoor, Hafiz Faisal Siddique, **Azam Ali** and Antonin Havelka, "Wrinkle free plaited knitted fabrics without pre-heat setting," **Journal of textile institute.** vol. 109, 2018. *[Impact factor = 1.1]*

[14] Sheraz Ahmad, M. Ashraf, **Azam Ali**, K. Shaker, M. Umair, A. Afzal, Y. Nawab, and A. Rasheed, "Preparation of conductive polyethylene terephthalate yarns by deposition of silver & copper nanoparticles," **Fibres and Textile Eastern Europe**. vol. 25, pp. 25–30, 2017. *[Impact factor = 0.677]*

[15] Salman Naeem, Vijay Baheti, Jiri Militky, and **Azam Ali**, "Multifunctional polylactic acid composites filled with activated carbon particles obtained from acrylic fibrous wastes," **Polymer. Composites**. vol. 40, 2017. *[Impact factor = 2.268]*

[16] Mussadaq Azeem, Lubos Hes, Jakub Wiener, Muhammad Tayyab Noman, **Azam Ali**, Tariq Mansoor" Comfort properties of nano-filament polyester fabrics: thermo-physiological evaluation," **industria textilaˇ**. Vol 69, pp. 315-320. 2018. *[Impact factor = 0.540]*
[17] Muhammad Zaman Khan, Vijay Baheti, Munir Ashraf, Tanveer Hussain, **Azam Ali,** Amjed Javid, Abdur Rehman" Development of UV Protective, Superhydrophobic and Antibacterial Textiles Using ZnO and TiO2 Nanoparticles," **Fibers and Polymersˇ**., 2018. vol 19, PAGE 1647 *[Impact factor = 1.43]*
[18] Muhammad Zaman Khan, Vijay Baheti, Jiri Militky, **Azam Ali**, Martina Vikova" Superhydrophobicity, UV protection and oil/water separation properties of fly ash/ trimethoxy silane coated cotton fabrics. **carbohydrate. Polymer**. 2018. *[Impact factor = 6.0]*
[19] Tayyab Noman, Muhammad Azeem Ashraf, Hafsa Jamshaid and **Azam Ali**, A Novel Green Stabilization of TiO_2 Nanoparticles onto Cotton " **Fibers and Polymers**. vol 19, pp. 2268-2277. 2018. *[Impact factor = 1.43]*
[20] Tayyab Noman, Muhammad Azeem Ashraf, Hafsa Jamshaid and **Azam Ali**," Synthesis and applications of nano-TiO_2: a review" Environmental Science and Pollution Research, DOI: 10.1007/s11356-018-3884-z *[Impact factor = 2.914]*
[21] Muhammad Zaman Khan, Vijay Baheti, Jiri Militky, **Azam Ali**," Superhydrophobicity, Self-cleaning properties of polyester fabrics coated with flower-like TiO 2 particles and trimethoxy (octadecyl)silane. **Journal of industrial textile**. 2019. DOI: /10.1177/1528083719836938,. *[Impact factor = 1.884]*
[22] Muhammad Zaman Khan, Vijay Baheti, Jiri Militky, **Azam Ali**," Superhydrophobicity, Improvement of liquid moisture management in plaited knitted fabrics. **Tekstil ve Konfeksiyon** 28(3):182-188,. *[Impact factor = 0.17]*

