Fibre Interface Molecular Engineering for Textile-based Wearable Electronics

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<th>Abbreviation</th>
<th>Text</th>
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<tbody>
<tr>
<td>ELD</td>
<td>electroless deposition</td>
</tr>
<tr>
<td>PAMD</td>
<td>polymer-assisted metal deposition</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>TA</td>
<td>tannic acid</td>
</tr>
<tr>
<td>PDA</td>
<td>polydopamine</td>
</tr>
<tr>
<td>PU</td>
<td>polyurethane</td>
</tr>
<tr>
<td>ICP</td>
<td>Inherently conducting polymer</td>
</tr>
<tr>
<td>PPy</td>
<td>polypyrrole</td>
</tr>
<tr>
<td>PANI</td>
<td>polyaniline</td>
</tr>
<tr>
<td>PA</td>
<td>polyacetylene</td>
</tr>
<tr>
<td>PTh</td>
<td>polythiophene</td>
</tr>
<tr>
<td>PVA</td>
<td>polyvinyl alcohol</td>
</tr>
<tr>
<td>PET</td>
<td>polyethylene terephthalate</td>
</tr>
<tr>
<td>SI-ATRP</td>
<td>surface-initiated atom-transfer radical polymerisation</td>
</tr>
<tr>
<td>FRP</td>
<td>free radical polymerisation</td>
</tr>
<tr>
<td>PMETAC</td>
<td>poly[2-(methacryloyloxy)-ethyl]-trimethylammonium chloride</td>
</tr>
<tr>
<td>PAA</td>
<td>poly(acrylic acid)</td>
</tr>
<tr>
<td>PVBVN</td>
<td>poly[1,1'-bis(4-vinylbenzyl)-4,4'-bipyridinium-dinitrate]</td>
</tr>
<tr>
<td>PMEP</td>
<td>poly(methacryloyl-ethyl phosphate)</td>
</tr>
<tr>
<td>P4VP</td>
<td>poly(4-vinylpyridine)</td>
</tr>
<tr>
<td>VTMS</td>
<td>vinyltrimethoxysilane</td>
</tr>
<tr>
<td>PAN</td>
<td>polyacrylonitrile</td>
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<tr>
<td>PI</td>
<td>polyimide</td>
</tr>
<tr>
<td>PS-b-PtBA</td>
<td>polystyrene-b-poly(tert-butyl acrylate)</td>
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<tr>
<td>Abbreviation</td>
<td>Full Name</td>
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<tr>
<td>--------------</td>
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<tr>
<td>PTFE</td>
<td>poly(tetrafluoroethylene)</td>
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<tr>
<td>PVDF</td>
<td>poly(vinydene fluoride)</td>
</tr>
<tr>
<td>FEP</td>
<td>poly(tetrafluoroethylene-co-hexafluoropropylene)</td>
</tr>
<tr>
<td>PEG</td>
<td>poly(ethylene glycol)</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate)</td>
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<tr>
<td>PDMS</td>
<td>polydimethylsiloxane</td>
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Abstract

Textile-based wearable electronics, as the next generation of wearable devices, have attracted considerable interest. Conductive fibres are the building blocks for developing these flexible and wearable devices. Electroless deposition (ELD) is a traditional method to deposit metal nanoparticles on different materials by autocatalytic chemical reduction of metal cations in a liquid bath. However, there are no catalytic sites on the fibre surface to initiate the ELD. To solve this problem, this research aims to coat polyphenols including dopamine, tannic acid and curcumin on the fibre surface via π-π stacking and then served as the platform to capture catalysts via cation-π interaction for depositing metal nanoparticles on fibres.

By introducing the polyphenols-assisted ELD, conductive yarns and fabrics were obtained and the resistance of Ni-coated cotton yarns reached 0.05 Ω/cm. The fibre interface molecular engineering provided strong adhesion forces between the metal layer and the fibre surface, resulting in durable metal-coated yarns and fabrics. On the other hand, the surface morphology of metal deposits on fibres was controlled in nanoscale by adjusting the ELD time to yield the metal coatings with multilayers shape on fibre surface in which unfilled gaps between metal nanoparticles prevented the metal films from cracking under bending. In addition, the Kelvin structure model was proposed to illustrate the relationship between the conductivity and flexibility of metal-plated fabrics. As a result, the normalised resistance of Ni-deposited fabrics (20 min ELD) was only 1.6 after 1000 mechanical bending cycles (bending radius = 0.1 mm). To construct these metallised substrates into wearable sensors, the fibrous structure was utilised. Based on the change of fibre-to-fibre contacts in metal-coated yarns and 3D fibrous sponges under mechanical deformations, fibre-shaped wearable electronics including finger bending sensors, arm bending sensors, pressure sensors, touch sensors and human-machine interfaces for monitoring human motions were obtained by collecting different resistance values. The research indicated that polyphenols-assisted ELD can metallise other flexible substrates and extend the applications of conductive and flexible samples.
Declaration

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Preface to the Alternative Format Thesis

This thesis is presented in the University of Manchester’s alternative format for a PhD thesis. This style is chosen as it most clearly demonstrates the different aspects of the conducted research. The structure consists of an introduction, literature review, research strategy and methodology, descriptions of the published papers, collections of papers, discussions on papers and conclusions with suggestions for future work. To aid the reader, references from the introduction and literature review are collected at the end of the thesis. The alternative format allows the writing of the thesis to be conducted in parallel with produced papers for publication.
Acknowledgements

Firstly, I would like to express my sincere gratitude to my main supervisor, Dr Xuqing Liu for his patience, creative thinking and immense knowledge. Through countless examples, he taught me the most important criterion for a qualified researcher is being critically thinking and daring to question authorities scientifically. He also taught me how to rationally make and follow plans and being precise with parameters of experiments and format of writings. My PhD study would be less organised without him.

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Most importantly, I give the most appreciation to my family for their tremendous support. Without their encouragement and love, it is impossible to complete this project successfully.
Chapter 1. Introduction
1.1 Introduction

In recent years, textile-based wearable electronics such as fabric antennas, fibre-shaped energy harvesting and storage devices, fibre-enabled sensors, fibre-based displays and fibre actuators have attracted considerable attention due to the lightweight, flexibility and conformable property of textiles. To develop these engineering prototypes, one critical step is the fabrication of conductive fibres that are the upstream materials of fibre-based wearable devices. In accordance to the structure of conductive fibres, they can be divided into three subclasses: intrinsically conductive fibres, hybrid conductive fibres and nanocoated conductive fibres. Intrinsically conductive fibres such as metal wires, conductive polymer fibres and carbon-based fibres are fibrous materials with inherent conductivity. Metal fibres, fabricated by using tensile forces to stretch metals, own low resistivity. For example, the resistivity of Cu at 20 °C is $1.68 \times 10^{-8} \Omega \cdot \text{cm}$. However, metallic filaments are stiff and rigid, leading to the increased resistance of fibre-shaped electronics after repeated bending cycles. Conductive polymer fibres, synthesized from inherently conducting polymers (ICPs) including polypyrrole (PPy), polyaniline (PANI), polyacetylene (PA), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and polythiophene (PTh) via solution spinning, are inherently flexible and can be tuned to have specially tailored chemical, physical and electronic properties by molecular design. Nevertheless, compared with metals, the resistivity of conducting polymer fibres is relatively high. For instance, according to the report of Foroughi and co-workers, the resistivity of continuous PPy fibres is only $3 \times 10^4 \Omega \cdot \text{cm}$. Carbonaceous fibres such as carbon nanotube (CNT) fibres, graphene fibres and carbon fibres present advantages over metal wires and conducting polymer fibres. In detail, carbon-based fibres are more flexible than metal fibres and have lower resistivity ($1 \times 10^4 \Omega \cdot \text{cm}$) than conducting polymer fibres. Despite that, the production of CNT and graphene fibres is still in the laboratory scale and the intrinsic black colour of carbon fibres hampers the aesthetic applications. Hybrid conductive fibres made of inherently conductive fibres and nonconductive
polymeric fibres can be fabricated by different techniques including spinning, drawing and filling. Spinning is to directly blend metal filaments into textile yarns. For example, Perumalraj et al.\textsuperscript{29} produced Cu-cotton fibres by wrapping Cu wires with cotton fibres as the sheath material via friction spinning. However, hybrid yarns with this structure are less flexible than the raw cotton yarns due to the presence of the metallic core. Fibre-drawing process is to embed metal or alloy wires into a polymer fibre. For instance, Mazhorova et al.\textsuperscript{30} manufactured a hybrid conductive fibre with the alloy core and polycarbonate cladding by firstly filling liquid melt of bismuth-tin alloy (melting temperature \(\sim 140 \degree C\)) into a polycarbonate tube to produce a fibre preform, followed by a heating-and-drawing step in a scientific polymer-fibre-drawing tower. Nevertheless, this method requires that metal or alloy components in these fibres should have a melting temperature similar to that of polymer materials. Filling is to disperse conductive particles such as CNT, carbon black and conducting polymers into textile yarns. For example, Xue et al.\textsuperscript{31} fabricated conductive polyvinyl alcohol (PVA) fibres with CNT fillers by wet-spinning the PVA/CNTs solution. However, the homogeneous dispersing of conductive fillers into nonconductive polymers is hard to achieve, causing the relatively high resistance of the resultant fibres (250 \(\Omega/cm\)).

Nanocoated conductive fibres are produced by depositing conductive nanomaterials (serving as conductive pathways for transferring electrons) on fibre substrates (playing roles of soft backbones). In general, conductive nanocoating strategy consists of two parts: coating materials and fabrication technologies. For coating nanoparticles, although several inherently conductive candidates such as ICPs,\textsuperscript{32-34} CNTs,\textsuperscript{35} graphene\textsuperscript{36,37} and carbon black\textsuperscript{38} have been developed in recent decades, metal is still considered as the best material in terms of conductivity, stability, compatibility and cost.\textsuperscript{39-41} For example, the normalised conductivity/cost ratio of Ni (1.4 \(\times 10^{-2}\)) is much higher than PEDOT/PSS (1.3 \(\times 10^{-8}\)) and graphite (8 \(\times 10^{-4}\)).\textsuperscript{42} For textile metallisation methods, compared with physical vapour deposition (PVD),\textsuperscript{43} chemical vapour deposition (CVD)\textsuperscript{44} and electrodeposition,\textsuperscript{45} electroless deposition (ELD) is particularly attractive because it can deposit uniform, continuous and compact metallic
nanoparticles on both the outer and inner surfaces of fibre assemblies without the use of vacuum chamber (required in PVD and CVD) and external electricity (needed in electrodeposition).\textsuperscript{46} In detail, ELD is an autocatalytic redox chemical reaction in which metal cations in the metal salt solution are reduced into metallic nanoparticles and coated on the catalytically active surface sites of the substrate at ambient environments.\textsuperscript{47} However, metal films would be easily delaminated from polymeric substrates if catalysts were captured on the flexible surfaces via weak physisorption. Thus, to strongly immobilise catalysts on fibres, the fibre interface molecular engineering (FIME) strategy that focuses on surface modification of fibres is essential because the designed fibre interface not only plays a role of the adhesive interfacial layer between metal nanoparticles and fibres via covalent bonds or other tethering forces, but also enhances the uptake efficiency and selectivity of catalysts.\textsuperscript{48} Based on these advantages, polymer-assisted metal deposition (PAMD) that includes FIME, catalysts absorption and ELD of metal nanoparticles is widely used to metallise fibres (Figure 1).\textsuperscript{49} In the FIME step, different methods such as etching,\textsuperscript{50} irradiation,\textsuperscript{51} and plasma activation\textsuperscript{52} have been used to graft polymers on fibres. Nevertheless, these modification processes involve complex steps and are limited with strict reaction conditions. In addition, these approaches cause damage to raw fibres by changing surface chemical groups of fibres. To address these problems, this research developed a simple, versatile and non-destructive fibre modification process to assist ELD for fabricating conductive fibres and fibre-based wearable electronics.

Figure 1. The conventional process for PAMD. Briefly, the polymers are firstly grown from a fibre substrate, followed by anchoring the catalyst, and finally a thin metal layer is formed on the catalysed areas in the ELD bath.\textsuperscript{49}
1.2 Aim and Objectives

The main aim of this project is to fabricate durable metal-coated yarns and fabrics for textile-based wearable electronics. In order to achieve the aim, the objectives of this research are as follows:

• The first objective was to develop fibre interfaces that can be directly attached to different fibre surfaces by using a simple and non-destructive method at ambient environments for capturing catalysts and then initiating electroless deposition (ELD) of metals on fibres. To fabricate conductive yarns and fabrics, the chemical properties of surface-modified and catalyst-absorbed fibres, mechanical and electrical properties of metal-coated yarns were studied.

1. The chemical structure of fibres after fibre interface molecular engineering (FIME) and catalyst absorption was to be determined respectively.
2. The surface morphology and the resistance value of metal-coated yarns at different ELD times were to be investigated.
3. The durability and the electrical performance of metal-plated yarns were to be inspected to study the implementation of conductive yarns for playing a role of interconnects in a circuit and monitoring human finger motions.

• The second objective was to combine ELD with screen printing for fabricating patterned conductive fabrics. To develop conductive patterns on fabrics, different printing gels, the effect of printed metal pattern on fabric and electrical properties of the partially metal-coated fabric were examined.

1. Recipes of different printing strategies by adjusting the volume of deionised water, catalyst and polymer in the gel were to be inspected.
2. The surface morphology of the patterned conductive fabric was to be explored.
3. The human finger touch sensing performance of the partially metallised fabric was to be tested.

• The third objective was to produce 3D conductive fibrous sponges that could be utilised for tracking the external pressure and movements of the human arm. To yield conductive sponges, the chemical properties of polymer-modified and catalyst-
anchored sponges, mechanical and electrical properties of metal-coated sponges were discussed.

1. The chemical structure of fibrous sponge after surface modification and catalyst immobilisation was to be investigated, respectively.

2. The surface morphology of metal-coated sponge was to be studied.

3. The durability of metal-coated sponges at different ELD times and their sensory attributes related to pressure as well as bending were to be determined for examining the functions of conductive sponges to detect external pressure and human arm bending.

• The fourth objective was to construct human-machine interface (HMI) textiles by integrating metal-coated stretchable yarns with signal processing units. To prepare stretchable and flexible HMIs, the chemical properties of surface-modified and catalyst-captured core-spun yarns, mechanical and electrical properties of metal-based composite yarns were inspected.

1. The surface chemical composition of covered yarns after the growth of fibre interface and anchoring of catalysts was to be characterised, respectively.

2. The surface morphology of metal-coated core-sheath filament was to be explored.

3. The durability, mechanical properties and strain-sensing behaviour of metallised compound yarns with the core-wrap structure were to be investigated for demonstrating the HMI application.
1.3 Novelty of the Research

The novelty of this research is to employ polyphenols as the fibre interfaces to modify fibre surface and immobilise catalysts for the electroless deposition (ELD) of metal nanoparticles on fibres. Based on the polyphenols-assisted ELD method, some key findings were proposed in this project. Firstly, the resultant metal-coated yarns and fabrics were very durable under mechanical deformations including bending, stretching and hand washing because the designed fibre interface provided tethering forces between the metal layer and the fibre surface. Secondly, the morphology of deposited metal nanoparticles on the fibre surface was successfully illustrated by using the Kelvin structure model. Thirdly, the growth of metal nanoparticles on fibres was controlled by adjusting the ELD time to optimise the flexibility and conductivity of metal-coated fibres for the first time. Fourthly, screen printing technique was combined with polyphenols-assisted ELD in a successful manner to produce the fabrics with metal patterns for detecting the touch of human fingers. Fifthly, the successful fabrication of fibre-based wearable sensors that could monitor finger movements, external pressures and arm bending was achieved because the change of fibre-to-fibre contact in the metallised yarns and the 3D fibrous sponges under mechanical deformations resulted in the varied resistance signals.
1.4 Thesis Layout

Followed by the introduction, Chapter 2 reviews different polymer interfaces and catalytic sources in polymer-assisted metal deposition (PAMD) method, patterned metal conductors by combining PAMD with printing techniques, PAMD on different substrates and their applications. After reviewing the previous works, the research gaps are addressed in section 2.4.

Chapter 3 is research strategy and methodology. Different fibres are firstly coated with dopamine in tris buffer, tannic acid in deionised water and curcumin in ethanol, respectively. Palladium ions are then captured by surface-modified fibres in the catalytic solution. Finally, Ni or Cu nanoparticles are deposited on catalytic fibres in the ELD bath. Various characterisation techniques including Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), X-ray diffraction (XRD), tensile test and 2-point resistance measurement are reviewed.

Chapter 4 is the descriptions of published papers, in which the basic information of published papers and the contribution of authors are discussed.


Chapter 6 is the discussion on the papers. The novelty of each research paper is studied and the important results of these research papers are critically analysed.

Chapter 7 concludes the thesis and future work is recommended in this chapter.
Chapter 2. Literature Review
2.1 Polymer Interface and Catalytic Moiety for PAMD

The surface-grafted polymer plays an important role in polymer-assisted metal deposition (PAMD) for fabricating robust and high-performance metallic yarns and fabrics because it allows the establishment of a stable metal/textile interfacial structure to ease the mechanical mismatch between rigid metal layers and flexible fibre surfaces. In the past decades, many advances have been made to develop polymer interfaces as powerful anchoring layers for absorbing catalytic moieties and then activating electroless deposition (ELD) on substrates. Several surface modification methods such as surface-initiated atom-transfer radical polymerisation (SI-ATRP),\textsuperscript{53} in-situ free radical polymerisation (FRP),\textsuperscript{54} self-crosslinking polymerisation,\textsuperscript{55} plasma,\textsuperscript{56} and radiation-induced polymerisation\textsuperscript{57} have been employed to graft polymers on flexible substrates including polymeric films\textsuperscript{58} and textiles\textsuperscript{59}. Compared with self-assembled monolayers,\textsuperscript{60} polymers can provide a large number of binding sites along the polymer chains for immobilising catalytic moieties, resulting in the significantly increased rate of ELD with high concentration of the applied catalyst. More importantly, these polymers with multilayers can interpenetrate the network of deposited metal nanoparticles in ELD to enhance the mechanical stability of metal-deposited samples.\textsuperscript{61} Different kinds of polymers (cationic, anionic and nonionic) are discussed in the subsections below. In each subsection, the synthetic method of the grafted polymer and the ELD process are elaborated.
2.1.1 Cationic Polymer Interface and Catalytic Moiety

Cationic polymer interfaces are defined as positively charged polyelectrolytes which have strong affinity to capture catalytic anions in an aqueous solution for electroless deposition (ELD). Examples of cationic polymers are poly[2-(methacryloyloxy)-ethyl]-trimethylammonium chloride (PMETAC) and poly[1,1′-bis(4-vinylbenzyl)-4,4′-bipyridinium-dinitrate] (PVBVN), with chemical structures illustrated in Figure 2.

Figure 2. Chemical structures of two cationic polymers: (a) PMETAC and (b) PVBVN.