8.2 Publications in International Conferences

[1] **Azam Ali**, Electrically conductive textile sensors made by silver and copper nanoparticles" Oral presentation at the "International Conference on Advances in Functional Materials in UCLA (AAAFM-UCLA), 2019 at the University of California, Los Angeles, USA
[2] **Azam Ali**, Blanka Tomkova, Vijay Baheti, Jiri Militky, Musaddaq Azeem, Study the functional properties of silver nanoparticles coated fabric
91st, Textile Institute World Conference, Leeds UK, 2018
[3] **Azam Ali**, Vijay Baheti, Abdul Jabbar, Sundaramoorthy Palanisamy, Jiri Militky, Effect of jute fibre treatment on moisture regain and mechanical performance of composite materials AUTEX 2017, Greece
[4] **Azam Ali**, VeronikaTunakova, Vijay Baheti, Jiri Militky. Preparation of Conductive Yarns by Deposition of Silver & Copper Nanoparticles
95th International Conference on Innovative Engineering Technologies (ICIET) Rawalpindi, Pakistan, 29th-30th May, 2017
[5] **Azam Ali**, Vijay Baheti, Jiri Militky. Metallized Textile with Copper and Silver particles, STRUTEX 2018
[6] **Azam Ali**, Vijay Baheti, Jiri Militky. Copper and silver coated textile for smart applications, 47th Textile Research Symposium, 17 – 19 June 2019, Liberec
[7] Muhammad Zaman Khan, Vijay Baheti, Jiri Militky, **Azam Ali**, Sajid Faheem, Development of Multifunctional Polyester fabrics, functionalize with TiO2 nano particles AUTEX 2018, Turkey, ID no 3194
[8] Hafiz Faial Siddique, Adnan Mazari, Antonin Havelka, **Azam Ali**, Improve Hydrophobic Analysis of Nanofilament polyester fabric AUTEX 2018, Turkey

[9] Musaddaq Azeem, Blanka Tomkova, Jakub Wiener, **Azam Ali**, Thermal and Tactile Comfort of Nanofilament Fabric
91st, Textile Institute World Conference, Leeds UK, 2018
[10] Abdul Jabbar, **Azam Ali**, Muhammad Usman Javaid, Jiri Militky, Investigation of mechanical and thermomechanical properties of nanocellulose coated jute/green epoxy composites AUTEX 2017, Greece
[11] Sundaramoorthy Palanisamy, Veronika Tunakova, **Azam Ali**, Jiri Militky, Study on effect of moisture content and electromagnetic shielding effectiveness of cotton knitted fabric treated with various liquid media. 9th Central European Conference 2017
[12] Sundaramoorthy Palanisamy, Veronika Tunakova, **Azam Ali**, Jiri Militky, Daniel Karthik Study on textile comfort properties of polypropylene blended stainless-steel woven fabric for the application of electromagnetic shielding effectiveness
AUTEX 2017, Greece

8.3 Book Chapters
[1] **Azam Ali,** Vijay Baheti, Jiri Militky "Metal coated multifunctional fabrics" Recent trends in fibrous material sciences, volume 5, page 392, ISBN 978-80-7494-493-2 (2019)
[2] Salman Naeem, Sayed Qammar Zia, Vijay Baheti, Jiri Militky, **Azam Ali** "Electrical Conductivity of PLA Films Reinforced with Carbon Nano Particles from Waste Acrylic Fibers" Advances in Natural Fibre Composites, Springer (2018)
[3] Abdul Jabbar, Jiri Militky, **Azam Ali** "Investigation of Mechanical and Thermomechanical Properties of Nanocellulose Coated Jute/Green Epoxy Composites" Advances in Natural Fibre Composites pp 175-194, Springer (2018)
[4] Vijay baheti, Jiri militky, **Azam Ali** "Production of activated carbon particles at optimized carbonization conditions, Recent trends in fibrous material sciences volume 5, page 372, ISBN 978-80-7494-493-2 (2019)

Citations
Article 1: Azam Ali, Nhung. H.A Nguyen, Vijay Baheti, Munir Ashraf, Jiri Militky, Tariq Mansoor and S. Ahmad, "Electrical conductivity and physiological comfort of silver coated cotton fabrics," **Journal of textile institute.** vol. 109, pp. 1–9, 2017.
[No of citations = 15]

Article 2: Azam Ali, Vijay Baheti, Jiri Militky, Muhammad Zaman Khan, Veronika Tunakova, and Salman Naeem, "Copper coated multifunctional cotton fabrics," **Journal of industrial textile.** vol. 48, pp. 448–464, 2017.
[No of citations = 14]

Article 3: Azam Ali, Vijay Baheti, Jiri Militky, Muhammad Zaman Khan, "Utility of silver-coated fabrics as electrodes in electrotherapy applications," **Journal of applied polymer science**. vol. 135, pp. 46357, 2018.
[No of citations = 10]

Article 4: Azam Ali, Vijay Baheti, Jiri Militky, Muhammad Zaman Khan, Sayed Qamer Zia Gilani, "Comparative Performance of Copper and Silver Coated Stretchable Fabrics" **Fibers and Polymers**. vol. 19, 2018.
[No of citations = 9]

Article 5: Azam Ali, Vijay Baheti, Jiri Militky, Muhammad Usman Javaid, "Enhancement in ageing and functional properties of copper-coated fabrics by subsequent electroplating," **Applied physics A**, vol. 124, pp. 651, 2018.

[No of citations = 4]

Article 6: Azam Ali, Vijay Baheti and Jiri Militky, "Energy Harvesting Performance of Silver Electroplated Fabrics" **Journal of materials chemistry and physics of solids**, Vol. 231, pp. 33-40. 2019.

[No of citations = 2]

Resume

Azam Ali

Address: 17 Listopadu, 584/2, 46015, Liberec, Czech Republic.
Email: mehr_azam91@yahoo.com
Contact media: Cell # +420-774357957,
Whatsapp: +92 3217033644**,**
Skype: live:mehr_azam91
Linked in: https://www.linkedin.com/in/azam-ali-a1b07261/
Nationality: Pakistani

Vision and skills

2 years of industrial experience in wet-processing department of textile. An enthusiastic, adaptive and fast-learning individual with a broad and acute interest in the synthesis mechanisms of nanomaterials (by sol gel process, insitu deposition, vacuum and arc spraying, electroless and electroplating method). Analytical and surface characterization, development of functional and multifunctional textiles, smart textiles, hydrophobic textiles, fabric-based electrodes for electrotherapy and energy harvesting. Making carbon and graphite particles by carbonization of waste materials and making the composites by hand layup, vacuum bagging and resin transfer method. I particularly enjoy collaborating with scientists of different disciplines to develop robust skills and solve new challenges attain professional excellence in dynamic and challenging organization by actively exercising my unique skills and abilities and bringing to bear my integrity.

Education

Ph.D. (Textiles & Materials Engineering) 2015-continue Technical University of Liberec, Czech Republic
Dissertation topic: Surface deposition of metals on textile structures
Characterization tools: XRD, FTIR, SEM, EDX, ICP-AES, Electrical and thermal conductivity, EMI shielding Antibacterial test, Air and Water vapor permeability, Ageing

Major subjects: Nanotechnology, Advance materials, Analytical techniques, Smart materials, Metrology, Textile raw materials and chemistry, Statistical analysis, Heat and mass transfer. Science for making composites. **Research Area:** Nano-particles preparation. Analytical characterization. Electrically conductive polymers and textiles, conductive composites, Development of flexible electrodes for electrotherapy, medical devices and energy harvesting (Tribo-electrification and Piezo-electricity method)
M.Sc. (Textiles Engineering) 2012-2014 National Textile University, Faisal Abad, Pakistan **Dissertation topic:** Development of natural fiber hydrophobic composites **Characterization tools:** SEM, EDX, Tensile testing, Impact testing, ageing **Major subjects**: Technical textile, Medical textile, Research methodology, Non-woven, High-performance fibers, Analytical techniques, protective textiles, nanotechnology, Smart textile, composites fabrication
B.Sc. (Textiles Engineering) 2006-2010 The University of faisalabad, Faisal Abad, Pakistan **Dissertation topic:** To study the effect of catalyst concentration and curing conditions on resin finish **Characterization tools:** SEM, EDX, Tensile testing, Impact testing, crease recovery **Major subjects**: Nano materials finishing, Applied chemistry, Polymer chemistry, Textile Dyeing, Textile printing, Textile finishing, Textile raw materials, Applied mathematics, Textile testing, Applied physics, Applied chemistry, Electrical engineering, Electronics, Hydraulic pressure, Thermodynamics etc.
F.Sc. GC University Faisalabad, Pakistan **Main Subjects:** Physics, Chemistry, Math

Summary: Experience: Textile Products Specialist (Textile Engineering)

2 years of industrial experience in wet-processing department of textile.

6 years of experience as a Researcher.