PMETAC is the most widely reported cationic polymer for polymer-assisted metal deposition (PAMD). The group of Zheng reviewed the mechanism of PMETAC-assisted ELD on textiles, as shown in Figure 3. In the first step, the pristine fibre surface is modified with a layer of functional organosilane initiators by self-assembly for the subsequent surface-initiated polymer brush grafting. Generally, surfaces with hydroxyl or oxide groups can be spontaneously reacted with silane. However, man-made fibres such as nylon and polyethylene terephthalate (PET) do not possess such groups on the surface. Therefore, prior to the silane deposition, exposing them to oxygen plasma is required to render the surface hydrophilic. After silane modification on fibre surface, the “Grafting-from” strategy that involves mainly two polymerisations [surface-initiated atom transfer radical polymerisation (SI-ATRP) and in-situ free radical polymerisation (FRP)] for the growth of polymer chains from silane-modified surface, is usually adopted to ensure the high brush grafting density of PMETAC brushes. PMETAC brushes are assemblies of macromolecular chains covalently tethered one end on a substrate surface and with sufficiently high grafting density of polymer brushes, these chains are forced to be stretched away from the tethered sites on the surface of the target substrate to form a brush-like configuration, in which a large number of
functional groups on polymer chains can be further utilised in the subsequent chemical reactions. To decide which polymerisation for brush grafting, the type of silane deposited in the first step needs to be identified. When Br-terminating silane initiator is plated on fibre surface, SI-ATRP is used to grow polymer chains. In typical SI-ATRP, free radical species generated from the oxidation of the metal ligand that concomitantly abstracts the halogen atom from the initiator attack monomers and subsequently trigger polymer chain propagation. Advantages of SI-ATRP include a high level of control over polymer graft architecture and grafting density. When vinyl-terminating silane is plated on fibre surface, in-situ FRP is used to grow polymer chains. Typical in-situ FRP involves free radical species generated by thermal decomposition or photolysis of the initiator attack monomers and then allow polymer chains to propagate. One advantage of in-situ FRP is that it is capable of producing brush-grafted fibres in a large scale because the whole grafting process is conducted at ambient conditions. After the formation of brushes on fibre surface, $[\text{PdCl}_4]^{2-}$ ions are captured by the PMETAC-grafted fibre via ion exchange because quaternary ammonium groups in the PMETAC brushes have high affinity toward $[\text{PdCl}_4]^{2-}$. In the final step, palladium-bearing species loaded fibres are immersed into the ELD bath for the metal deposition, where areas anchored with catalytic moieties act as effective sites for depositing conformal metal films. Cu and Ni are mostly reported metals in the PMETAC-assisted ELD strategy due to their relatively low cost comparing to Ag and Au. It should be noted that PMETAC brushes show a particular ability to control the amount of anchored $[\text{PdCl}_4]^{2-}$ by simply changing the concentration of $[\text{PdCl}_4]^{2-}$ and the loading amount of catalytic moieties can highly affect the quality and thickness of the deposited metal layers. Although PMETAC brushes exhibit the ability to conduct ELD on textiles, complex steps such as plasma treatment and silane deposition are needed in the modification process. In addition, the vacuum chamber for oxygen plasma treatment is required and the plasma treatment damages fibre structure because it changes the surface chemistry of fibres by adding oxygen groups.
Figure 3. Typical PMETAC brushes assisted ELD on a textile substrate. (a) A raw textile is modified with a layer of functional organosilane, as illustrated in (b). (c) The grafting of polymer brushes from organosilane-modified textile surface by SI-ATRP or in-situ FRP. (d) Anchoring of catalytic moieties on brushes. (e) ELD on catalysed areas. (f) The illustration of metal layers on a textile.\(^{63}\)

Cui et al.\(^{69}\) demonstrated the successful grafting of PVBVN on the polyimide (PI) surface for the fabrication of Ag-coated PI films (Figure 4). In detail, Ar-plasma treatment was firstly conducted on PI films, which were then exposed to the air to form peroxides and hydroperoxides on the PI surface. Subsequently, PVBVN brushes were grafted on the surface-modified PI films via UV-induced copolymerisation of VBVN. Finally, PVBVN-grafted PI films were immersed into the silver nitrate solution and
exposed to UV irradiation in which conformal and uniform Ag layers were coated on the PI surface without a plating bath because viologen derivatives on PVBVN brushes undergo the photo-induced reduction of silver ions in the silver salt solution. Nevertheless, the influence of UV irradiation is difficult to control (for example, eye and skin problems to experimental users). Moreover, Ar-plasma treatment damages the surface structure of PI film and the vacuum chamber is required for this technique.

Figure 4. The schematic illustration of the fabrication process of PVBVN-assisted ELD to coat Ag nanoparticles on the PI film.  

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2.1.2 Anionic Polymer Interface and Catalytic Moiety

The anionic polymer interfaces are defined as negatively charged polyelectrolytes which can immobilise the catalytic cations in the aqueous solution for electroless deposition (ELD). Examples of anionic polymer matrixes include poly(acrylic acid) (PAA) and poly(methacryloyl-ethyl phosphate) (PMEP), with chemical structures illustrated in Figure 5.

![Chemical structures of two anionic polymer interfaces: (a) PAA and (b) PMEP.](image)

Kobersterin et al.\(^7\) proposed the surface-grafted PAA for Ni ELD by using \([\text{Pd(NH}_3\text{)}_4]^2^+\) as catalytic moieties (Figure 6). In this report, a di-block copolymer, polystyrene-b-poly(tert-butyl acrylate) (PS-b-PtBA), was firstly spin-coated on the surface of a PS substrate and the self-assembly process was promoted by annealing at 100 °C under vacuum in which the PS chains in the di-block copolymer interpenetrated the PS substrate. A photoacid generator was then used to photochemically pattern the surface-modified PS substrate under UV irradiation through a shadow mask, leading to the regions of hydrolysed PAA and unhydrolyzed PtBA because of the photocleavage of tert-butyl ester to carboxylic acid. Finally, the PAA blocks grafted PS substrate were used to site-selectively immobilise \([\text{Pd(NH}_3\text{)}_4]^2^+\) for depositing Ni pattern on the PS substrate in the ELD bath. However, this method is limited by the specifically synthesised block copolymer (the first block must be the same as the polymeric substrate). Furthermore, the requirement of UV irradiation and vacuum atmosphere increases the cost of the modification process and the adverse effects of UV light on the human body are undesirable. Besides, the high temperature (100 °C) at annealing is energy-consuming.
Figure 6. The schematic illustration of PAA-assisted Ni ELD. (a) Self-assembly of PS-b-PtBA on a PS substrate. (b) UV-induced PAA grafting on PS-b-PtBA modified PS through a contact mask. (c) The selective anchoring of \([\text{Pd(NH}_3]_4]^2+\) ions on PAA-grafted PS. (d) The selective deposition of Ni nanoparticles on PS.\(^{70}\)

Garcia et al.\(^{71}\) reported the ligand induced electroless plating (LIEP) of Cu on different polymeric substrates such as PS, acrylonitrile–butadiene-styrene (ABS) and polybutadiene (PB) by PAA enabling ELD (Figure 7). In detail, PAA brushes were firstly covalently-grafted on the target substrate by the GraftFast technique. In GraftFast, aryl diazonium salts were reduced in the presence of iron powder to generate surface-active aryl radicals, leading to the initiation of the radical polymerisation of the vinylic monomer in the monomer solution.\(^{72}\) The PAA-modified substrate was then immersed into the Cu\(^{2+}\) source, in which carboxylate groups in PAA brushes allowed the chelation of metal cations. Subsequently, sodium borohydride was used as a reducing agent to
reduce chelated Cu\textsuperscript{2+} ions into Cu\textsuperscript{0} catalytic seeds that were absorbed on the brushes. Finally, these metal seeds acted as efficient catalysts to initiate the growth of copper particles on substrates in the ELD bath. Despite that this strategy eliminates the use of costly palladium-bearing catalyst, the adding of extra reductant can cause the nonuniform and large-size metal seeds, leading to the poor catalytic performance of the catalyst-immobilised substrate in the ELD bath.\textsuperscript{73}

Figure 7. The schematic illustration of PAA-assisted ELD for depositing Cu nanoparticles on the surface of PS, ABS and PB.\textsuperscript{71}

Liu et al.\textsuperscript{74} reported the PMEP-assisted ELD for manufacturing bimetallic layers on a silicon wafer. In detail, microcontact printing was used to graft binary polymer brushes consisting of two oppositely charged polyelectrolytes [PMEP and poly[2-(methacryloyloxy)-ethyl]-trimethylammonium chloride (PMETAC)] by surface-initiated atom transfer radical polymerisation (SI-ATRP) on the target substrate. The quaternary ammonium groups in positively charged PMETAC showed strong affinity to [PdCl\textsubscript{4}]\textsuperscript{2−} species and the phosphate groups in negatively charged PMEP could anchor [Pd(NH\textsubscript{3})\textsubscript{4}]\textsuperscript{2+} species. The ion-paring-oriented binding not only guarantees a large amount of catalysts for efficient metal deposition but also diminishes nonspecific absorption by neighbouring component, which is essential for fabricating highly selective bimetallic patterns. Based on this unique property, oppositely charged catalytic-active metal ions were then captured by the binary polyelectrolyte brushes modified sample, respectively, and used for the subsequent site-selective ELD of two different metals (Cu and Ni), as shown in Figure 8. Nevertheless, the nitrogen protection
throughout the entire polymerisation in SI-ATRP technique for coating PMETAC and PMEP chains on fibres limits the large-scale production of metallised samples and the SI-ATRP process is time-consuming (24 h).\textsuperscript{75}

Figure 8. The schematic illustration of binary polyelectrolyte brushes for the selective uptake of palladium seeds to activate the subsequent ELD of Cu and Ni on the silicon wafer.\textsuperscript{74}
2.1.3 Nonionic Polymer Interface and Catalytic Moiety

Apart from the ionic polymer interfaces mentioned above, nonionic polymer brushes which are neutrally charged polyelectrolytes in an aqueous solution possess special functional groups with binding mechanism for anchoring catalytic moieties and subsequently initiating the electroless deposition (ELD) even though they are non-charge-bearing. Examples of nonionic polymer interfaces are poly(4-vinylpyridine) (P4VP) and polyacrylonitrile (PAN), with chemical structures illustrated in Figure 9.

![Chemical structures of two nonionic polymer brushes: (a) P4VP and (b) PAN.](image)

Yang et al.\textsuperscript{76} demonstrated the P4VP-assisted ELD of Ni on poly(vinylidene fluoride) (PVDF) and poly(tetrafluoroethylene) (PTFE) films (Figure 10). In detail, fluoropolymer films were firstly pre-treated with Ar plasma and then exposed to air to facilitate the formation of peroxides and hydroperoxides on the target surfaces. P4VP polymer chains were subsequently grafted on the films via UV-induced grafting copolymerisation. Surface-modified substrates were then immersed into the PdCl\textsubscript{2} solution, in which palladium species complexed with the nitrogen moiety in the pyridine ring on the P4VP brushes, resulting in the strong chemisorption of palladium species on the grafted polymer brushes. Finally, Ni ELD bath was conducted on the catalytic samples to allow the growth of Ni nanoparticles on PVDF or PTFE. However, this method still requires UV irradiation and Ar plasma treatment, leading to the use of additional instruments, damage to substrate surface and potential health problems to UV light users.
Yu et al.\textsuperscript{77} reported the PAN-assisted ELD via UV radiation to fabricate Cu-deposited poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) films (Figure 11). In detail, Ar plasma treatment was firstly used to modify the substrate surface and the plasma-treated FEP film was then exposed to air to form functional groups for copolymerising with the PAN brushes under UV irradiation. Due to the lack of chemical groups on PAN chains to anchor catalysts for ELD, cyano groups on the PAN-grafted surface were subsequently amidoximated by using hydroxylamine hydrochloride to introduce amidoxime groups on the sample, which were capable of complexing with palladium species. Next, the amidoximated PAN brushes were subjected to sensitisation in SnCl\textsubscript{2} solution, followed by activation in the PdCl\textsubscript{2} solution for yielding a conformal copper layer on the substrate surface in the ELD bath. Nevertheless, this approach needs Ar plasma and UV light to complete the surface modification of PAN brushes on FEP film. In addition, extra steps including the introducing of amidoximated groups on PAN brushes and sensitisation are required before anchoring catalysts.
Figure 11. The schematic illustration of PAN-assisted ELD to deposit Cu nanoparticles on the FEP film.\textsuperscript{77}
2.2. Metal Pattern on Textile with PAMD

Based on the discussion in Section 2.1, metallised textiles can be theoretically fabricated by using polymer-assisted metal deposition (PAMD) for different applications including electromagnetic shielding, electrostatic discharge and conductive wires. Nevertheless, textile substrates coated with metal patterns are always demanded for constructing flexible electronic circuits. To print precise metal tracks on textile surfaces, resist-based lithographic techniques that have been developed for a long time in semiconductor industries should be considered. These methods involve multiple steps such as etching, masking, resist patterning, life-off and annealing. Nonetheless, these techniques are incompatible with textiles because most polymeric fibre substrates cannot withstand the harsh chemical environment in the etching solution and the high temperature in the annealing step (~900 °C). Concerning the difficulties to use transitional patterning methods for fabricating metal-printed textiles, recently, the roll-to-rolling printing with the continuous manner and the high throughput, to realise the great production capacity of patterned conductive textiles, comes into the spotlights because it is fast, accurate and less facility-demanded (only printing equipment is required). In the textile industry, the printing sectors are in fact well-established, especially the fabrication of different patterns on fabrics by using screen printing and inkjet printing. PAMD is also capable of manufacturing patterned metal-coated fabrics by printing techniques, which can be realised by either two strategies: catalytic moiety ink patterning or copolymer ink patterning.
2.2.1 Catalytic Moiety Ink Patterning

The catalytic moiety ink patterning strategy is to pattern the catalytic moieties that are responsible for growing metallic traces on textile substrates. Figure 12 shows the mechanism of this approach that only the areas immobilised with catalysts can result in metal deposition to yield well-defined metal coatings on fabrics. In the first step, the pristine fibre substrate is coated with a layer of functional organosilane, followed by grafting of polymer brushes from the organosilane initiators. Printing of ink containing catalytic moieties is then conducted on the brushes-modified substrate. Catalysts then diffuse from the ink to the polymer brushes and subsequently the localised brush area is loaded with catalytic moieties. Finally, electroless deposition (ELD) is used to obtain patterned metal coatings on the surface of textile.
Figure 12. The schematic illustration of the catalytic moiety ink patterning strategy for manufacturing metal patterns on textiles. (a) Raw textile substrate is plated with a layer of functional organosilane as shown in (b). (c) The grafting of polymer brushes from the organosilane initiators. (d) Ink that contains catalytic moieties is subsequently printed on the textile and catalytic moieties then diffuse from the ink to the grafted polymer chains. After diffusion, localised brush area is loaded with catalytic moieties. (e) ELD is conducted to obtain patterned metal nanoparticles on the textile surface to manufacture printed metal layer on the textile as shown in (f).

To apply this strategy for the fabrication the well-defined metal pattern on textiles, the catalytic moieties must be prepared as printable ink with suitable viscosity for different printing techniques such as screen printing and inkjet printing. Guo et al. reported the matrix-assisted catalytic printing for the fabrication of patterned metal conductors on flexible substrates (Figure 13a). In this study, poly(ethylene glycol) (PEG), poly[2-(methacryloyloxy)-ethyl]-trimethylammonium chloride (PMETAC) and [PdCl4]^2− were chosen as the delivering matrix polymer, the receiving matrix polymer and the
catalytic source, respectively. In the first step, the oxygen plasma was used to render the substrate surface hydrophilic for the subsequent silanization with octenyltrichlorosilane through a condensation reaction to form vinyl-terminating initiators on the surface. The surface-modified flexible substrate was then immersed into a polymerisation solution to deposit PMETAC chains on the target surface via in-situ FRP. On the other hand, Printable inks were prepared by mixing PEG, (NH₄)₂PdCl₄, ethanol and deionised (DI) water in various ratios based on different printing techniques including dip-pen nanolithography (DPN), screen printing and inkjet printing, as shown in table 1. There are several reasons to select PEG as the moiety carrier and thickening agent. Firstly, it could absorb water and was soluble in water. Secondly, it could carry but did not react with the catalysts. Thirdly, the viscosity of the catalytic could be optimised for a wide variety of printing methods by adjusting the molecular weight (Mw) and concentration of PEG. For examples, the ink for screen printing must be viscous, while the ink for inkjet printing should be at low viscosity and moderate surface tension. For DPN technique, the ink is required to be at low viscosity at the inking state, and at high viscosity during DPN patterning. As-prepared inks were subsequently printed on the surface-tethered substrate by using these printing methods to allow [PdCl₄]²⁻ anions diffuse into PMETAC brushes. Finally, ELD was conducted to deposit metallic nanoparticles on the ink-printed areas for the production of patterned metal conductors on substrate surface. As shown in Figure 13b, various metal patterns with feature size ranging from nanometre to metre scales were plated on different substrates including Cu dot arrays on polyethylene terephthalate (PET) films, serpentine Cu on polydimethylsiloxane (PDMS), Ag, Au and Ni electrodes on PET films, Cu interconnects on polyimide (PI) films and Cu patterns on cotton fabrics. Nevertheless, the catalytic inks must be freshly prepared before use and long-time usage of such inks results in not only the loss of their reactivity but also blockage or corrosion of the printing nozzles and tubing. In addition, the oxygen plasma treatment is required for substrates that do not contain hydroxyl or oxide, leading to the damage on the substrate surface by changing chemical functional groups on surface of target substrates.
Table 1. Recipes of catalytic inks for DPN, inkjet printing and screen printing

<table>
<thead>
<tr>
<th></th>
<th>DNP</th>
<th>Inkjet printing</th>
<th>Screen printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG</td>
<td>10 mg&lt;sup&gt;(a)&lt;/sup&gt;</td>
<td>20 mg&lt;sup&gt;(b)&lt;/sup&gt;</td>
<td>5 g&lt;sup&gt;(c)&lt;/sup&gt;</td>
</tr>
<tr>
<td>DI water</td>
<td>-</td>
<td>10 g</td>
<td>2.3 g</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.8 g</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(NH₄)₂PdCl₄</td>
<td>2.5 mg</td>
<td>14 mg</td>
<td>23 mg</td>
</tr>
</tbody>
</table>

<sup>(a)</sup>M<sub>w</sub> ≈ 300 g/mol and 1540 g/mol, 1:1 weight/weight; <sup>(b)</sup>M<sub>w</sub> ≈ 400 g/mol; <sup>(c)</sup>M<sub>w</sub> ≈ 4000 g/mol

Figure 13. (a) The schematic illustration of the matrix-assisted catalytic printing process. (b) Various metal patterns were fabricated on different substrates including Cu dot arrays on PET films, serpentine Cu on PDMS, Ag, Au and Ni electrodes on PET films, Cu electrode on cellulose paper, Cu interconnects on PI films and Cu patterns on cotton fabrics.}\(^{85}\)


2.2.2 Copolymer Ink Patterning

The copolymer ink patterning strategy is to print the copolymers on the textile surfaces on which metal nanoparticles are intended to deposit. Figure 14 is the schematic illustration of this method that only the area grafted with copolymers can initiate electroless deposition (ELD) to produce metal patterns on textiles. In detail, the pristine textile is first printed with a layer of bifunctional copolymer ink on textile surface. The copolymer is made of two major components (a metal-platable part and a UV-curable part). Afterwards, the self-crosslinking and surface grafting of the copolymer on substrate are simultaneously triggered by UV radiation under ambient conditions. Catalysts are then anchored on the localised brush area in the catalytic source for the subsequent ELD to obtain patterned metal traces on the surface of textiles.
Figure 14. The Schematic illustration of copolymer ink patterning strategy for fabricating patterned metal conductors on textile. (a) Raw textile substrate is printed with a layer of bifunctional copolymer ink, as shown in (b). (c) The illustration of metal-platable part and UV curable part in the copolymer. (d) The simultaneous self-crosslinking and surface grafting of copolymer on textile surface by using UV irradiation at ambient conditions. (e) Catalytic moieties are loaded on the localised brush area. (f) ELD to produce the patterned metal traces on the textile surface as shown in (g) and (h). Areas without printed copolymer cause none of plated metal, as shown in (h) and (i).
To apply this strategy for manufacturing metal traces on textiles, the selection of copolymer that contains UV reactive ligands and metal-platable groups is vital. Yu et al.\textsuperscript{91} reported the use of poly(4-methacryloyl benzophenone-co-2-methacryloyloxy ethyltrimethylammonium chloride) [P(MBP-co-METAC)] as the copolymer ink for printing metal patterns on flexible substrates. Importantly, P(MBP-co-METAC) could be deposited on the polymeric substrate via one-step curing. Under UV irradiation, the rapid generation of free radicals at the carbonyl position of the MBP units occurred, enabling the coupling with neighbouring organic species via a classic hydrogen abstraction reaction. This resulted in the simultaneous self-crosslinking and surface grafting of the copolymer under ambient conditions. Subsequently, the surface-modified substrate was immersed into the (NH\textsubscript{4})\textsubscript{2}PdCl\textsubscript{4} aqueous solution, where the METAC fragments on the copolymer-modified substrate absorbed PdCl\textsubscript{4}\textsuperscript{2-} for the following metal deposition on the substrate surface in the ELD bath, as shown in Figure 15a. To combine this copolymer with printing techniques, 2-methoxyethanol was chosen as the main solvent for making copolymer ink because of good compatibility with P(MBP-co-METAC) and excellent wettability on both hydrophilic and hydrophobic substrates (for example, the contact angle of raw PET sheet was 85° while after the surface modification, the contact angle of P(MBP-co-METAC) was only 38°). The recipes of copolymer inks for soft lithography moulding and inkjet printing were (2 wt.%) and (0.5 wt.%) P(MBP-co-METAC) in 2-methoxyethanol, respectively. The copolymer gel for screen printing was 5 mL of (10 wt.%) P(MBP-co-METAC) in 2-methoxyethanol, 10 mL DI water and 40 g of PEG (M\textsubscript{w} ≈ 4000 g/mol). After printing copolymer inks on the flexible substrates by these techniques, PdCl\textsubscript{4}\textsuperscript{2-} ions were subsequently captured on the quaternary ammonium groups of the copolymer-tethered substrates via the strong electrostatic interactions in the catalytic source. Finally, ELD of Cu was conducted to deposit high-density metal patterns on target substrates. Figure 15b-d revealed the scheme of each printing technique (in the top), the optical images of the printed copolymer (in the middle) and resulted Cu patterns (in the bottom) on polyethylene terephthalate (PET) films (b, d) and cotton fabrics (c). Although the self-
crosslinking and grating of the copolymer are fast (~10 min) in this strategy, the UV lamp is required in the irradiation treatment and the influence of UV irradiation is difficult to control, especially for the eye and skin problems to researchers.

Figure 15. (a) The schematic illustration of fabricating metallic patterned textiles via copolymer ink patterning. Printing metal electrodes by using (b) Soft lithography moulding, (c) Screen printing and (d) Inkjet printing. Upper row gives the scheme of each printing technique, while middle and bottom rows show the optical images of the printed copolymer and resulted Cu patterns respectively on PET films (b, d) and cotton fabrics (c). Scale bars are (b) 150 µm, (c) 1 cm and (d) 100 µm.91
2.3. PAMD on Different Substrates and Their Applications

Based on the discussion in Section 2.1 and 2.2, polymer-assisted metal deposition (PAMD) has been introduced as a highly productive method for fabricating fully metal-coated substrates and well-defined metal patterns on the surface of target substrates. Importantly, crucial components of this technique include not only the polymer interfaces, but also the different kinds of substrates. Flexible and stretchable substrates such as textiles, plastics, 3D sponges, natural leaves and elastomers have a significant impact on the properties of soft electronics that are produced by PAMD because of their unique structures. For example, due to the hierarchical nature of structurally defined yarns and fabrics, they have fatigue resistance and damage tolerance. The working mechanism of resisting fatigue and damage is that by transforming a large deformation into numerous fibres, the induced internal strain in every single fibre is small and there is no crack propagation in assemblies. Thus, these crack arrestors can still maintain structural integrity after several washing cycles. In this section, key examples of PAMD on different soft materials and their applications in flexible and stretchable electronics are discussed.
2.3.1 Textiles

Textiles with inherently flexibility and wearability, are essential substrates for manufacturing flexible and wearable electronic devices. However, traditional vacuum deposition cannot plate an uniform layer of metal film over the textile surface because fibre substrate owns rugged surface and irregular geometry. In contrast, polymer-assisted metal deposition (PAMD) as the full-solution strategy is considered as an promising method for fabricating fibre-shaped metal conductors on a wide variety of textile materials including natural and synthetic fibres, yarns and fabrics. Liu et.al reported the successful fabrication of conductive cotton yarns and fabrics by using poly[2-(methacryloyloxy)-ethyl]-trimethylammonium chloride (PMETAC) brushes as the interfacial layer between cotton fibre surface and deposited metal films, as shown in Figure 16a. In the fabrication, Br-terminating silanes were deposited on cotton fibres to allow the surface-initiated atom transfer radical polymerisation (SI-ATRP) for the grafting of PMETAC brushes on the fibre surface. The PMETAC brushes grafted cotton yarns and fabrics were subsequently immersed in the catalytic source to load [PdCl$_4$$^{2-}$] via ion exchanging because the quaternary ammonium groups of PMETAC have a strong ability to capture metal anions. Finally, Ni or Cu nanoparticles were deposited on cotton substrates in the electroless deposition (ELD) bath. From the scanning electron microscope (SEM) image of Cu-coated cotton fibre in Figure 16b, it was clear to see that Cu particles were homogeneously plated on both upper and inner surface of cotton fibres that have the hollow structure. This integral and continuous metal coating significantly decreased the resistance of Cu-coated cotton yarns, reaching as low as 1 $\Omega$/cm. These Cu or Ni-coated cotton yarns and fabrics were durable under repeated stretching-releasing (Figure 16c) and washing (Figure 16d) because of the formation of polyelectrolyte-bridged metal/cotton hierarchical structures. The application of metallic cotton yarns was demonstrated as conductive wires in textile electronics by connecting a battery and a light-emitting diode (LED) bulb, as shown in Figure 16e. Nevertheless, SI-ATRP is not feasible for scaling up the production of metallised cotton fibres due to the requirement of oxygen-free atmosphere and long polymerisation time (24 h).
Figure 16. (a) The schematic illustration of ELD on PMETAC modified cotton surface through SI-ATRP. (b) The SEM image of the copper coated cotton fibre. Durability tests of (c) hand washing and (d) stretching-releasing cycles (resistivity = 1/conductivity) on the Cu-plated cotton fabric. (e) The digital images of the textile-based electronic circuit: conductive yarn was used as the interconnect for powering a commercial LED.95
To achieve the industrial production of metal-coated textiles by using PAMD, Wang et al. proposed the in-situ free radical polymerisation (FRP) technique to graft PMETAC brushes for depositing metal nanoparticles on different textile substrates. The fabrication process is illustrated in Figure 17a. In detail, the textile substrate was firstly impregnated in a vinyltrimethoxysilane (VTMS) aqueous solution to attach double-bond silane molecules to the target textiles such as cotton, nylon and spandex through a condensation reaction. Man-made filaments should be exposed to the oxygen plasma before silanization to ensure that all textile substrates have abundant hydroxyl groups for grafting VTMS. Subsequently, the VTMS-modified textile was immersed in the aqueous solution that contained METAC and potassium persulfate (KPS) was then added in the solution to initiate the growth of PMETAC brushes on fibre surface under ambient conditions through in situ FRP. Ni or Cu nanoparticles were finally deposited on the catalysed areas through ELD after the immobilisation of $[\text{PdCl}_4]^{2-}$ species on the PMETAC-grafted textile. The SEM image of Cu-plated nylon fabric in Figure 17b revealed the homogeneous, compact and continuous coating on the fibre surface. The sheet resistance of Cu-coated cotton fabric was 10 Ω/sq and the resistance value of such fabric decreased under different bending radii due to more compact fibre-to-fibre contacts (Figure 17c). The normalised resistance of the Cu-deposited cotton fabric only showed a small increase after 1000 continuous cycles of bending ($r = 5 \text{ mm}$) (Figure 17d) because of the designed polymer interface. For the demonstration, Cu-coated cotton yarns were wrapped around the pencil to power the light-emitting diode (LED) in a flexible circuit, as shown in Figure 17e. Compared with SI-ATRP, in situ FRP is more favourable for high-throughput and roll-to-roll fabrication of metallised textiles due to several advantages. Firstly, the silane deposition in in-situ FRP is conducted in aqueous solution. Secondly, the grafting of PMETAC on textiles is performed under ambient conditions. Thirdly, the polymerisation of PMETAC brushes in in-situ FRP is much quicker, leading to the high yield of conductive textiles. The comparison of in-situ FRP and SI-ATRP is shown in Table 2. However, for synthetic fibres, the oxygen plasma treatment is still required before depositing silane initiators on the man-made
Table 2. Comparison of in-situ FRP and SI-ATRP for grafting PMETAC brushes

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<th>in-situ FRP</th>
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<tr>
<td>Silane modification</td>
<td>VTMS in water</td>
<td>Br-terminating trichlorosilane in anhydrous toluene</td>
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<td>Polymerisation</td>
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Figure 17. (a) The schematic illustration of PMETAC-assisted ELD via in-situ FRP. (b) The SEM image of Cu-deposited nylon fabric. The durability tests of (c) different bending radii and (d) repeated bending cycles (r = 5 mm) (R/R₀ is the normalised resistance) on the Cu-deposited cotton fabric. (e) The digital image of conductive yarns wrapped around a pencil in an electrical circuit that contains the LED.¹⁶
2.3.2 Plastic Thin Films

Plastic thin films are ideal candidates for flexible electronics because of their intrinsically flexibility and metal pattern can be easily realised on these substrates by combing polymer-assisted metal deposition (PAMD) with printing techniques.\(^97\) Liang et al.\(^98\) used the microfluidic patterning technique to deposit metal structures on the polyethylene terephthalate (PET) film via PAMD (Figure 18a). In detail, the plasma treated PET substrate was firstly coated with a layer of vinyltrimethoxysilane (VTMS) via silanization, followed by grafting poly[2-(methacyryloyloxy)-ethyl]-trimethylammonium chloride (PMETAC) on the VTMS-modified sample by in-situ FRP in a solution containing potassium persulfate (KPS) initiators and METAC monomers. A catalytic source was then infused into the polydimethylsiloxane (PDMS) microchannel via the peristaltic pump at a flow rate of 0.1 mL·min\(^{-1}\), in which PdCl\(^{2-}\) ions were captured by quaternary ammonium groups of PMETAC chains on the surface-modified PET. A typical Cu electroless solution in the microchannel at a flow rate of 0.1 mL·min\(^{-1}\) was finally applied to fabricate the Cu pattern on flexible PET film (denoted as Cu/PET). The resistance of Cu/PET was 20 Ω/sq. Apart from Cu, Ag and Ni pattern could be also successfully plated on the PET substrate by using the same method (denoted as Ag/PET and Ni/PET). Figure 18b and 18c showed that optical images of the PDMS microchannel and the as-prepared Cu/PET sample. The microscope of Cu pattern on PET in Figure 18d showed a clear boundary between pristine PET and Cu pattern. Scanning electron microscope (SEM) images in Figure 18e-g revealed that closely packed Ni nanoparticles were formed in the patterned area, while other areas remained uncoated. The bending test with gradually decreased radius of curvature was used to evaluate the flexibility of the patterned metallised PET. From Figure 18h, Cu/PET showed the good normalised resistance under different bending radii, while the resistances of Ni/PET and Ag/PET increased under bending with the radius of curvature that was smaller than 3.11 mm. In addition, these patterned metal interconnects showed excellent fatigue resistance at bending with selected radius (Figure 18i). Taking these advantages, as-fabricated flexible printed conductors were
used as interconnects in the electrical circuit to stably illuminate the light-emitting diode (LED) at different bending curvatures (Figure 18j and 18k). Although the microchannel technique reduces usage of chemicals, plasma treatment destructs the surface chemistry of raw PET film.
Figure 18. (a) The schematic illustration of fabricating the metal-patterned PET substrate. The digital image of (b) PDMS microchannel stamp and (c) Cu pattern on PET. (d) The microscope image of Cu pattern on PET. (e-g) SEM images of Ni/PET. The durability tests on Cu/PET, Ni/PET and Ag/PET by using (h) different bending radii and (i) cyclic bending with selected radius ($R/R_0$ is the normalised resistance). (j) The Ag/PET was used as the interconnect to power the LED lamp in a bendable circuit. (k) The I-V characteristics of the LED circuit at different bending radii.
2.3.3 3D Sponges

In flexible and stretchable electronics, 3D substrates with the spongy structure are frequently involved because of their 3D interconnected network. Polymer-assisted metal deposition (PAMD), as a bottom-up method, shows obvious advantages in growing continuous metal layers on 3D sponges because this strategy is independent from the size and architecture of the substrate.\textsuperscript{99,100} Yu et al.\textsuperscript{101} proposed the fabrication of conductive 3D polyurethane (PU) sponges. The fabrication is shown in Figure 19a and 19b. In the first step, PU sponges were dipped into an ethanol solution of poly[2-(methacryloyloxy)ethyl trimethylammonium chloride-co-3-(trimethoxysilyl)propyl methacrylate] [P(METAC-co-MPTS)] that was prepared by the “one-pot” radical polymerisation process. After hydrolysis and curing steps, the copolymer chains were grafted on PU sponges, followed by immersing [P(METAC-co-MPTS)]-modified PU sponges into an aqueous solution of (NH\textsubscript{4})\textsubscript{2}PdCl\textsubscript{4} for loading catalytic moieties on brushes. These catalytic samples were then immersed into electroless deposition (ELD) baths of Au and Cu to prepare Au-plated and Cu-deposited PU sponges (denoted as PU-Ag and PU-Cu), respectively. Binary-metals-coated PU sponges (denoted as PU-CuAg) were also obtained by a second ELD of Ag on the top of PU-Cu. All PU-metal samples were finally infiltrated with polydimethylsiloxane (PDMS) precursors and cured at 70\degree C to prepare PU-metal-PDMS. Digital images of these samples were shown in Figure 19c and 19d. From SEM images in Figure 19e and 19f, it could be seen that metal nanoparticles were homogeneously coated on PU surfaces. Because the whole fabrication process was conducted in solutions, large-sized samples could be prepared. Figure 19g showed the PU-Cu brick (9 cm × 10 cm × 4 cm) with sheet resistance of 0.57 \Omega/sq and Figure 19h was the PU-CuAg-PDMS sponge sheet (15.5 inch).
Figure 19. (a) The schematic illustration of fabricating 3D conductive sponges. (b) The cross-linking reaction of the copolymer coating and the ion exchange process. Optical images of (c) PU-metal and (d) PU-metal-PDMS. SEM images of (e) PU-CuAg (inset is the cross-section of CuAg film on PU sponges) and (f) PU-CuAg-PDMS (inset is the cross-section of PU-CuAg-PDMS). Optical images of (g) PU-Cu pricks before (top) and after cutting into half (bottom) and (h) the PU-CuAg-PDMS sheet.\textsuperscript{101}