PROFESSIONAL EXPERIENCE:

Proficiencies:

Organization: Sitara Textile Mills [6 months]
Designation: Training engineer

Organization: Arif Textile Mills [2½ year]
Designation: Assistant Manager
Time dedicated: September 2010~ January, 2012

- Textile pretreatments
- Dyeing
- Finishing
- Trouble shooting and mechanical maintenance supervision

Organization: National Textile Research Center (NTRC), NTU, Pakistan [2 Years]
Designation: Research Associate
Time dedicated: 2013 ~ September, 2015

- Preparation of
    - Nanoparticles of Copper, Silver, Zinc and Magnesium, Magnesium hydroxide

  - Micro particles of carbon and graphite from waste materials
  - Multifunctional textiles (hydrophobic, oil and water repellency)
  - Flame retardant fabrics (by making and imparting magnesium oxide and magnesium hydroxide nanoparticles)
  - Antibacterial fabrics
- Development of
  - Electrically conductive yarns and textiles by imparting metal particles
  - Making electrically conductive polymers and stretchable fabrics by imparting carbon based fillers
  - Stretchable electrodes
- Development of
  - Electrically conductive green composites
  - Hydrophobic natural fiber reinforced composites
  - Shape memory composites
- Carbonizing acrylic and Kevlar waste materials to make electrically conductive fillers
- Working on ageing properties of composites

Additional Expertise In Subjects

- Smart textile
- Composites
- Carbonization to make carbon fibers
- Heat and mass transfer through Porous Media
- Clothing Comfort
- Textile Fibrous material Properties
- Textile processing
- Statistical Data analysis (Regression Analysis using MINITAB)
- Sound knowledge of data analysis using Software: MINITAB, ORIGIN Pro, MS Word, MS Excel and MS Power Point, Python (Basics only), Irfan View, ImageJ, Chem sketch window, Blender Animation.

RESEARCH SCORE

- Research gate score **20.46**
- h-index **7**

AWARD and MEMBERSHIPS:

- Best poster award INTERNATIONAL PH.D. STUDENTS DAY, within workshop for PhD students. 12 November, 2019, Liberec, Czech Republic
- Membership of Pakistan Engineering Council

LANGUAGE PROFICIENCY:

URDU: Native Speaker
ENGLISH: First Language (CEFR Level C2), IELTS: Academics clear
HINDI : Speak well
GERMAN and CZECH: Learning at my own

INTERNATIONAL TOURS:

- 10 days stay in University of California Los Angles, USA

- 10 days stay in Greece for international conference AUTEX
- 10 days stay in Leeds for 91st, Textile Institute World Conference, Leeds UK
- Small tours regarding research project in France and Sweden
- Small tours regarding research project in Poland

INTERESTS AND ACTIVITIES:

- Scientific Novelties
- Habitual to play football and cricket
- Exploring advance ideas in Textile materials and Finishes.
- Event organizer for conferences

Recommendation of the supervisor

Supervisor's recommendation on PhD thesis of Azam Ali, M.Sc.

Date: 16.12.2020

Thesis title: **Surface deposition of metals on textile structures**

The PhD thesis of Azam Ali is oriented to preparation of electrically conductive metal particles on surface of smart textiles. He studied mainly electromagnetic shielding, antimicrobial and electrical conductivity and changes of electrical resistance) during stretching (possible application in electrotherapy) by using cuprous, silver and other type of particles deposited on surfaces. He focused not only on functional properties but as well on the durability changes due to washing. Special applications as Joule heating and electrodes for triboelectric generators were deeply investigated as well.

The thesis is written according to standard format and all the aims are accomplished. The candidate has done all his work quite systematically, on outstanding level, with specific objectives. He organized and analyzed data scientifically. Discussion of the results is logical and there are comparisons of achieved results with the results of other published works. The quality of figures and tables is good and understandable. The language level of the thesis is good and meets the PhD level. Some of his results are quite innovative and were already published in journals with excellent impact factor.

His publication activities in high impact factor journals show that he is an exceptionally good young researcher. During his research work at TUL on the PhD theme, he has published 22 papers in high ranked impact factor journals, 4 book chapters and 12 articles in conference proceedings.

During his studies he proved himself as a diligent and fully competent person.