As-made PU-CuAg-PDMS samples were demonstrated as interconnects to power light-emitting diode (LED) arrays by two different approaches. In the first strategy, these 3D porous metals-coated sponges were cut into desirable ribbons to connect LEDs that were glued onto PU-CuAg-PDMS with conductive silver epoxy. From Figure 20a and 20b, it could be observed that the 2D LED array worked good even when being fully
rolled, bent and twisted into different shapes and the I-V characteristics of the LED array at different tensile strains showed no significant difference. In the second strategy (Figure 20c), a shadow mask was firstly used to cover on a piece of [P(METAC-co-MPTS)] coated PU sponge. The half-cured PDMS was then printed on the copolymer-modified PU sponge via screen printing, leading to that only the uncovered areas were infiltrated with PDMS. The spreading of PDMS was prevented by the applied pressure on the shadow mask in this procedure. The PDMS pattern was formed after curing at 70 °C for 1h, followed by absorbing catalysts in the catalytic source for the subsequent ELD. As a result, CuAg nanoparticles were only deposited on the masked areas. LEDs were finally glued on the PU-CuAg interconnects and PDMS was used to encapsulate the whole assembly. Figure 20d and 20e revealed that the patterned circuit exhibited excellent stability upon stretching up to 30%. Despite the fruitful realisation of metal-coated 3D sponges in this study, there are still some disadvantages. Firstly, precise control of the molar ratio between METAC and MPTS as well as the viscosity of the copolymer solution is required to achieve the uniform metal coating. Secondly, the storage of polymers and the preparation of their solutions need air-dried condition. Thirdly, the PDMS filtration is needed in order to obtain good stretchability of the final products.
Figure 20. (a) The schematic diagram of the circuit with four LEDs (top) and the optical image of LED arrays by using PU-CuAg-PDMS ribbons under twisting, folding, rolling and stretching states (bottom). (b) I-V characteristics of the as-prepared circuit at different tensile strains. (c) The schematic illustration of patterning the PU-CuAg-PDMS integrated with LEDs. Optical images of (d) 1D and (e) 2D LED arrays by using as-fabricated patterned interconnects at 30% tensile strain. 101
Liang et al.\textsuperscript{102} reported metallised 3D PDMS sponges by PAMD (Figure 21a). In detail, sugar cubes as hard templates were firstly dipped into a mixture of PDMS prepolymer and its curing agent, followed by vacuum pumping to infiltrate PDMS into the sugar templates and baking at 65 °C to obtain PDMS-sugar cubes. These PDMS-sugar templates were then stirred in hot water to form PDMS sponges by removing the exposed sugar. PDMS sponges were particularly suitable for the fabrication of 3D stretchable and compressible electrodes because not only the material itself could be stretched, but also the sponge-like structures were highly stretchable. Afterwards, such sponges were exposed to air plasma for forming hydroxyl groups on the surfaces, followed by coating a thin layer of vinyltrimethoxysilane (VTMS) via silanization. Next, PMETAC-modified PDMS sponges were obtained by immersing VTMS-PDMS sponges into the polymerisation solution containing potassium persulfate (KPS) and METAC via in-situ free radical polymerisation (FRP). Catalytic moieties were then immobilised on PMETAC chains of PMETAC-grafted PDMS sponges for subsequent Cu ELD to obtain Cu-plated PDMS sponge (denoted as Cu-PDMS). Binary-metals-coated PDMS sponges were also fabricated by second ELD of Ag and Au on the top of Cu-deposited PDMS sponges (denoted as Ag/Cu-PDMS and Au/Cu-PDMS), respectively (Figure 21b).
To evaluate the mechanical properties of as-made metal-coated PDMS sponges, tensile and compression tests were used to investigate the resistivity of such sponges upon stretching and compressing (Figure 22a). As shown in Figure 22b, it could be seen that the resistance of Ag/Cu PDMS sponges (0.36 Ω/cm) almost kept constant for 5000 stretching-releasing cycles, especially at the tensile strain less than 40% because of the excellent stretchability of the porous PDMS. Figure 22c revealed that there was no obvious change in the resistance of as-prepared metallised PDMS sponges at less than 30% compression strain due to the good compressibility of PDMS with the spongy
structure. However, further increasing the compression strain to 50% caused the
dramatical increase of the resistance (~8 times) because the accumulation of
microcracks in metal coatings was formed upon repeated cycles of the large extent of
compression. Based on these properties, Ag/Cu-PDMS sponges were used as building
blocks in circuits to illuminate LED arrays under different mechanical deformations. In
detail, a thin film of half-cured PDMS was firstly casted together with three pieces of
aligned 3D porous conductors to form a model, in which these sponges were
immobilised and separated from each other. The as-made sponge-LED circuits were
then obtained after curing the model and inserting two LEDs into the conductive
sponges. These sponge-LED circuits were stable when being subjected to stretching
from 0 to 30% (Figure 22d), bending (Figure 22e) and twisting (Figure 22f). However,
the baking process for the preparation of 3D PDMS sponge requires the oven and is
energy-consuming. Moreover, the plasma treatment before silanization causes the
damage to the 3D PDMS sponge by destructing its intrinsically chemical groups on the
surface.
Figure 22. (a) The schematic illustration of stretching and compressing of the Ag/Cu-PDMS sponges ($L_0$ is the original length and $\Delta L$ is the extended length). The Durability tests of Ag/Cu-PDMS sponges at different (b) tensile strains and (c) compression strains ($R/R_0$ is the normalised resistance). Optical images of sponge-LED circuits under (d) stretching, (e) bending and (f) twisting.\textsuperscript{102}
2.3.4 Bio-inspired Substrates

Flexible substrates from nature are suitable to be coated with metal layers by polymer-assisted metal deposition (PAMD) because they are green and eco-friendly. Yu et al. proposed the bio-inspired chemical fabrication of vein-based transparent electrodes (VTEs) based on plant leaves and PAMD technology. The fabrication is illustrated in Figure 23a. In the first step, commercially available veins were immersed into a diluted ethanol solution of poly[2-(methacryloyloxy)ethyl trimethylammonium chloride-co-3-(trimethoxysilyl)propyl methacrylate] [P(METAC-co-MPTS)], followed by hydrolysis and curing to graft the copolymer chains on the vein surfaces. Palladium-bearing species were then anchored on the polymer-modified veins in the catalytic source via ion exchange. Cu nanoparticles were finally coated on the catalytic areas of the veins in the electroless deposition (ELD) bath. Figure 23b and 23d showed freestanding raw veins and VTEs, respectively. The scanning electron microscope (SEM) image of the bare veins in Figure 23c illustrated that they were mainly made of 2D continuous polygonal unit cells and there were interconnected subnetworks within each unit cell. Figure 23d and 23e revealed that after the metal deposition, the hierarchical structures in veins were retained and Cu nanoparticles on the surface VTEs were uniform and conformal.
As-prepared VTEs were conductive and transparent. As illustrated in Figure 24a, the bulk resistance of VTE measured randomly at several spots of the VTEs were ~4 Ω, indicating the low resistance of VTEs. Because the transmittance (T) and the sheet resistance (R_s) of VTEs were mainly dependent on the density of raw veins, two typical VTEs with different vein densities (denoted as VTE I and VTE II) were studied. Figure 24b showed that the R_s and T of VTE I with lower vein density were 0.9 Ω/sq and 83%,
respectively, and VTE II with increased density (~10%) exhibited decreased $R_s$ (0.25 Ω/sq) and $T$ (73%). The resistance change of VTEs at different strains in one stretching cycle was evaluated in Figure 24c. From the diagram, it could be observed that the normalised resistance ($R/R_0$) of VTEs remained stable until 50% strain but the $R/R_0$ value rapidly increased to 1.5 at 60% strain and this sample became nonconductive at 70% strain. However, the transmittance was independent of the strain deformations. The tensile fatigue resistance of VTEs was conducted by applying 30%, 40% and 50% maximum strains with 1000 stretching-releasing cycles, respectively. The results showed that there was no increase in the normalised resistance after continuous stretching-releasing cycles (Figure 24d). This was attributed to the deformation of the polygonal unit cells of the veins: the cells elongated along the strain direction and narrowed perpendicular to the strain direction, which could be seen in Figure 24e-h. Importantly, patterned VTEs could be fabricated to make 2D light-emitting diode (LED) arrays. In detail, transparent polydimethylsiloxane (PDMS) was firstly printed onto the polymer-grafted vein via screen printing. After curing, PdCl$_4^{2-}$ ions were selectively captured by brushes due to the presence of the PDMS mask for subsequent ELD. Finally, LEDs were glued onto patterned VTEs. As shown in Figure 24i and 24j, as-prepared LED arrays worked well at releasing and deformed states due to the stable performance of VETs at large deformations. However, the hydrolysis and curing are needed in the polymer grafting process, increasing the consume of energy.
Figure 24. (a) Bulk resistance measurements at different areas of VTEs. (b) Optical transmittance of veins and VTEs (inset showed the digital images of two veins with different densities and the scale bars were 400 µm) (Ω/□ is the same as Ω/sq). (c) The normalised resistance \( R/R_0 \) and the normalised transmittance \( T/T_0 \) of VTEs at different tensile strains. (d) The durability test of VTEs at 30%, 40% and 50% maximum strains. (e-h) The deformation of veins at different strains ranging from 0-70%. Digital images of transparent and flexible LED arrays based on patterned VTEs under (i) releasing state and (j) deformed state.
2.3.5 Elastomers

Elastomers that can be stretched to a large extent are usually used in flexible and stretchable electronics. Polymer-assisted metal deposition (PAMD), as an efficient approach to deposit metal films on different substrates, can be considered for fabricating stretchable conductors by either creating wavy structures of metal layers on elastomers or directly coating metal nanoparticles on stretchable candidates with crater-like topographies. Wang et al.\textsuperscript{104} reported Cu-coated polydimethylsiloxane (PDMS) with ultrahigh tensile strain and stable metallic conductance enabled by prestrained polyelectrolyte nanoplatforms (Figure 35a). In detail, the presynthesized PDMS substrate by mixing PDMS prepolymer and the curing agent in a ratio of 10:1 and curing at 70 °C were firstly exposed to oxygen plasma to render the surface hydrophilic. Silane initiators were then immobilised on the surface-modified elastomer by a condensation reaction in the vapour phase. Next, surface-initiated atom transfer radical polymerisation (SI-ATRP) was used to grow dense surface-tethered polymers [poly[2-(methacryloyloxy)-ethyl]-trimethylammonium chloride (PMETAC) brushes] on PDMS, followed by capturing catalytic moieties in an aqueous solution of (NH\textsubscript{4})\textsubscript{2}PdCl\textsubscript{4} via ion exchange due to high affinity to quaternary ammonium groups of PMETAC. Afterwards, the PDMS substrate was uniaxially stretched to a certain strain and then immersed into the electroless deposition (ELD) bath of Cu for producing the Cu-coated PDMS. Finally, as-prepared Cu-deposited PDMS was released from the prestrain to from the buckle structure on the PDMS substrate. The resistance of the Cu-coated PDMS with wavy structure was $1 \times 10^{-5} \Omega/cm$. The deposition rate of Cu nanoparticles on prestrained PDMS was about 14 nm/min when ELD time was longer than 5 min. After 20 min plating, the thickness of the Cu layer was approximately 320 nm (Figure 25b). Typically, longer electroless plating resulted in thicker Cu films and the thickness was proportional to ELD time. Scanning electron microscope (SEM) images in Figure 25c and 25d showed that plated Cu nanoparticles on prestrained PDMS were compact, uniform and continuous and after releasing the applied strain, clear buckled structures could be seen in the PDMS surface.
Figure 25. The schematic illustration of fabricating highly stretchable metallic conductors with prestrained polyelectrolyte nanoplatorms ($L_0$ is the original length and $\Delta L$ is the extended length). (b) The diagram of conductivity (squares) and thickness (dots) of Cu films at different ELD times (conductivity = 1/resistivity). SEM images of the surface morphology of (c) Cu layers at the prestrain stage and (d) buckled Cu layers when the prestrain (30%) was released (inset showed the cross-sectional view of Cu wrinkles).\textsuperscript{104}

To test the stretchability of the as-made elastomeric conductor under reversible stretching-releasing cycles, the conductivity of the conductive PDMS fabricated at 70% uniaxial prestrain and 20 min ELD was measured when this sample was stretched to 70% and then released to the original length for 50 cycles. From Figure 26a and 26b, it could be seen that the conductivity value only dropped by 10-15% when the Cu-coated
PDMS was fully stretched to 70% strain, whereas the value recovered when the tensile force was released. Optical images of the surface morphology of the Cu layer in Figure 26c revealed that the amplitude of these buckles decreased during stretching, while there was no obvious change in the wavelength, indicating only a small bending deformation and tiny effective strain (< 1%) of Cu layer. Based on the superior stretchability, the PDMS composite was used as electrical wires to power the light-emitting diode (LED) in an electrical circuit. From the I-V characteristics in Figure 26d and digital images in Figure 26e, it could be observed that the current decreased from 12 to 8 mA when the circuit was stretched to 70% strain and the I-V characteristics fully recovered when the stress was released. Importantly, the buckled Cu-coated off-the-shelf rubber band could be readily stretched to 300% by applying the 300% prestrain at the catalytic rubber before ELD (Figure 26f).
Figure 26. (a) The changing in conductivity (denoted as $P/P_0$) of the as-prepared stretchable conductor with increased tensile strain up to 70% (conductivity = 1/resistivity). (b) The changing in conductivity (denoted as $P/P_0$) of the Cu-coated PDMS at 70% prestrain under cyclic stretching (70% strain) and relaxing (0% strain) tests (conductivity = 1/resistivity). (c) Optical images of the surface morphologies of the buckled Cu layer at different tensile strains. (d) I-V characteristics of the LED integrated circuit with as-made PDMS conductors as interconnects. Digital images of (e) The LED-circuit at 0 and 70% strain and (f) The Cu-plated rubber band with ultrahigh stretchability (300% strain).\textsuperscript{104}

Particularly, this approach was feasible to demonstrate patterned stretchable conductors by employing mask lithography and sewing technology. For the mask process, the PDMS was firstly covered by a shadow mask and then exposed to oxygen plasma.
Therefore, only uncovered areas would be activated for the subsequent silanization, SI-ATRP, catalysts absorption and ELD at prestrain (Figure 27a). Optical images in Figure 27b showed the buckled Cu lines at 30% and 0% strain and the patterned substrate illuminated the LED in a circuit that could be reversible stretched and released, as shown in Figure 27c. For the sewing process, a simple circuit pattern could be formed by sewing Cu-coated spandex yarns onto a piece of fabric to power the LED, as shown in Figure 27d. Nevertheless, the preparation of PDMS substrate needs curing at oven. In addition, the plasma treatment requires vacuum chamber and the changing in the chemical groups destructs the surface of PDMS.

Figure 27. (a) The schematic illustration of fabricating patterned stretchable conductors via masking. (b) Optical images of Cu lines at stretching (top) and relaxing (bottom) state. Digital images of the LED-integrated circuit (c) with patterned PDMS conductors under stretching (30%) and relaxing and (d) with conductive spandex fibres sewn on a piece of Lycra fabric.\textsuperscript{104}
Guo et al.\textsuperscript{105} reported the biomimicking topographic elastomeric petals (E-petals) for omnidirectional stretchable and printable electronics via PAMD. The fabrication process of E-petals is shown in Figure 28a. In the first step, fresh rose petals were fixed onto a plastic petri dish via taping and used as moulds (Figure 28b and 28c). Next, a mixture of PDMS prepolymer and its curing agent was poured onto the petals of yellow roses and then degassed in a vacuum desiccator. After curing the PDMS solution at room temperature, cured PDMS was subsequently peeled off from the moulds to obtain E-petals (Figure 28d). The SEM image in Figure 28e showed that there were pentagonal and hexagonal micropapillaes on the surface of rose petal moulds, which were separated by a web of trench, and nanofolds spread from the centre to the edge on the top of these micropapillaes. On the other hand, SEM images in Figure 28f and 28g revealed an inverted structure of E-petals to that of natural rose petals. PMETAC-assisted ELD was finally applied to coat a uniform and conformal Cu thin film on as-made E-petals, denoted as ELD-Cu/E-petals (Figure 28h). The resistance of ELD-Cu/E-petals was $2 \times 10^{-5} \ \Omega$/cm. SEM images of ELD-Cu/E-petals in Figure 28i and 28j showed clear topographic microcraters and nanofolds on the surface of conductive E-petals and the thickness of the Cu layer (~120 nm). To evaluate the omnidirectional stretchability of ELD-Cu/E-petals, these samples were clamped with a pair of stainless-steel rings and the omnidirectional stretching was induced by punching a stainless-steel ball into the centre of these Cu-deposited elastomers. As shown in Figure 28k, the normalised resistance ($R/R_0$) of these samples increased to 1.5 after the first 300 cycles and then maintained stable until 1000 cycles in the omnidirectional stretching test (the applied strain was 13%) due to the crater-like topographies on ELD-Cu/e-petals. Based on the excellent mechanical properties, ELD-Cu/E-petal interconnects were integrated into an electrical circuit with the LED. Figure 28l revealed that there was no obvious change in the LED intensity even though the conductive samples deformed largely under punching.
Figure 28. (a) The schematic illustration of fabricating E-petals. Digital images of (b) A fresh yellow rose petal, (c) Rose petals taped on the bottom of a petri dish and (d) E-petals. SEM images of (e) Natural rose pedals, (f) Topography and (g) Cross section of
E-petals. (h) The digital image of ELD-Cu/E-petals. SEM images of (i) The topographic structure of ELD-Cu/E-petal PDMS and (j) The cross section of Cu-plated PDMS, showing the thickness of the Cu layer. (k) The normalised resistance (R/R₀) of ELD-Cu/E-petals during 1000 cycles of omnidirectional tensile tests. (l) Digital images of the LED circuit by using as-prepared conductive pedals under releasing (left) and with punching (right).

Apart from conductive interconnects, E-petals could be also readily used for printable electronics by using PAMD and printing techniques. As proof-of-concept, a strain sensor based on printed stretchable metal electrodes was fabricated for potential applications of electronic skins in this work (Figure 29a). In detail, six pairs of interdigitated electrodes with interconnects and contacts made of a bilayer of Cu (the bottom layer) and Ag (the top layer) via catalytic printing strategy were firstly printed on E-petals. Graphene oxide (GO) was then spin-coated on the Ag/Cu electrodes, followed by reducing GO to reduced GO (rGO) in hydrazine vapour atmosphere to form the final strain-sensing device. As shown in Figure 29b, the resistance of the device increased to 2.2 folds during the first 300 stretching (20% strain)-relaxing cycles and then stabilised, while the resistance at 0% strain remained unchanged after 800 cycles. Figure 29c revealed that the current of the printed electrodes was a first-order function of the tensile strain under a constant bias. Based on this, when the device was attached to a joint of the index finger, four different bending gestures could be identified by monitoring the current change of the strain sensor (Figure 29d and 29e). Nevertheless, the oxygen plasma treatment is needed in the PMETAC-assisted ELD for rendering the surface of E-petals hydrophilic, which destructs the surface chemistry of the elastomers.
Figure 29. (a) The schematic illustration of fabricating printed strain sensors on E-petals. (b) The normalised resistance ($R/R_0$) of the strain sensor during repeated stretching-relaxing cycles (inset showed the digital image of the device). (c) The current change of the device during the tensile tests. (d) The demonstration of the printed strain-sensing device. (e) The current change of the device at four different states in (d).
2.4 Summary and Research Gaps

Polymer-assisted metal deposition (PAMD) is an efficient approach to deposit metal nanoparticles on substrates for producing flexible and stretchable electronics. Basically, this technique contains three steps to achieve soft metal conductors: modifying substrates with polymer interfaces, capturing catalytic moieties on the polymer-grafted substrates and plating metal layers on the catalytic areas in an electroless deposition (ELD) bath. The substrates applied for PAMD can be chosen from a wide range of materials such as plastic thin films, elastomers, textiles, 3D sponges and natural veins. Moreover, traditional lithographic approaches including dip-pen writing, microfluid patterning, moulding, masking, inkjet printing and screen printing are compatible with PAMD for producing well-defined metal patterns on flexible substrates by using catalytic ink strategy or copolymer ink strategy.

Based on the discussion in section 2.1, 2.2 and 2.3, different polymer interfaces and polymerisation methods for coating metals on various flexible and stretchable substrates with PAMD are summarised in Table 3. The polymer interface is an important part in the whole process of PAMD because the grafted polymer can form interpenetrated polymeric networks between flexible substrates and metal nanoparticles, which provides a powerful adhesion to overcome mechanical failures and instability when the flexible conductors are stretched or folded by minimising the cracking of the metal layer from the substrate surface.\textsuperscript{106-108} Although surface modification on substrates by using polymer interfaces has been comprehensively studied in previous researches, there are still some key questions. Firstly, for UV-induced coating of polymers such as PVBVN, PAA, P4VP, PAN and [P(MBP-co-METAC)], the specific instrument in the irradiation treatment increases the cost and the influence of UV light to experimental user (eye and skin problems) is difficult to control. Secondly, the hydrolysis-induced polymerisation of [P(METAC-co-MPTS)] requires air-dried atmosphere, which is not suitable for industrial production. Thirdly, to graft PMEP and PMETAC brushes on target substrates that do not contain hydroxyl or oxide groups via SI-ATRP, complex steps including oxygen plasma treatment and Br-terminating silane
deposition are required before the growth of PMETAC chains. Furthermore, the nitrogen protection in SI-ATRP technique for coating polymer brushes on the substrate surface limits the large-scale production. Fourthly, although FRP is capable of grafting PMETAC brushes on the surface of fibre substrates at ambient environments, this technique still needs the fibre surface to be hydrophilic for depositing the vinyl-terminating silanes and subsequently initiating the growth of PMETAC chains on fibres. For man-made filaments, the oxygen plasma treatment is needed to create hydroxyl or oxide groups on the surface of fibre, which results in the damage to the substrate surface by changing the surface chemical groups. On the other hand, in previous reports, most metal-coated substrates manufactured by PAMD are used as simple conductive wires and electrodes. The research works of textile-based human-body monitoring sensors by using metallised yarns and fabrics are limited.