The conclusions of the thesis are interesting, novel and ready to be used in practice. I therefore strongly recommend the thesis for final defense.

Prof. Ing. Jiří Militký, CSc. EURING
Supervisor

Opponents's reviews

Opponent's review

Title: *Surface Deposition of Metals on Textile Structures*

Author: Azam Ali, M.Sc.

This presented thesis deals with the current topic of preparation of conductive textiles, which contain applied layers of copper or silver particles and their subsequent use in the field of conductive materials.

Thesis contains 103 pages divided into 8 main chapters and contains 10 tables and 69 pictures.

At the beginning of this thesis, four main goals of experimental work were defined, in-situ deposition of copper or silver on cotton fabric / knitted fabric usable for electromagnetic shielding, electroless plating for further copper deposition and study of silver deposited knitted fabrics as an electrode usable for TrEG self-powered device.

The chapter of literature review of current knowledge in the field of textile materials containing conductive metal layers, their preparation, and various uses, follows. Attention was paid mainly to the issue of electromagnetic shielding and the use of conductive textile materials in medicine. The search is clear and a sufficient amount of resources has been used.

Using methods of preparation and testing conductive materials are sufficiently described for possible repetition. Personally, in order to determine the concentration of metal on the fabric, I would choose not only the SEM EDX, but also the determination of the metal by elemental analysis from the ash of the cotton fabric. On the other hand, this method is destructive for sample.

In the experimental part of present thesis, firstly copper or silver layers were prepared by chemical reduction on the surface of a cotton fabric or knitted fabric. For metal identification appropriate physical methods was used. A positive effect of higher amounts of copper or silver on the determined values of surface resistivity, electromagnetic shielding and antibacterial activity was described.

The effect of extension on the above properties was also observed for the silver coated knitted fabric. The subsequent electroless copper plating over previously deposited copper or silver coated fabrics was the next part of the experimental work, when a significant increasing of conductivity was achieved.

One type of these samples, silver electroplated knitted fabric was used as an electrode for triboelectric generators, where the values of electrical resistance and voltage and current flowing due to the stretching of the knitted fabric were monitored. In the last part of the thesis, presented results were compared with the values published in the literature. This thesis contains the chemical description of individual processes.

Formally, this thesis contains some typing errors, e.g.:

p. 41 ... for 12 minutes; ... g/L

p. 58 Table 6: Oxygen (O) should probably be the correct element instead of potassium (K)

p. 59 ... see 42

I miss of SH and SE in the list of abbreviations. Some citations in the bibliography are not complete, e.g. number 60, 106, 114.

The thesis presents interesting results of experimental work in the field of preparation of textile materials with a conductive layer usable not only as an electromagnetic shield, but also in the field of

medicine. The doctoral student demonstrated good scientific work and published his results sufficiently. He is the co-author of 22 articles in impact journals (11 of them as the main author), 6 chapters in books and presented his results at international conferences.

I also appreciate the proposal for the future direction of further research.

My questions:

1. Why do you choose knitted fabric with Polyamide for Triboelectric generators?
2. Is the difference between deposition of metal particles on cotton and polyamide surface?
3. Did you measure electrical resistivity dependence of number of repeated extensions for silver electroplated knitted fabrics?
4. Did you determine values of durability under washing for higher temperature than 40 degree Celsius?
5. Could you explain increasing standard deviation during increasing Extension presented on Figure 64b, p. 80?

In conclusion, I **recommend** this thesis for the defense.

In Pardubice on July 8, 2020

Ing. Michal Černý, Ph.D.

TECHNICAL UNIVERSITY OF LIBEREC
Faculty of Textile Engineering

Referee´s report on PhD. thesis of

Azam Ali

„ Surface Deposition of Metals on Textile Structures “

Professor Miroslav Černík

The presented thesis consists of 106 pages divided into 7 chapters. The thesis´s main objective was to investigate the preparation, properties and applications of surface-modified textiles with electrical conductivity, EMI shielding, ohmic heating capability, and antibacterial properties. The thesis has standard parts - Introduction, Thesis objectives, Literature review, Methodology, Results and discussions, Conclusions and Future works. In the end, there are References and a List of author´s publications. The author´s list of publications is extensive.