It is a challenge to set up a novel fibre interface molecular engineering (FIME) strategy that can be used for one-step modification on various fibres at ambient conditions without damaging the pristine fibre structure and provide strong adhesion forces between the metal layer and the fibre surface. In addition, the fabrication of fibre-shaped sensors that can track human-body movements is required for developing textile-based wearable electronics.
Table 3. The summary of PAMD technology

<table>
<thead>
<tr>
<th>Polymer interface</th>
<th>Polymerisation method</th>
<th>Metal</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMETAC</td>
<td>SI-ATRP, in-situ FRP</td>
<td>Cu, Ni, Ag, Au</td>
<td>cotton, nylon, spandex, PET, Kevlar, PDMS, PI, cellulose paper</td>
</tr>
<tr>
<td>PVBVN</td>
<td>UV irradiation</td>
<td>Ag</td>
<td>PI</td>
</tr>
<tr>
<td>PAA</td>
<td>UV irradiation</td>
<td>Ni, Cu</td>
<td>PS, PB, ABS</td>
</tr>
<tr>
<td>PMEP</td>
<td>SI-ATRP</td>
<td>Ni</td>
<td>silicon wafer</td>
</tr>
<tr>
<td>P4VP</td>
<td>UV irradiation</td>
<td>Ni</td>
<td>PVDF, PTFE</td>
</tr>
<tr>
<td>PAN</td>
<td>UV irradiation</td>
<td>Cu</td>
<td>FEP</td>
</tr>
<tr>
<td>[P(MBP-co-METAC)]</td>
<td>UV irradiation</td>
<td>Cu, Ni, Ag, Au</td>
<td>PET, cotton</td>
</tr>
<tr>
<td>[P(METAC-co-MPTS)]</td>
<td>hydrolysis</td>
<td>Cu, Ag, Au</td>
<td>PU, vein</td>
</tr>
</tbody>
</table>

PMETAC = poly[2-(methacryloyloxy)-ethyl]-trimethylammonium chloride, PVBVN = poly[1,1'-bis(4-vinylbenzyl)-4,4'-bipyridinium-dinitrate], PAA = poly(acrylic acid), PMEP = poly(methacryloyl-ethyl phosphate), P4VP = poly(4-vinylpyridine), PAN = polyacrylonitrile, [P(MBP-co-METAC)] = poly(4-methacryloyl benzophenone-co-2-methacryloxyloxy ethyltrimethylammonium chloride), [P(METAC-co-MPTS)] = poly[2-(methacryloyloxy)ethyl trimethylammonium chloride-co-3-(trimethoxysilyl)propyl methacrylate], PET = polyethylene terephthalate, PDMS = polydimethylsiloxane, PI = polyimide, PS = polystyrene, PB = polybutadiene, ABS = acrylonitrile–butadiene-styrene, PVDF = poly(vinylene fluoride), PTFE = poly(tetrafluoroethylene), FEP = poly(tetrafluoroethylene-co-hexafluoropropylene), PU = polyurethane, SI-ATRP = surface-initiated atom transfer radical polymerisation and in-situ FRP = in-situ free radical polymerisation.
Chapter 3. Research Strategy and Methodology
3.1 Research Strategy

The aim of this research is to use novel fibre interfaces to modify fibres by one-step polymerisation at ambient conditions without damaging the raw fibre structure and provide adhesive forces between metal thin films and fibre substrates for the large-scale production of durable conductive yarns and fabrics that can be applied in textile-based wearable electronics. In this research, surface modification on various fibres by using nature-inspired polyphenols including dopamine, tannic acid (TA) and curcumin for producing metal-coated textiles that were used as conductive interconnects and fibre-enabled motion sensors was investigated. The reason for choosing these polyphenols as the fibre interface was that they could form an adhesive layer on different fibres by one-step dip doping at room temperature without destructing the intrinsic fibre structure and anchor catalysts for the subsequent electroless deposition (ELD) of metal nanoparticles on fibres. For example, polydopamine (PDA) could attach to various solid surfaces by the spontaneous polymerisation of dopamine in an alkaline solution. However, dopamine was expensive (£2.6/g) and the polymerisation time was long (24 h). To solve this problem, TA was proposed to modify fibres and 3D sponges via dip doping in the aqueous solution because the coating process of TA on fibres was quick (30 min) and the price of TA was low (£0.2/g). Nevertheless, TA was unstable in the aqueous solution during long-term storage due to the macromolecular-aggregation and self-precipitation characteristics of polymers. To address this issue, curcumin, as a small molecule, was introduced to modify the elastic compound yarns in the ethanol solution via dip coating because the curcumin solution could be stored for more than three months.

In Chapter 4, the descriptions of published papers including Mussel-Inspired Flexible, Durable, and Conductive Fibres Manufacturing for Finger-Monitoring Sensors, A Nature-Inspired, Flexible Substrate Strategy for Future Wearable Electronics and Ultra-elastic Yarns from Curcumin-Assisted ELD toward Wearable Human-Machine Interface Textiles were introduced. After understanding the basic information of these papers, the detailed research works on fibre surface modification were to be studied.

In Chapter 5 (publication number one), a robust thin film of PDA was coated on fibres
in the dopamine solution at pH 8.5. Afterwards, catalysts were immobilised on the PDA layers of surface-modified fibres. The chemical structures of PDA-coated fibres and catalysts-absorbed fibres were to be inspected. For the ELD of Cu or Ni on the catalytic fibres, the resistance of metal-deposited yarns at different ELD times was to be analysed. The surface morphology of metal-plated fibres was to be examined. The structure and size of deposited metal nanoparticles were to be determined. The durability performance of metallised yarns was to be characterised under mechanical deformations. For the applications of conductive interconnects and motion sensors, the electrical performance of conductive yarns was to be explored.

In Chapter 5 (publication number two), TA was used as the fibre interface to modify flexible substrates including textiles and 3D sponges in an aqueous solution, followed by the catalyst anchoring. The surface chemical structures of TA-modified and catalysts-anchored substrates were to be studied. After the ELD of metal, the surface morphology and resistance value of metal-coated substrates at different ELD times were to be investigated. The mechanical properties of metal-plated substrates were to be explored. The crystalline structure and particle size of plated metal thin films were to be characterised. To combine the TA-assisted ELD with screen printing, the recipes of printing inks and the morphology of metal pattern on textiles were examined. For the applications of pressure sensors and motion sensors, the electrical performance of the cotton fabric with metal pattern and metallised 3D sponges was to be determined.

In Chapter 5 (publication number three), curcumin was applied to modify core-spun yarns in an ethanol solution and catalysts were then captured on the curcumin-modified elastomeric yarns in the catalytic solution. The surface chemical composition of curcumin-coated and catalysts-immobilised yarns was to be investigated. After the deposition of metal nanoparticles on stretchable yarns in the ELD bath, the resistance and surface morphology of metal-deposited yarns were to be studied. The crystalline plane and size of deposited metal layers were to be explored. The durability of metallised composite yarns was to be determined. To understand the working mechanism of strain-sensing core-spun yarns, the theoretical model of conductive
elastomeric yarns under mechanical deformations was to be examined. For constructing the human-machine interface (HMI) textiles, the electrical performance of conductive stretchable yarns was to be analysed.

The experimental materials in this research, experimental processes for manufacturing conductive fibrous substrates and the characterisation methods for analysing chemical structure and surface morphology of samples, investigating the crystal structure of deposited metal nanoparticles on samples, testing mechanical properties and detecting resistance value of samples are explained in the next section.
3.2 Research Methodology

3.2.1 Materials

All fibre substrates such as cotton, wool, nylon and polyethylene terephthalate and the screen for producing the metal pattern on cotton fabric were obtained from the Dye House at the University of Manchester (UK). Chemicals including dopamine hydrochloride, tris(hydroxymethyl) aminomethane, tannic acid, curcumin, ethyl alcohol, polyethylene glycol, ammonium tetrachloropalladate (II), lactic acid, sodium citrate, nickel sulfate hexahydrate, dimethylamine borane, sodium hydroxide, copper sulfate pentahydrate, potassium sodium tartrate and formaldehyde were purchased from Sigma-Aldrich (UK). Polyurethane sponge was purchased from Foam Partner Company (UK). Ecoflex was purchased from Smooth-on Company (UK). Cotton glove was purchased from Samine Company (China). Hue lightbulb was purchased from Philips Company (UK). Robotic hand and signal processing units were purchased from Youngbot Company (China).

3.2.2 Fibre Interface Design

For the polydopamine (PDA) coating on fibre surface, dopamine hydrochloride was dissolved in the 0.01 mol/L tris(hydroxymethyl) aminomethane buffer (pH 8.5) to prepare the polymerisation solution (2 g/L). Cleaned substrates were then dipped into the dopamine solution and the non-specific micro-particle deposition on fibres was prevented by stirring and/or vertical sample orientation. The pH-induced oxidation of dopamine changed the colour of the solution to dark brown. After a predetermined reaction time of 24 h, the adherent PDA film coated fibres were rinsed thoroughly with deionised (DI) water and dried with a N₂ gas stream.

For the tannic acid (TA) modification on fibres and polyurethane (PU) sponges, TA was dissolved in DI water to prepare the polymerisation solution (5 g/L). After dipping cleaned substrates into the TA solution for 30min, the TA-coated substrates were rinsed with DI water for several times and then dried under a stream of N₂.
For the grafting of curcumin on core-spun yarns, curcumin was dissolved in ethanol absolute to prepare a curcumin solution (5 g/L). Cleaned samples were then immersed into the solution for 30 min and the curcumin-coated samples were rinsed with DI water for several times, followed by N₂ drying.

3.2.3 Immobilisation of Catalysts

Catalysts were immobilized by immersing the surface-modified samples into a 5mM (NH₄)₂PdCl₄ aqueous solution and placed in a dark environment for 15 min. The physical absorption of catalysts was removed by rinsing with deionised water.

3.2.4 Metallisation by ELD

The Ni electroless plating was performed in an electroless deposition (ELD) bath containing 4:1 mixture of freshly prepared solutions A and B at room temperature. Solution A consisted of 10 g/L lactic acid, 20 g/L sodium citrate and 40 g/L nickel sulfate hexahydrate prepared in advance. Solution B was a freshly prepared reductant solution containing 1 g/L dimethylamine borane in deionised (DI) water. After mixing, the solution was adjusted with ammonia to pH ~8. The Cu electroless deposition was performed in plating bath containing 1:1 volumetric proportion of nickel-to-reductant stocks at room temperature. A copper stock solution consisting of 12 g/L sodium hydroxide, 13 g/L copper sulfate pentahydrate and 29 g/L potassium sodium tartrate was prepared in advance. A fresh reductant solution containing 9.5 mL/L potassium sodium tartrate in DI water was prepared separately. After ELD, all samples were washed for several times and dried with compressed air.

3.2.4 Metal Pattern on Cotton Fabric

There are two strategies to fabricate well-defined metal conductive patterns onto flexible cotton fabrics via screen printing. In strategy A, the substrate was firstly coated with tannic acid (TA), which played a role of the receiving matrix polymer.
(NH₄)₂PdCl₄ was then screen printed onto the TA-modified substrate with the help of polyethylene glycol (PEG), functioning as the delivering matrix polymer. After printing, catalyst patterns were formed on the substrate with a thin layer of TA because the inorganic catalytic salts diffused from the PEG into TA upon the contact between the two matrix polymers. Metal patterns were finally manufactured by electroless plating on the catalytic areas. In strategy B, TA was initially screen printed with the aid of the PEG onto the raw substrate to form TA patterns. The substrate partially modified by TA was subsequently immersed into the (NH₄)₂PdCl₄ aqueous solution and catalytic patterns were then formed on the ink-patterned area because only TA-modified area could capture catalysts. ELD was finally conducted on the catalyst-immobilized area to fabricate metal patterns on flexible substrates. Printing gels were prepared by mixing PEG, TA, (NH₄)₂PdCl₄ and deionised (DI) water in different ratios, as shown in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>Strategy A</th>
<th>Strategy B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tannic acid</td>
<td>-</td>
<td>0.125 g</td>
</tr>
<tr>
<td>(NH₄)₂PdCl₄</td>
<td>0.051 g</td>
<td>-</td>
</tr>
<tr>
<td>PEG (Mₜ = 8000 g/mol)</td>
<td>9 g</td>
<td>10 g</td>
</tr>
<tr>
<td>DI water</td>
<td>4.6 g</td>
<td>5 g</td>
</tr>
</tbody>
</table>

Mₜ = molecular weight

3.2.5 Construction of Textile-based Wearable Electronics

For the application of conductive interconnects, a simple electrical circuit containing Ni or Cu-coated yarns and fabrics, a commercial light-emitting diode (LED) and a 9 V alkaline battery was established. For the application of finger-bending sensors, Ni-deposited cotton yarns were sewn into four finger parts of a cotton glove and when fingers bent at different gestures, the resistance signals of Ni-coated cotton yarns were detected by a multimeter. For the application of human-touching sensors, a simple
circuit containing metal-coated yarns and fabrics, a 9 V alkaline battery, a commercial LED and the screen-printed Ni interdigital electrode was built. For the application of pressure sensors, different weights were placed on the top of metallised 3D sponges and the resistance changes of the conductive sponges were collected by a multimeter. For the application of arm-bending sensors, the conductive 3D sponge was attached to human arm and when the arm moved at different gestures, the resistance values of metal-deposited 3D sponges were collected by a multimeter. For the application of HMI textiles, smart glove made by fixing Ni-coated core-spun yarns on cotton glove via Ecoflex filtration was integrated with signal processing units for controlling the movements of robotic hand and the light colour of Philips hue lightbulb.

### 3.2.6 Characterisation Techniques

Fourier transform infrared spectroscopy (FTIR) is a powerful analytical technique for identifying types of chemical bonds in a molecule by producing an IR spectrum that represents a molecular fingerprint with absorption peaks corresponding to the vibrational frequencies of functional groups in a molecule. The basic components of an FTIR spectrometer are shown in Figure 30. In the Michelson interferometer that is employed in most FTIR spectrometers, a beam splitter is firstly used to divide radiation beam from the IR source into two parts, in which one part is transmitted towards a moving mirror and another part is refracted towards a stationary mirror. When the divided beams are reflected back to the beam splitter, constructive/destructive interference patterns are formed because of the difference in the optical path length travelled by two components of the beam. After the selective absorption of IR energy by a sample that is located between the beam splitter and the detector, fluctuations in the intensity of energy reach to the detector, followed by digitalising to yield an interferogram that contains all the information required to produce the IR spectrum of the sample. Finally, a conventional IR spectrum is obtained by using Fourier transformation to convert the time domain information into frequency domain information. In this research, FTIR is used to investigate the chemical groups in the
surface of raw fibres and surface-modified fibres.

Figure 30. The schematic illustration of an FTIR spectrometer.\textsuperscript{111}

X-ray photoelectron spectroscopy (XPS) is a useful surface-sensitive technique for identifying chemical information of a material such as elemental composition, chemical state, overall electronic structure and density of electronic states based on the photoelectric effect.\textsuperscript{112} The basic components of XPS are illustrated in Figure 31. In a typical XPS test, a monoenergetic source of radiation is firstly used to excite a specimen surface in the ultrahigh vacuum (UHV) chamber. The most commonly employed X-ray source is Al Kα radiation with corresponding energy of 1486.6 eV.\textsuperscript{113} When an atom in the sample absorbs an X-ray photon, a photoelectron is emitted from the sample surface. Afterwards, the kinetic energy of the emitted photoelectron is measured by the energy
analyser. Because the photo energy of X-ray is known and the energy analyser is applied to measure the emitted photoelectron’s kinetic energy, the binding energy of the electron in the sample (i.e., the energy required to remove the electron from the material surface) can be calculated by using Equation (1):

\[ BE = h\nu - KE \]  

where \( BE \) is the binding energy of the electron in the sample, \( h\nu \) is the photo energy of the X-ray and \( KE \) is the kinetic energy of the emitted photoelectron. A typical XPS spectrum is a plot of the number of electrons detected at a specific binding energy. In this research, XPS is used to characterise the surface elements of the catalysts-immobilised polymeric substrates.

Scanning electron microscope (SEM) is an efficient technique for producing images that contain information of the surface topography and composition of the sample. The main components of SEM including electron source, accelerating node, electromagnetic lenses, a vacuum chamber and detectors are shown in Figure 32.
During a typical SEM imaging process, electrons are firstly produced at the top of the column. Afterwards, these electrons accelerate down and pass through a combination of lenses and apertures to produce a focused beam of electrons. Controlling the position of the electron beam on the sample is achieved by using scan coils that situate above the objective lenses. When the focused beam of electrons hits the surface of the sample, it penetrates the sample to a depth of a few microns, depending on the accelerating voltage and the density of the sample. As a result, secondary electrons, backscattered electrons and characteristic X-rays are formed by the electron-sample interaction. These signals are then collected by detectors to form images on the computer screen. In this research, SEM was used to characterise the surface morphology of raw fibres and metal-coated fibres.
Figure 32. The schematic illustration of the SEM measurement.\textsuperscript{118}

X-ray diffraction (XRD) is a widely used diffraction method for determining the crystal structure of powder samples.\textsuperscript{119} The basic components of XRD instrument (called X-ray diffractometer) including X-ray source, divergent slit, sample holder, receiving slit and X-ray detectors are shown in Figure 33. In the diffractometer, the X-ray radiation generated by an X-ray tube firstly moves through the divergent slit. Afterwards, the divergent X-ray strikes the sample where the radiation is diffracted in various directions. A convergent beam is then formed at the receiving slit. In the final step, the count and intensity of diffracted X-rays from the specimen are recorded by the detector. The specimen on the sample holder can rotate in the path of incoming X-rays at an angle of
theta (Bragg angle). Simultaneously, the rotation of the detector rotates is at twice the speed of the specimen (2θ) to accomplish the geometry of diffraction. By continuously changing the incident angle of the X-ray beam, a diffractogram of intensity versus diffraction angle (2θ) is obtained. By comparing the spectrum with a database that contains more than 60,000 diffraction spectra of known crystalline substances, the crystal structure and quality of the sample can be identified. Moreover, based on the broadening of the diffraction peak in the diffractogram, the crystallite size can be calculated by using Equation (2):

$$ t = \frac{n \lambda}{B \cos \theta} \quad (2) $$

where \( t \) is the mean size of the ordered crystalline domains, \( n \) is a shape factor without limitations of dimension; \( \lambda \) is the X-ray wavelength; \( B \) is the full width at half maximum intensity and \( \theta \) is the Bragg angle. In this research, XRD was used to determine the crystal structure and the particle size of deposited metal nanoparticles on the fibres.