First pages
Before the introduction, there are Contents, List of tables, List of figures, List of abbreviations, and List of symbols. The last two lists are incomplete, and the list of symbols contains only 4 symbols, and even very strange.

Thesis significance, scope and objectives
The author made here an introduction to his work and explained the objectives of the study. The work was split into four major parts – an deposition of Cu particles on plain woven cotton fabrics; an deposition of Ag particles on cotton fabric and knitted fabric; electroless platting on NPs coated woven fabrics; development of tribo-electic generators for energy harvesting (platting of Ag on stretchable knitted fabrics). Unfortunately, these topics look as four various subjects without any unification bridge.

Literature review
There is a sufficient number of literature sources divided into ten parts. Even the whole chapter is well written, some parts and Figures are disputable. Directly, Fig.1 shows a range of electric resistivity for different materials, but the ranges are too broad to me (e.g., metals are always in a range of 10^{-5} or smaller resistivity, not from the value in the presented interval); Fig. 2 shows just basis of Ohm´s law, which is too basic for the PhD. thesis. Part 3.5 (Research on electrically conductive metalized fabric) presents many figures. I think the literature part should explain previous work and the most critical literature findings related to the topic. It should not repeat figures published previously (at least in such quantity).

Methodology
There is a vast variety of methods used for the preparation, characterization and application of the fabrics. Four different materials were prepared – Cu particles on textiles, Ag particles on textiles, Cu plating on coated fabrics and electrode Ag plating. There are other methods like antibacterial testing, heating performance, and durability besides electric and electromagnetic testing. I am not sure if all these methods are essential for the final topic of the thesis.

Results and discussions
The chapter summarizes all results of the thesis. For each conductive structure, several measurement was performed – electric conductivity, SEM analysis, mechanisms of attachment,

electromagnetic shielding, antimicrobial properties, and durability of fabrics. Figure 33 repeats the scheme of Fig.22, and again in the chemical formulae, the student shows an ignorance of basic chemical nomenclature (Cu^{+2}, etc.). His knowledge of chemistry, based on many errors in the text, is too basic.

Conclusions

This chapter summarizes the findings of the previous chapters. The author repeated major conclusions for each material, but generalization of the results and especially comparing different techniques is missing. I expected more conclusions from the study – get advantages and drawbacks of each technique and their detailed comparison from various points of view. The future work planned here is also in terms of individual studies of particular techniques.

Referee remarks, question and conclusions

QUESTIONS

1. Prior deposition of Ag particles, cotton fabric was dipped into NaOH. According to Fig. 23, for this pretreatment Na^+ ions are essential. Why? What were the mechanisms of this step?
2. Antibacterial tests in Fig. 36: Has the student performed the tests? Describe details about the 95% confidence interval. Was is determined from the repetition of the experiments? How many parallel experiments have you carried out? Are the error bars calculated separately for each of the values?
3. Equation (9) and (10): I do not understand these equations? Could you give an example, how equation (9) works? The stability constant equation is also wrong.
4. Cathode reactions mentioned on page 79 considers the complete deprotonation of EDTA. This deprotonation depends on the solution pH. At which conditions, such a situation appears?

Imperfections and recommendations

The thesis is written in good English but with significant typing errors.
Example on p.13: Micrometric metal are did not cause…; nanoparticles are shown displayed in…; was dip. Chemical formulae are sometimes wrongly written (e.g., p.18, Cu^{+2}, SO_4^{-2}, e for electron w/o the negative charge).

Referee´s conclusion

The presented thesis of Azam Ali has all the formal parts and shows the author is able to carry out scientific work. The thesis shows four different techniques of fabrics´ surface modification, various characterization techniques and potential applications. The work significantly contributes to knowledge in the subject. The work´s fundamental disadvantage is in fragmentation, where the general idea is the application of various techniques, but without their comparison and generalization. The author also showed a problem with the understanding of chemical processes applied in the thesis. The language is acceptable and entirely understandable.

Besides imperfections, errors and weak points, the thesis meets the criteria to be taken to the defense.

Miroslav Černý

In Liberec (Czech R.) on February 14, 2021

Professor Miroslav Černík