![Figure 33. The schematic illustration of the XRD instrument.](image)

Fabric stiffness test is a widely used technique for studying the fabric stiffness. The working principle of this method is shown in Figure 34. During the test process, the
specimen is firstly supported on a horizontal platform in a direction perpendicular to one edge of the platform. The sample is then moved lengthwise until the leading edge of the fabric makes an angle of 41.5° to the horizontal platform. The length of the fabric protruding beyond the platform edge, which equals to the twice the bending length of the sample, is measured by ruler. The flexural rigidity can be calculated by using Equation (3):

$$G = MC^3$$

(3)

where $G$ is the flexural rigidity, $M$ is the mass per unit area of the fabric and $C$ is the bending length. In this research, the fabric stiffness test was used to explore the flexural rigidity of metal-coated fabrics.\textsuperscript{124}

![Diagram](image)

\textbf{Figure 34. The working principle of the fabric stiffness test.}\textsuperscript{125}

- $F$ = external force
- $L$ = length of fabric projecting
- $\theta$ = angle to which fabric bends

Tensile test is a conventional technique for measuring the mechanical properties of a sample including breaking strength and maximum elongation.\textsuperscript{126} The image of tensile testing machine, Instron 3345, is shown in Figure 35. The main components in this machine are load frame, foot panel and jog control panel. The load frame consists of a frame base, a moving crosshead, one column and a top plate. The foot pedal is used to mount the specimen on the grips of the crosshead and the base. The jog panel controls the movement of the crosshead along the column. The tensile test involves placing the specimen in the machine and extending the sample at a predetermined speed until the
failure. During the test process, the elongation against the applied force is recorded by computer. In this research, tensile test is used to study the maximum elongation and the breaking strength of pristine core-spun yarns and metal-coated elastic yarns.

Figure 35. The image of the tensile testing machine.

The two-point measurement is a traditional technique to examine the surface resistance of a sample by using the multimeter. The image of the Keithley 2000 multimeter is shown in Figure 36. The resistance test involves connecting two probes to the surface of the specimen. The resistance value is displayed in the screen of the multimeter. To obtain the plot of resistance versus time, a remote interface is applied to link the multimeter with the laptop. In this research, the multimeter was used to investigate the
In this section, different techniques for characterising samples were discussed. The surface chemical structures of samples were characterised by FTIR and XPS. For the FTIR, raw fibre substrates and polyphenols-modified fibre substrates were tested. For XPS, the catalytic samples after Pd$^{2+}$ absorbing in the (NH$_4$)$_2$PdCl$_4$ source were examined. The surface morphology of metal-coated samples with different thicknesses of metal films was studied by SEM. For the raw polymeric substrates, the sputtering of Au was required. The crystal structure and particle size of deposited metal nanoparticles on fibres at different electroless deposition (ELD) times was studied by XRD. The mechanical properties of metal-plated yarns and fabrics were determined by tensile test and the fabric stiffness tester. For the tensile test, metal-coated stretchable yarns (90 min ELD) were explored. For the stiffness test, Ni-coated cotton fabrics at different ELD times were investigated. The surface resistance of metal-deposited textiles and 3D sponges was inspected by two-point measurement. Metal thin wires without motion-sensing function were used to connect the metallised samples with the probes in the
multimeter for detecting the changes of resistance when metal-coated samples were deformed during human motions. All the instruments used in this research are summarised in Table 5.

Table 5. List of instruments used for characterisation

<table>
<thead>
<tr>
<th>Characterisation technique</th>
<th>Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fourier transform infrared spectroscopy (FTIR)</td>
<td>Nicolet 5700 FTIR, Thermo Electron Corporation, USA</td>
</tr>
<tr>
<td>X-ray photoelectron spectroscopy (XPS)</td>
<td>Kratos Axis Ultra Hybrid, Shimadzu, Japan</td>
</tr>
<tr>
<td>Scanning electron microscope (SEM)</td>
<td>Ultra-55 Scanning Electron Microscope, ZEISS, Germany</td>
</tr>
<tr>
<td>X-ray diffraction (XRD)</td>
<td>PANaytical X’Pert Pro, Bruker, USA</td>
</tr>
<tr>
<td>Fabric stiffness test</td>
<td>Fabric stiffness tester Model 112, Taber, USA</td>
</tr>
<tr>
<td>Tensile test</td>
<td>Instron 3345, Instron, USA</td>
</tr>
<tr>
<td>Two-point measurement of resistance</td>
<td>Keithley 2000 multimeter, Keithley, USA</td>
</tr>
</tbody>
</table>
Chapter 4. Descriptions of Published Papers
4.1 Dopamine-assisted ELD


In this publication, dopamine was used to coat surface-adherent polydopamine (PDA) films on different fibres by dip doping in an alkaline solution. The chemical structures of raw fibres and PDA-coated fibres were investigated by Fourier-transform infrared spectroscopy (FTIR). Afterwards, the surface-modified fibres were immersed into a catalytic source to capture catalysts on the fibre surface. The element composition of catalytic samples was explored by X-ray photoelectron spectroscopy (XPS). Finally, the metal nanoparticles were deposited on fibres in the electroless deposition (ELD) bath. The surface morphology and the crystal structure of metal-coated fibres were studied by scanning electron microscope (SEM) and X-ray diffraction (XRD), respectively. The surface resistance of metal-deposited yarns was characterised by multimeter. The durability of these conductive yarns was tested under different mechanical deformations including bending and hand washing. These metallised yarns were demonstrated as interconnects to power the light-emitting diode (LED) in a flexible circuit. By integrating metal-plated yarns with cotton glove, the finger motions were tracked based on the resistance changes of the metal-coated yarns.

The structure of the project was designed by me, jointly with Xuqing Liu. The majority of experiments including FTIR, SEM, resistance test, electrical circuit design and sewing was conducted by me. XPS and XRD were tested under the help of Ben Spencer and John Warren, respectively. The thorough first draft of the manuscript was written by me. The collaboration on the multiple iterations of the paper was finished by Xuqing Liu and me to produce the final version, which was then submitted and published after major corrections.
4.2 TA-assisted ELD


This publication introduced tannic acid (TA) as the fibre interface to modify textiles and 3D sponges in an aqueous solution. The chemical structures of pristine samples and TA-coated samples were investigated by Fourier-transform infrared spectroscopy (FTIR). Subsequently, catalysts were anchored on the surface-modified samples in the solution containing palladium-bearing species. X-ray photoelectron spectroscopy (XPS) was used to study the element composition of catalytic samples. In the final step, metal nanoparticles were deposited on fibres and 3D sponges in the electroless deposition (ELD) bath. Metal patterns on the fabric were produced by using screen printing technique. scanning electron microscope (SEM) and X-ray diffraction (XRD) were applied to determine the surface morphology and the crystal structure of metal-coated samples, respectively. The multimeter was used to characterise the surface resistance of metal-deposited samples. The flexural rigidity of conductive fabrics was determined by using fabric stiffness tester. The durability of metallised fabrics was tested under repeated bending cycles. The Kelvin structure model was proposed in this work to illustrate the relationship between conductivity and flexibility. For applications, the cotton fabric with metal patterns was used as touching sensors and the metal-plated 3D sponge was applied as pressure sensor as well as the arm bending sensor.

The structure of the project was designed by me, jointly with Xuqing Liu. The majority of experiments including FTIR, SEM, resistance test, screen printing and fabric stiffness test was finished by me. XPS and XRD were tested under the help of Ben Spencer and John Warren, respectively. The thorough first draft of the manuscript was written by me. The collaboration on the multiple iterations of the paper was conducted by Xuqing Liu, Bin Xu, Evelyn Chalmers and me to produce the final version, which was then submitted and published after major corrections.
4.3 Curcumin-assisted ELD


In this publication, curcumin, a natural textile dye, was used to modified core-spun yarns in an ethanol solution. Fourier-transform infrared spectroscopy (FTIR) was applied to investigate the chemical structures of raw samples and curcumin-coated samples. In the next step, catalysts were immobilised on the curcumin-modified samples in the catalytic solution. X-ray photoelectron spectroscopy (XPS) was used to explore the element composition of catalyst-anchored samples. Finally, elastic yarns were coated with metal thin films in the electroless deposition (ELD) bath. The surface morphology and the crystal structure of metallised samples were studied by scanning electron microscope (SEM) and X-ray diffraction (XRD), respectively. The surface resistance of metal-plated stretchable yarns was characterised by multimeter. The tensile test was used to inspect the mechanical properties of metal-deposited samples. The durability of conductive samples was tested by different methods such as stretching, hand washing and placing in air. The principle of resistance changes of conductive core-spun yarns under mechanical deformations was determined by using a theoretical model. By integrating such yarns with cotton glove via Ecoflex filtration, this device was used as the human-machine interface (HMI) to control robotic hand and the colour of light. The structure of the project was designed by me, jointly with Xuqing Liu and Bin Xu. The majority of experiments including FTIR, SEM and resistance test was finished by me. XPS and XRD were tested under the help of Ben Spencer and John Warren, respectively. The signal processing units and designed different triggers for the human-machine interfaces were constructed by Ruohao Li. The theoretical model to illustrate the change of resistance with external tensile force was established by Xiaoteng Liu. The thorough first draft of the manuscript was written by me. The collaboration on the multiple iterations of the paper was conducted by Xuqing Liu and me to produce the final version which was then submitted and published after major corrections.
4.4 Other Publications

4.4.1 Review of PAMD for E-textiles

Zhu, C.; Li, Y.; Liu, X. Polymer Interface Molecular Engineering for E-Textiles. 
*Polymers* 2018, 10, 573. DOI: 10.3390/polym10060573

This publication reviewed different surface modification techniques in polymer-assisted metal deposition (PAMD) for manufacturing conductive textiles and their applications in E-textiles. The polymer matrix, polymerisation method, metal coating and substrate of each modification method were critically analysed. Limitations of these approaches were studied and the suggestions for the development of high-performance E-textiles were discussed.

The writing of the review was conducted by me, jointly with Xuqing Liu, and Yi Li. The design of the structure of review and the writing of the framework were finished by Xuqing Liu and Yi Li. The paper was written by me and finalised by Xuqing Liu.

4.4.2 Conductive Fibres for Detecting Physical Rehabilitation


The contribution to this paper by me was minor. The preparation of conductive fibres based on dopamine-assisted electroless deposition (ELD), which were used as wearable magnetic induction sensors for monitoring physical rehabilitation was conducted by me. Some suggestions, revisions and comments of the manuscript were proposed by me.

4.4.3 Highly Conductive and Adhesive Polypyrrole Hydrogels

The contribution to this paper by me was minor. The principle of the complex formation of PDA through the self-assembly of dopamine in the tris buffer and the increasing the conductivity of polypyrrole (PPy) hydrogels by adding PDA molecules was proposed under my help. The establishment of the stretchability test of PPy hydrogels with electropolymerized PDA to show the recoverable nature of these gels was finished under my help.

4.4.4 Conference Poster Presentation

Zhu, C.; Li, Y.; Liu, X. Q. Chemical Functionalization of Fiber Surface Towards Future Wearable Electronics. The 12th Textile Bioengineering and Informatics Society, 2019, Suzhou, China
Chapter 5. Collection of the Papers
5.1 Publication Number One

Mussel-Inspired Flexible, Durable, and Conductive Fibers Manufacturing for Finger-Monitoring Sensors
Mussel-Inspired Flexible, Durable, and Conductive Fibers Manufacturing for Finger-Monitoring Sensors

Chuang Zhu, Xinyi Guan, Xi Wang, Yi Li, Evelyn Chalmers, and Xuqing Liu*

Here a bioinspired facile and versatile method is reported for fabricating highly durable, washable, and electrically conductive fibers and yarns. Self-polymerized dopamine plays as adherent layers for substrates and then captures Pd\textsuperscript{2+} catalyst for subsequent metal deposition on substrates. The Pd\textsuperscript{2+} ions are chelated and partially reduced to nanoparticles by polydopamine (PDA)-modified substrates and the catalytic performance is investigated in surface electroless deposition. Importantly, this is the first report about PDA as both ligand and enhancement in Pd catalyst system, and the mechanism of their excellent catalytic performance is studied by X-ray photoelectron spectroscopy. This approach can be extended as a general method for fabricating conductors from all kinds of substrates and precursory research about PDA/Pd catalyst application in surface catalysis.

1. Introduction

In recent years, fiber-based wearable electronics such as fiber-shaped energy harvesting and storage devices, wearable displays, deformable antenna, and fiber computers/processors have attracted a great deal of attention.\cite{1–6} For realizing these devices, one critical step is the fabrication of conductive components such as interconnects on flexible and stretchable fibers/fiber assemblies.\cite{7} Although several novel materials, including conductive polymers, carbon nanotubes (CNTs), and graphene, were developed in recent decades, metal is still considered as the best coating material in terms of conductivity, stability, compatibility, and cost.\cite{8,9} Compared with other substrate materials such as plastics and elastomers, fibers, and paper have the unique porous structures. Thus, the desired coating materials should penetrate into the fibrous structures.\cite{10–12}

Several attempts have been made to metalize fibers such as thermal evaporation, atomic layer deposition, magnetron sputtering, and galvanic deposition.\cite{13–17} But the fabrication via above-listed methods does not have chemical bonds or other tethering force between the metallic layers and the surface of fibers. The inherently poor adhesion between metal nanoparticles and flexible substrates limits the widespread application of conductive fibers. Additionally, for flexible substrates with the particular 3D structure, such as sponges, the electroconductivity is poorly containable because the 3D structure, as a spatial mask, decreases the uniformity and continuity of the deposited metal films initiated by gravity.\cite{18} Recently, Liu et al. reported the polymer-assisted metal deposition by surface-initiated atomic transfer radical polymerization.\cite{19} The designed polymer interface introduces covalent bonds between the surface of fibers and grafted polymer brushes and viscoelastic and high-swelling intrinsic properties of polymers provide the nanometer-scale mechanical interlocking of deposited nanoparticles within brushes. Although the resultant conductive yarns are highly durable and washable, the polymerization requires an inert N\textsubscript{2} protection and complex steps. Moreover, the target substrates have to contain abundant hydroxyl groups. On the other hand, with the booming development of novel materials, which can be employed in wearable electronics as their variety of performances, how to develop a new surface modification method which can be used in virtually any substrate and create conductive composites is important.

According to Lee’s report,\cite{20} dopamine which mimics the adhesive chemistry of mussel plaque detachment allows the spontaneous deposition of nanoscale-thin, surface-adherent films of poly(dopamine) (PDA) on virtually all material surfaces such as polymers, ceramics, semiconductors, and novel metals by simple dip-coating in an alkaline solution. More importantly, secondary reactions can be used to produce a variety of ad-layers on the top of PDA, including metal films by electroless metalization.\cite{21} In some reports, silver (Ag) was coated on different fibers, such as polyester polyethylene terephthalate (PET), meta-aramid, glass, cotton, and polyurethane, via PDA-assisted electroless deposition (ELD).\cite{22–26} However, in accordance with Zheng’s review work,\cite{27} silver, as a conductive coating material, is much more expensive than copper and nickel. More importantly, according to the European Commission and its nonfood Scientific Committee on Emerging and Newly Identified Health Risks, there are still some arguments related to the toxicity of silver nanoparticles and additional adverse effects caused by the use of silver nanoparticles should be further evaluated.

To address the challenges, we report here a simple, versatile, and scalable approach for preparing highly durable, washable, and electrically conductive fibers and yarns by electroless nickel (Ni) plating on fiber surfaces modified with PDA as adhesive layers. Copper (Cu) can be an alternative coating choice due to the high conductivity and low price. However, the
oxidation of the Cu layer can cause the slow decrease in conductivity when the sample is placed in air. Thus, nickel, as an air-stable conductive metal, is mainly discussed in this report. In detail, PDA that tethers one end on the surface via covalent and noncovalent bonds is first grown from fibers by dip doping in tris buffer. Subsequently the grafted PDA interface anchors the catalyst in an aqueous solution. The captured catalyst final activates electroless plating metallization. The as-made conductive yarns can be demonstrated as interconnects to power light-emitting diodes (LEDs) and also can be used to track finger motions. In principle, this effective approach can be extended as a general method for producing conductors from all kinds of substrates.

2. Results and Discussion

2.1. The Graft of PDA onto Substrates and Catalyst Immobilization

As proof-of-concept, we synthesized PDA by pH-induced polymerization, which strongly adheres to the surface of various substrates and provides a platform for secondary reactions. The PDA modification can control the coating thickness by varying deposition time and is recognized as an environmentally friendly chemical approach. The procedure is illustrated in Scheme 1. In a typical experiment, we first immobilized the PDA interface on fiber surfaces by dip doping in tris buffer for 24 h at room temperature. Then, the samples were washed with distilled (DI) water several times and dried with a N2 gas stream.

Fourier transform infrared spectroscopy (FTIR) was applied in this work to confirm the successful PDA-coating process. From Figure 1a, cotton as a natural cellulose, without any treatment and modified by PDA were compared. The new peak at 1612 cm−1 is attributed to the N–H bending vibration in primary amine groups of PDA. From Figure 1b, PET as one of the most widely used synthetic fibers, without any surface modification and modified by PDA were analyzed and attributed. The new peak at 1232 cm−1 is attributed to the C–O stretching vibration in catechol groups of PDA. The peaks at 1635 and 3284 cm−1 are attributed to N–H bending state and N–H stretching state in primary amine groups of PDA, respectively. The successful wrapping of PDA on wool surface is also detected by FTIR (see Figure S1, Supporting Information).

After PDA modification, the PDA-coated samples were immersed into a 5 × 10−3 M (NH4)2PdCl4 aqueous solution for 2 h, where Pd2+ moieties were anchored within the PDA interface. The captured palladium moieties/particles provide effective catalytic sides for subsequent ELD. The proposed mechanism of dopamine polymerization has been known but when adding Pd (II) to PDA-modified substrates, the binding mechanism between PDA and Pd (II) should be explained. Thus, X-ray photoelectron spectroscopy (XPS) was applied to investigate the surface composition of the Pd/PDA-PET composite. The XPS survey spectrum reveals region scans for all elements detected in the catalytic sample (see Figure S2, Supporting Information). The C 1s spectrum in Figure 2a shows three peaks assigned to C–C (284.8 eV), C–O/C–N (286.4 eV), and C=O (288.9 eV) species originating from the PDA layer.[28] From the N 1s spectrum (Figure 2b), the peak at 402.0 eV was assigned to the component of primary amine (R–NH2), which is associated with dopamine. The peak at 399.7 eV was attributed to the secondary amine component (R–NH–R), which is associated with both PDA and accepted intermediates. The peak at 398.6 eV was assigned to the tertiary/aromatic amine functionality, which was associated with 5,6-dihydroxyindole and 5,6-indole-quinone.[29] Additionally, the O 1s region
in Figure 2c is fit with two oxygen signals assigned to C=O (531.9 eV) and C–O (533.2 eV) species, which were from the PDA layer.[28] In Pd 3d region (Figure 2d), two spin–orbital doublets (Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ peaks) are shown, indicating there are two electronic states of palladium, i.e., Pd (0) (binding energy 333.9 and 343.3 eV) and Pd (II) (binding energy 339.1 and 346.4 eV). This confirms that Pd$^{2+}$ ions were chelated by the primary amine groups of PDA and the catechol groups of PDA reduced some Pd$^{2+}$ ions into Pd nanoparticles, which were encapsulated within PDA layers.[30]

It is interesting to note that in comparison with previous reports,[28,31] there is an increase of the binding energy of palladium in our report. The first reason for the increase in binding energy is due to the electronic environment around Pd catalysts. PDA, due to the characteristics of its π bond, causes the outer electrons of the palladium ions to participate in the π-metal stacking, resulting in an increase in binding energy. On the other hand, it is important that the palladium nanoparticles we reported were reduced by PDA, not further reduced by other reducing agents such as sodium borohydride. Therefore, the reduced palladium nanoparticles were nearly not agglomerated, resulting in the larger binding energy.[32] The smaller catalytic nanoparticles also contribute to the larger specific surface area of catalytic region, leading to the increased performance of the catalyst in the followed ELD. To prove that, extra NaBH$_4$ was added in the catalyst solution to further reduce palladium ions into palladium particles on the surface of PDA-PET and when this sample was immersed in the ELD bath, only a few
weak bubbles were formed, suggesting a very low reaction rate. Therefore, on the surface of a substrate, PDA plays a role of reducing and stabilizing palladium ions with an adhesive force. Importantly, the stabilized Pd$^{2+}$ can enhance the catalytic action in ELD, causing the good performance of metal coating.

### 2.2. Surface Characterization

Since the surface morphology of the obtained copper or nickel coatings may affect the electrical, mechanical, and optical properties of the conductive fibers that are produced, scanning electron microscopy (SEM) was employed to characterize the morphology of thin copper or nickel films in detail. The SEM photographs of the nickel coating on cotton (c, e) and PET (d, f) fibers and pure cotton (a) and PET (b) fibers are shown in Figure 3. Compared with Figure 3c,d–f, a significant change on the surface of raw materials (Figure 3a,b) can be observed after nickel electroless plating. And it can be clearly seen that uniform and continuous nickel nanoparticles were compactly dispersed on the surface of PET and cotton fibers. The homogeneous distribution of Ni nanoparticles on the fiber surface would enhance the electrical performance of as-made conductive fibers. Additionally, the longer ELD time caused the bigger size of nickel nanoparticles. The detailed change of the size of nickel nanoparticles on cotton fibers with the increased ELD time is also analyzed by SEM (see Figure S3, Supporting Information).

Particularly, for cotton fibers which have the natural hollow structure, conventional methods initiated by gravity such as physical vapor deposition and chemical vapor deposition can only coat metal nanoparticles on the outer layer of cotton fibers because of the directional limitation. This causes that the coating layer is not continuous and fully covered on multidirectional surfaces. However, in this report, cotton fibers are immersed into aqueous solutions throughout, which ensures the inner layer can be modified by PDA and coated with nickel nanoparticles in ELD. Figure 4 shows that the nickel particles deposited not only on the upper surface of the fibers but also

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**Figure 3.** SEM photographs of cotton and PET fibers a,b) without any treatment and c–f) with the nickel coating (electroless plating time for cotton and PET is 10 min).
on the surface of inner fibers. And electrical properties of the prepared metallic cotton yarns and fabrics would be enhanced by this integral and continuous coating.

X-ray diffraction (XRD) is a conventional and simple technique to reveal the size and the shape of the unit cell for any crystalline compound. In previous reports,[19,33] no discussions were related to the size and the shape of deposited nickel nanoparticles on the surface of fibers. Accordingly, this report reveals the XRD patterns of nickel particles on the cotton surface at different ELD time. From Figure 5a, the main peak at 2θ value of 44.48° was observed from these two patterns. According to the standard powder diffraction card of Joint Committee on Powder Diffraction Standards, the value corresponds to the (111) crystal plane of Ni. Based on the powder diffraction file (PDF) card of the JADE-SCAN software, the characteristic face-centered cubic crystalline structure of deposited nickel particles was also identified, implying the excellent conductivity of as-made nickel-deposited fibers. According to the Scherrer equation, the average size

![Figure 4. SEM photographs of nickel-coated cotton fibers with the unique hollow structure (electroless plating time is 10 min).](image)

![Figure 5. a) The XRD spectrum of the Nickel/PET composite. The SEM photographs of nickel-coated PET fibers at the low-voltage mode: b) electroless plating time is 30 min and c) 60 min.](image)
of nickel nanoparticles when the ELD time is 30 and 60 min is 16.6 nm in both cases. However, the size of nickel nanoparticles is clearly bigger when the ELD time is longer based on the SEM photographs as shown in the supporting information. To further investigate this, low-voltage scanning electron microscopy, as an intuitive measurement, was used to determine the size of nickel nanoparticles when ELD is 60 min. The low-voltage mode ensures more detailed information of the surface morphology but images are less 3D. From Figure 5b,c, it can be clearly observed that the grown big spheres are comprised of small nanoparticles, which are estimated to be 16–17 nm, which is coincident with XRD results. This means that nickel nanoparticles are deposited on fibers with the same size along the ELD, resulting in the uniform coating. Importantly, these granular nanoparticles are homogeneously and continuously arranged on the fiber surface with a compact distribution, leading to the perfect conductive property of nickel-plated composites.

2.3. Electrical Conductivity and Mechanical Durability

Compared with bare textile fibers which are well known to be insulated, the as-made Ni-coated fibers are electrically conductive. In this report, four types of conductive yarns are produced, including wool, cotton, nylon, and PET and the digital images of yarns are recorded (see Figure S4, Supporting Information). From Figure 6a, the electrical surface resistance of the cotton yarn decreases with increasing plating time, reaching as low as 0.05 Ω cm$^{-1}$ at 60 min ELD. And longer plating leads to heavier samples due to the increasing amount of plated metallic nanoparticles (see Figure S5, Supporting Information). However, a saturation plateau occurs at ~60 min. This can be attributed to catalyst poisoning. Clearly, extending the depositing time resulted in a conspicuous decrease in resistance, but a more brittle and stiff film with increased thickness. This can be explained by the decreased contact resistance between plated nanoparticles when they are more tightly packed with longer depositing time. However, no evidence is shown to prove this hypothesis.$^{[34]}$ Luckily, we found three different types of distributions of nickel nanoparticles on a single fiber using field emission gun scanning electron microscopy (FEG-SEM). The surface morphology of Ni nanoparticles on the cotton fiber when the ELD time is 15 min is shown in Figure 6b and it perfectly confirms the assumption. From the yellow area of the image, nickel nanoparticles were dispersed at a low rate of compact distribution, which can be defined as the first layer of nickel coating. Based on the blue area of the photograph, the plated nickel particles were more continuous on the surface of the cotton fiber, leading to the decreased resistance. This can be defined as the second layer. When depositing time increased further, nickel nanoparticles were more densely aggregated on the second layer, leading to the further decrease in resistance and the formation of subsequent layers such as the cyan area of the FEG-SEM image. With increased ELD time, the coated nickel film on fibers was thicker and more compact, creating higher conductivity at the expense of flexibility.

The electrical stability under multiple cycles of bending and washing is one of the most critical challenges of conductive yarns and fabrics. To investigate this, washing cycles using simple hand washing and squeeze drying and mechanical bending cycles using simple hand bending with a radius of 15 mm were employed to test the rubbing and bending robustness, respectively. No obvious increase of surface resistivity on the Ni/cotton conductive yarn was observed after five washing and drying cycles or 2000 simple mechanical bending cycles (see Figure S6, Supporting Information). This was due to the chemical bonds between the surface of fibers and the coated PDA layers.

2.4. Demonstrations of Ni Conductive Yarns

One of the most important applications for the as-prepared conductive yarns is used as conductive wires in electronic circuits because of their high conductivity and robustness. As a demonstration, a simple circuit was built by bridging a 9 V battery and one electrical contact of a blue LED with prepared conductive yarns. When the blue LED contacted the alkaline battery, the LED turned on immediately and illuminated for more than 20 min until the contact was disconnected (see Figure S7, Supporting Information). On the other hand, because of the high sensitivity to strain, these conductive yarns
can be used as a strain sensor to monitor tiny motions of the finger. As a proof-of-concept, we sewed nickel-coated cotton yarns into four finger parts of a commercial glove, as shown in **Figure 7a**. When the finger bent/unbent at different gestures, the conductive yarns sewn into glove were stretched/released, causing the increased/decreased contact area between conductive fibers (see Figure S8, Supporting Information). This gave corresponding resistance signal (obviously the larger/smaller area of contact between conductive cotton fibers would lead to the decrease/increase in resistance), detected by Keithley 2400 Source Meter. Three different hand gestures, including releasing, grasping, and holding, are tested in this experiment, as illustrated in Figure 7b. From Figure 7c, the resistance showed a quick decrease during bending fingers and the resistance recovered to its original value during unbending fingers. We could successfully monitor the motions of the finger through recording the resistance signal changes versus hand gestures. More importantly, these conductive yarns also can be attached to the finger parts of the robotic hand to track the robotic finger movements, as shown in Figure 7d,e. From Figure 7f, when the gesture of robotic hand changed from releasing to grasping, the resistance of attached conductive yarns reduced correspondingly because the stretching caused more internal connections between conductive staple fibers. And when the gesture of robotic hand changed from grasping to releasing, the resistance of attached conductive yarns increased since releasing reestablished the conductive network in the nickel layer.

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**Figure 7.** a) Digital photographs of conductive yarns sewn into the four finger parts of a glove. b) Digital photographs of three typical finger movements, including releasing, grasping, and holding. c) The resistance changes versus hand gestures when fingers move. d) Digital photographs of conductive yarns attached to the four finger parts of a robotic hand. e) Digital photographs of two typical finger movements, including releasing and grasping. f) The resistance changes versus hand gestures when the robotic hand moves.
3. Conclusion

In conclusion, this study demonstrates a novel, facile, and versatile approach for preparing durable, flexible, and electrically conductive yarns. PDA nanofilms are first coated on fiber surfaces by immersing them into an alkaline aqueous solution. PDA-modified fibers then anchor the catalyst via ion chelation and finally metal nanoparticles are deposited onto the catalytic area, resulting in the formation of polymer-brided conductive composites. This in situ plating method ensures that metallic nanoparticles are distributed on the surface of fibers continuously and uniformly. In addition, as the PDA coating serves as an adhesive layer, this leads to the superior electrical stability of as-made conductive yarns under repeated bending and washing cycles. Such manufactured conductive yarns can be used as the flexible electrical conductor in electrical circuits to power an LED and also a strain–stress sensor to monitor finger movements. The bioinspired polymerization of dopamine can be used for multifunctional coatings. Thus, PDA-assisted ELD can be a universal method for coating nickel or copper nanoparticles on virtually all material surfaces. PDA-assisted ELD is also a low-energy and green method throughout and the low price of nickel and copper makes mine can be used for multifunctional coatings. Thus, PDA-assisted ELD can be a universal method for coating nickel or copper nanoparticles on virtually all material surfaces. PDA-assisted ELD is also a low-energy and green method throughout and the low price of nickel and copper makes them perfect coating materials for producing conductive yarns on a large scale. Such conductive yarns should develop a wide variety of applications in fiber-based wearable electronics, radiation and electromagnetic protection, energy, architecture, and biomedical industries. Moreover, PDA/Pd catalyst was first employed in surface-catalyzed reactions and shows better performance than isolated Pd catalyst, and PDA as both adhesion and enhancement will show broadened application in other surface catalytic reaction.

4. Experimental Section

Materials: Dopamine hydrochloride, ammonium tetrachloropalladate(II) \[(\text{NH}_4)_2\text{PdCl}_4\] and all other chemicals were purchased from Sigma-Aldrich. All textile substrates were obtained from the Dye House at the University of Manchester. Each fiber substrate was ultrasonically cleaned in acetone and DI water for 30 min, respectively, then dried with a N₂ gas stream.

Dopamine Spontaneous Polymerization on the Surface of Fibers: Dopamine was dissolved in 0.01 mol L⁻¹ tris (hydroxymethyl) aminomethane (pH 8.5) buffer to prepare a dopamine solution (2 g L⁻¹). Cleaned substrates were dipped into the solution and the nonspecific microparticle deposition on surfaces was prevented by stirring and/or vertical sample orientation. The pH-induced oxidation of dopamine changed the color of the solution to dark brown. After a predetermined reaction time of 24 h, the adherent PDA film coated surfaces were filtered and rinsed thoroughly with ultrapure water and dried with a N₂ gas stream.

Metallization by ELD: The modified samples were immersed into a 5 × 10⁻³ M \[(\text{NH}_4)_2\text{PdCl}_4\] aqueous solution and placed in a dark environment for 15 min to load catalysts by chelation and reduction, followed by thorough rinsing with DI water to remove the physical absorption of catalyst inks. The Ni electroless plating was performed in an ELD bath containing 4:1 volumetric proportion of nickel-to-reductant stocks at room temperature. A nickel stock solution consisting of 10 g L⁻¹ lactic acid, 20 g L⁻¹ sodium citrate and 40 g L⁻¹ nickel sulfate hexahydrate was prepared in advance. A fresh reductant solution containing 1 g L⁻¹ dimethylamine borane in DI water was prepared separately. After mixing, the solution was adjusted with ammonia to pH = 8. After ELD, all samples were washed several times and dried with compressed air.

Characterization: The surface morphology of the samples was characterized by scanning electron microscopy (ZEISS Ultra-55 and TESCAN Mirra3). The surface resistance was measured by a two-point probe method with a Keithley 2400 Source Meter. The self-polymerization of dopamine in solution was investigated by UV–vis spectroscopy (M550 Double Beam Scanning UV/Vis Spectrophotometer). The coating of PDA on fibers was tested by Fourier transform infrared spectroscopy (NICOLET 5700 FTIR). The size and the shape of the unit cell for metallic particles on the fiber surface were determined by X-ray diffraction (PANalytical X’Pert Pro X’Celerator diffractometer).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords
c conducive fibers, electroless deposition, finger-monitoring sensors, polydopamine, surface catalysis

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Supporting Information

Mussel-Inspired Flexible, Durable, and Conductive Fibers Manufacturing for Finger-Monitoring Sensors

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The yarn was placed in contact with the battery and LED.
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5.2 Publication Number Two

A Nature Inspired, Flexible Substrate Strategy for Future Wearable Electronics
A Nature-Inspired, Flexible Substrate Strategy for Future Wearable Electronics

Chuang Zhu, Evelyn Chalmers, Liming Chen, Yuqi Wang, Ben Bin Xu, Yi Li, and Xuqing Liu

1. Introduction

Recently, there has been rapidly increasing interest in the development of flexible wearable electronics such as tiny motion-monitoring sensors,[1–5] wearable energy harvesting and storage devices,[6–13] electronic skins,[14] and medical implants.[15–19] The fabrication of flexible conductive materials is one critical step for realizing these devices. Currently, most flexible conductive materials are made by coating metallic layers (Au, Ag, Cu, and Ni) on flexible substrates such as textiles,[20,21] polyethylene terephthalate (PET) films,[22–24] poly(dimethylsiloxane) (PDMS),[25–27] sponges,[25,28] and plant leaves.[29,30] Compared with other metal coating candidates, nickel and copper are still considered as the best materials because of their low cost and high electrical conductivity. Many methods of depositing a layer of conductive metals on flexible substrates have been studied, including physical vapor deposition (PVD),[31] chemical vapor deposition (CVD),[32,33] electroplating,[34] and electroless deposition (ELD).[35,36] Expensive equipment and complex operation steps are required for PVD and CVD. Electroplating needs the conductive substrate to activate the metal deposition, which is not suitable for the major of polymeric substrates. In general, ELD is particularly attractive for the metallization of flexible surfaces because it can be conducted under ambient conditions on a large scale without the requirement of expensive equipment.

Notably, pretreatment of substrates is crucial in ELD. Polymer-assisted metal deposition (PAMD) is a full-solution processing strategy, in which the surface-grafted polymer is innovatively introduced to facilitate the ELD on polymer substrates. The polymer interface molecular engineering plays an important role in PAMD because the grafted polymer acts as an adhesion layer for the deposited metal film and improves the uptake efficiency and selectivity of the catalyst.[37] Several polymer interfaces, including poly[2-(methacyryloyloxy)-ethyltrimethylammonium chloride] (PMETAC),[38] and polydopamine (PDA),[39,40] have been reported in previous works. Although highly flexible and durable conductors are manufactured via ELD assisted by PMETAC, there are still some drawbacks existing in this method. The synthesis of PMETAC is very complex and the surface-grafting technique of PMETAC requires N2 protection. Additionally, plasma treatment is required when the target substrates do not contain abundant hydroxyl groups. In contrast to PMETAC, dopamine, a kind of biomaterial found in mussels, provides a promising opportunity by allowing the self-deposition of adherent PDA films on...
virtually all material surfaces via simple dip coating in an alkaline solution without any pretreatment. More importantly, catalysts can be anchored by PDA interfaces for subsequent ELD. Therefore, such a phenol-rich material seems like an ideal alternative candidate for PMETAC-assisted metal deposition. Nevertheless, dopamine is expensive and the PDA modification process is time consuming (24 h), which are less favored for industrial production.

To address this need, we here report a facile, low-cost and universal method for fabricating high-performance compliant flexible conductive composites at industrial scales. The key-enabling feature of this strategy is the introduction of tannic acid (TA) as the designed interface via dip coating and subsequent catalyst-activated ELD. Inspired by textile dyeing and coloration processes, TA can form mordant combinations (TA + metal salts) on the fiber surface through the interaction of the TA anions and metal cations such as Fe$^{3+}$, indicating the metal ion chelating/reducing ability of TA. Compared with PDA, TA is abundant in many plants such as gallnuts and the price of TA is relatively hundredfold lower than that of dopamine. Moreover, the time taken for the TA coating on almost all inorganic and organic surfaces is significantly shortened. Importantly, the TA aqueous solution is air stable and can be stored in the laboratory for more than one month. As proof-of-concept applications, as-prepared conductive yarns and fabrics are demonstrated as conductors to power the light-emitting diode (LED) in a simple circuit. This approach is compatible with typical surface lithography techniques (e.g., screen printing) for making desired conductive patterns. In addition, durable bending sensors based on Ni-coated polyurethane (PU) sponges obtained via ELD are used to detect arm motions. Interestingly, we found that there is an intrinsic link between conductivity and flexibility in flexible conductors created by solution deposition techniques. This intrinsic link is explained by the Kelvin Problem model in metallic grain growth and will be scientific law in the design of future flexible devices.

2. Results and Discussion

2.1. Surface Chemical Characterization

The fabrication of metal-coated flexible and stretchable conductors consists of TA coating, catalyst immobilization, and ELD, as illustrated in Figure 1. In brief, TA was first attached to flexible surfaces via intermolecular hydrogen bonds by immersing these cleaned substrates into the TA aqueous solution. Such a polymerized plant-based phenolic coating offers sufficient sites to anchor catalysts for subsequent ELD. Pyrogallol-rich solutions such as red wine, coffee, and red tea were also able to successfully coat pyrogallol moieties on flexible surfaces, immobilize catalysts, and then activate ELD.

Fourier transform infrared spectroscopy (FTIR) was used to confirm the coating of TA. Pristine and TA-modified cotton fabrics were compared because of cotton's wide use in daily life. From Figure 2a, the new peak at around 1715 cm$^{-1}$ is assigned to the C=O stretching of carbonyl groups in TA. The medium intensity band at 1605 cm$^{-1}$ is associated with the C=C stretching vibration of aromatic groups in TA. The raw polyurethane sponge and TA-coated PU sponge were analyzed due to its

Figure 1. The scheme illustration for the fabrication of flexible conductors via TA modification and electroless deposition.
unique 3D and hollow structure. From Figure 2b, the strengthened peak at 3270 cm\(^{-1}\) is attributed to the O–H stretching state of phenol groups in TA. After the TA modification, the TA-modified substrates were dipped into a \(5 \times 10^{-3} \text{ M} \) \((\text{NH}_4)_2\text{PdCl}_4\) aqueous solution for 15 min to anchor catalysts. The binding mechanism between TA and Pd(II) is very important in this catalytic system and will affect the catalytic performance. Therefore, X-ray photoelectron spectroscopy (XPS) was used to characterize the surface chemical composition in the Pd/TA-PET film. The proposed binding mechanism between TA and palladium ions is shown in Figure 2c. From Figure 2d, two spin–orbital doublets are shown in the Pd 3d spectrum, indicating two electronic states of palladium in the catalytic surface.\(^\text{[45]}\) The peaks at 337.6 and 347.4 eV are attributed to Pd(0) species and the peaks at 342.8 and 351.0 eV are assigned to Pd(II) species. However, these reduced Pd nanoparticles do not exhibit significant catalytic behavior because when extra reductants were added to reduce more Pd ions into Pd nanoparticles on the surface of TA-PET, the sample would not activate the ELD. Thus, chelated Pd ions in TA by phenol groups were the major cause that initiated the ELD. To investigate the effect of TA on binding catalysts, a raw PET film without any surface modification was immersed into the same seeding solution. The XPS results of the Pd-PET film show that the peaks in the Pd 3d signal spectrum have the same binding energy but the intensity of these peaks is much lower than that of the Pd/TA-PET film (Figure S1, Supporting Information). The Pd(0) and Pd(II) species in the Pd-PET sample might be anchored by cation–π interaction\(^\text{[46]}\) between benzene groups in PET and Pd ions. Therefore, it can be clearly seen that phenol groups in TA play an important role as a binder to anchor catalysts.

### 2.2. Surface Morphology Characterization

The electrical, mechanical, and optical properties of as-made conductive samples may be affected by the surface morphology of the deposited metal nanoparticles. Scanning electron microscopy (SEM) was thus employed to explore the morphology of the obtained metal coating. Fiber assemblies and sponges will
cause a decrease in uniformity and continuity of metal films deposited by gravity-initiated methods such as sputtering. This is because yarns and fabrics have the unique porous structure and PU sponges contain the particular 3D framework. For this reason, metal-coated cotton fibers and sponges, manufactured by our method, are discussed in the SEM characterization. The SEM photographs of pure cotton fibers (a), the untreated sponge (b), Ni-coated cotton fibers (c), and the nickel coating on the PU sponge (d) are shown in Figure 3. It can be clearly seen that the surface morphology of unmodified materials changed significantly after Ni ELD. As shown in Figure 3c,d, Ni nanoparticles were very homogeneously, continuously, and densely covered on the surface of these two substrates. The electrical performance of the as-prepared flexible conductors would be enhanced by the compact and uniform nickel nanoparticle film. More importantly, the coating layer is fully deposited on the multidirectional surfaces. In other words, homogenous and continuous nickel nanoparticles were compactly dispersed on both of the outer and inner layers of the substrates. This would also enhance the electrical properties of the as-made metallic flexible substrates. After Cu ELD, the surface of PET fiber substrates is also fully packed with dense aggregates of Cu nanoparticles (Figure S2, Supporting Information). The crystalline structure and size of nickel and copper nanoparticles deposited on flexible samples were detected by X-ray diffraction (XRD). From Figure 3e, nickel-coated samples show a characteristic peak at the 2θ value of 44.9°. According to the standard power diffraction card of Joint Committee on Powder Diffraction Standards (JCPDS), this peak is associated with the (111) crystal face of face-centered cubic (fcc) Ni (JCPDS no. 45-1027). The average size of the crystalline metallic Ni nanoparticles was ≈16.5 nm according to the Scherrer equation. The obtained data from XRD are coincident with the above-listed SEM results, in which the ELD time is 20 min. Figure 3f shows that the big clusters (300–500 nm) are made of numerous small nanoparticles (15–20 nm) when the ELD time is 60 min. This proves that Ni nanoparticles are deposited on samples with the same size throughout the whole ELD process. The XRD spectrum of Cu-coated samples shows three main peaks at 2θ values 43.9°, 51.0°, and 74.7° corresponded to the (111), (200), and (220) planes.

Figure 3. SEM photographs of cotton fibers and the PU sponge a,b) without any treatment and c,d) with the nickel coating (20 min ELD). Insets are magnified images. e) The XRD spectrum of Ni-deposited flexible substrates and f) the SEM photograph of Ni-coated samples (60 min ELD).
respectively, with the Cu nanoparticles also maintaining the same size during the ELD (Figure S3, Supporting Information). The average size of copper particles (the crystal plane is 111) was \( \approx 31.1 \) nm. We found that the Cu-deposited samples suffered a decrease of electrical conductivity after exposing them to air for 7 d. This is due to the oxidation of copper nanoparticles in air and it may be addressed by capping the metal by some developed methods in the electronic industry such as physical encapsulation.

### 2.3. Electrical Conductivity, Flexibility, and Mechanical Durability

It is well known that bare polymers are electrically insulating at room condition. In contrast, Ni-coated polymeric substrates prepared by our method are electrically conductive. In this report, highly conductive Ni films were homogeneously coated on sheets of cotton, wool, nylon fabric, PET films, PU sponges, and natural luffa sponges (Figure S4, Supporting Information). Surprisingly, the resistance of the single aramid fiber coated by copper can reach as low as \( 0.9 \, \Omega \, \text{cm}^{-1} \). And our results showed that the hydrophilic substrates containing amine groups can achieve higher conductivity due to more TA bonding on the substrates.\[44\] However, we found that the metal coating on amine-rich substrates such as wool is not very good, leading to lower conductivity. The reason might be that phenolic hydroxyl groups of TA molecules functionalize with protein molecules in wool to form complexes,\[45\] resulting in the decreased number of phenol groups available to immobilize catalysts. Thus, the formation of complexes between protein and TA would adversely affect the catalyst immobilization and subsequent ELD. From previous reports, the conductivity of metal-coated substrates increased with extending the ELD time.\[48\] However, limited reports discussed the flexibility of metal-coated samples during the ELD process in their intrinsic principle. Thus, British Standard (BS) 3356:1990, which is a method for determination of bending length and flexural rigidity of fabrics, and a two-point probe method were applied to test the bending length in warp direction and the surface resistance of Ni-coated cotton fabrics in different ELD times, respectively. From Figure 4a, it is clear to see that longer ELD leads to decreased surface resistance but increased bending length. After 10 min of plating, the surface resistance and the warp-wise bending length of Ni-coated fabric are \( 3230 \, \Omega \, \text{sq}^{-1} \) and 1.925 cm, respectively. Such a low value of the bending length indicates that this sample was very flexible. From Figure 4g, it can be seen that nickel nanoparticles were not fully covered on the fiber surface, indicating the excellent flexibility and the poor conductivity of the 10 min ELD sample. Thus, as shown in Figure 4c, when 1000 mechanical bending cycles (bending radius = 0.1 mm) were applied in the 10 min ELD sample, there was no obvious change in the surface resistance (\( R/R_0 = 1.1 \)). After 20 min of depositing, a quick decrease of surface resistance (\( 16.68 \, \Omega \, \text{sq}^{-1} \)) can be observed and the bending length in warp direction of our as-prepared fabric is 2.325 cm. The increased value of bending length demonstrates that this sample was less flexible than the 10 min ELD sample. From Figure 4h, although nickel nanoparticles were fully packed on the fiber surface with a multilayers-shaped structure, there were numerous gaps between these building blocks. These unfilled gaps could prevent the nickel films of the 20 min ELD sample from cracking under large bending, as illustrated in Figure 4b. Therefore, only a small increase of surface resistance (\( R/R_0 = 1.6 \)) in the mechanical bending test was illustrated in Figure 4d. With a longer plating time (30 min), the surface resistance and the warp-wise bending length of Ni-deposited sample are \( 5.29 \, \Omega \, \text{sq}^{-1} \) and 2.725 cm, respectively. The slow decrease rate of surface resistance was due to catalyst poisoning. The value of bending length increased continuously, indicating the stiffer Ni-coated fabric. From Figure 4i, nickel nanoparticles aggregated to form clusters on the surface of the coating layer, resulting in the brittle and stiff nickel film. As a consequence, the 30 min ELD sample showed a quick increase of the normalized resistance in the bending test from 1 to 3 in Figure 4e. After 60 min of electroless plating, the surface resistance showed a small decrease from 5.29 to 1.02 \( \Omega \, \text{sq}^{-1} \), which is due to the further catalyst deactivation. However, the value of the bending length in warp direction experienced a large increase from 2.725 to 3.925 cm, demonstrating higher stiffness of as-made samples. From Figure 4j, nickel nanoparticles continued to aggregate and form bigger and more compact clusters, causing a more brittle and stiff nickel film. The particle aggregation significantly increased the value of bending length but had a very limited impact on surface resistance. From Figure 4f, the 60 min ELD sample illustrated a dramatic increase of the normalized resistance in the mechanical bending cycles from 1 to 5, which is ascribed to the very low flexibility of the nickel-coated sample. After the bending test, the obvious cracking could be found in the nickel coating layer of the 60 min ELD fabric (Figure S5, Supporting Information). Hence, based on the above discussion, the optimized ELD time of Ni metallization for manufacturing flexible conductive fibers was 20 min and the nickel film exhibited the multilayer structure with a great number of unfilled gaps between nickel nanoparticles. Additionally, the deposition of the Ni coating on flexible substrates includes three stages: i) the nucleation period (loose coating, highest flexibility), ii) the growth of spherical nodules period (the multilayers shape, medium flexibility), iii) the aggregating of nanoparticles period (clusters, lowest flexibility) (Movie S1, Supporting Information) and the surface morphology of metal deposits can be controlled in nanoscale by varying ELD time. The cooper-coated samples showed the same growth process (Figure S6, Supporting Information) and we found that metal aggregates in the outer surface of the coating layer are bigger than particles in the inner surface of the metal coating layer (Figure S7, Supporting Information).

### 2.4. Kelvin Structure Model

To further explore the relationship between conductivity and flexibility of surface-deposited metallic coating on flexible substrates, we introduce the Kelvin structure model to understand this intrinsic connection. The Kelvin problem, posed by Lord Kelvin in 1887, to find space-filling arrangement of similar cells, of equal volume, is relevant to deposited conductive coatings in this research because deposited metallic cells have a honeycomb-like structure. Under the observation
of SEM (Figure 5a,c), the morphologies of deposited layers (20 min ELD and 60 min ELD) are similar to the arrangement of bubble foams (Figure 5b,d), as shown in Figure 5. At the beginning of the deposition, the clusters are isolated, so that the conductivity of coating is poor but shows excellent flexibility, due to less attachment of each isolated particle. During the increased deposition time, if the plating solution keeps a constant concentration, ideally, as a self-catalyzing reaction, the metallic clusters will undergo competitive growth and squeeze with neighbor clusters, to form honeycomb-like structure by minimizing energy, following the Aboav–Weaire empirical topological law. Similar to coarsening in soap films, the size of metallic clusters grows due to pressure differences between cells, which follows the Von Neumann’s law well. Neighbor
swapping and bubble disappearance are two primary reasons in topological changes in metallic coating deposition by reducing perimeter (Figure S8, Supporting Information).\[50\] From the observation of the cross-section of coating, the SEM image in Figure 5e shows that on the bottom of the coating, the clusters are small and incompact. However, the clusters on the top of the coating, during the coarsening process, are bigger and more compact, as shown in Figure 5f. During bending, the surface stress released from the top surface of films to the incompact bottom is smaller compared with homogeneous structures, such as copper foil. An opposite example is the metal block material. After repeated bending, there will be some defects in the metal block material, to release the stress from the bending. As the defects continue to grow and spread, it can cause material breakage.\[51\] This is the main reason why the ductility of the ductile metal film produced by the physical method is not high. Thus, this hierarchical structure makes the conductive fibers or films show both excellent conductivity and flexibility. Introducing the Kelvin structure model allows improvement in predicting the flexible and conductive properties of the chemical-deposited coating, in both ELD and electrodeposition.

2.5. Practical Demonstrations

As this chemical strategy is a universal nature-inspired method for metallizing virtually all material surfaces, it can be readily extended to making metal-coated conductive fibers, yarns, and fabrics. The most important application of as-made conductive textiles is demonstrated as conductive wires and substrates in integrated electronic circuits due to their excellent electrical conductivity and high robustness. For proof-of-concept purposes, we built a simple circuit by connecting a 9 V alkaline battery with one electrical contact of a red LED with manufactured Ni-coated nylon yarns and Cu-plated cotton fabrics. When the battery contacted to the other contact of LED, the LED switched on immediately and illuminated for more than 10 min until the disconnection of contact was made (Figure S9, Supporting Information). Notably, this method shows excellent

Figure 5. a) The SEM image of the morphologies of deposited layers at 20 min ELD. b) The arrangement of small bubble foams. c) The SEM photograph of the plated particles at 60 min ELD. d) The arrangement of big bubble foams. e) The SEM image of the cross-section of coatings. f) The scheme illustration of the size of particles in different layers.
compatibility with screen printing for preparing desired conductive patterns. As shown in Figure 6, there are two strategies to fabricate well-defined metal conductive patterns onto flexible polymeric substrates via screen printing. In strategy A, the substrate is first coated with TA, which plays a role of the receiving matrix polymer. Catalytic salt is then screen printed with the help of polyethylene glycol (PEG), functioning as the delivering matrix polymer, onto the TA-modified substrate. After printing, catalyst patterns are formed on the substrate with a thin layer of TA because the inorganic catalytic salts diffuse from the PEG onto the TA-modified substrate. After printing, catalyst patterns are formed on the substrate with a thin layer of TA because the inorganic catalytic salts diffuse from the PEG into TA upon the contact between the two matrix polymers. Metal patterns are finally manufactured by electroless plating on the catalytic area. However, in strategy B, TA is initially screen printed with the aid of the PEG onto the raw substrate to form TA patterns. The substrate partially modified by TA is subsequently immersed into the aqueous solution containing catalytic salts and catalytic patterns are formed on the ink-patterned area because only TA-modified area can capture catalysts. Electroless deposition (ELD) is finally conducted on the catalyst-immobilized area to fabricate metal patterns on flexible substrates. Printing gels were prepared by mixing PEG, TA, (NH₄)₂PdCl₄, and DI water in different ratios (Table S1, Supporting Information). Compared with normal polymer substrates, textiles endowed with conductive properties provide a more powerful platform for wearable electronics because they are lightweight and skin friendly.[52] Thus, metal patterns are fabricated on textile substrates in this report. As presented in Figure 6, the Ni interdigital electrode is fabricated onto the flexible cotton fabric via screen printing. Additionally, the SEM image of the Ni pattern obtained through ELD on the cotton fabric shows a clear boundary, as shown in Figure 6c. This indicates that the well-defined nickel pattern was fabricated using our strategy. Furthermore, to demonstrate potential applications of the proposed manufacturing route in wearable electronics, a simple circuit with our as-made conductive yarns and one conductive keypad was built for controlling the red LED light via human touch, as shown in Figure 6d. From Figure 6e, when the keypad was connected by the human finger, the red LED was illuminated. This phenomenon shows that the fabricated metal pattern can play the role of a stable conductor on textile substrates for practical use.

More importantly, when applying our approach to a piece of PU sponge, several Ni-metallized PU sponges with

Figure 6. a) The scheme illustration of the manufacturing of conductive patterns via screen printing. b) The digital photograph of the cotton fabric with screen-printed conductive interdigital electrode. c) The SEM photograph of the clear boundary between the cotton fabric and the Ni pattern. d) The designed simple circuit for controlling the LED light via human touch. e) The LED was lit when the keypad was connected.
different flexibility and conductivity can be obtained. As shown in Figure 7a, different weights from 0 to 100 g were placed on the top of the Ni-coated sponge, respectively. This would cause the change of resistance signal, which can be detected by the Keithley 2000 Multimeter. On the basis of the above study, 10 min ELD and 20 min ELD samples are very flexible and further extending ELD time leads to rigid and brittle samples. From Figure 7b,c, when the weight increased from 0 to 5 g, there was no obvious change in the surface resistance of 10 min ELD and 20 min ELD Ni-plated sponges. When the weight further increased, this would induce increasing pressure and cause more contact area in the 3D structure, increasing the conductive pathway. As a result, the resistance signal would decrease accordingly. When the weight was removed, the resistance recovered to its original value due to the reestablishment of the conductive network. The responses of the resistance signal are similar when repeating loading/removing of the weight because the high flexibility of these two Ni-coated sponges can prevent cracking under large deformation. As shown in Figure 7d,e, when the weight increased from 0 to 5 to 20 g, the surface resistance of 30 min ELD and 60 min ELD samples showed a small increase because the loaded pressure induced crack propagation in the brittle and stiff Ni film and the micro/nanocracks decreased the number of cracks, leading to a increased conductivity.
conductive pathways.\textsuperscript{[54,55]} When the weight further increased, although large and rapid crack propagation was promoted, more contact area occurred between sponge scaffolds, enabling dramatic increase of the conductive pathway and thus, the surface resistance decreased. However, when the 100 g weight was removed, the surface resistance experienced a significant increase because of the numerous irreversible cracking (Figure S10, Supporting Information) and the reduction of contact area, resulting in the loss of conductivity. More importantly, these two samples could not detect the tiny pressure after one cycle because the well-coated nickel film was destroyed. Thus, when the 5 g weight was placed on the top of these two samples again, no obvious change of resistance could be detected. When further increasing the weight, the resistance signal is similar to the 10 min and 20 min ELD samples. Only two cycles are shown in this test because the inherent flexibility of sponges is much lower than that of textiles and more cycles would lead to the resistance of 30 min ELD and 60 min ELD samples changing from low to infinity. To further investigate the ability of this resistance sensor in monitoring bending movements of the human arms, the 20 min ELD Ni-coated PU sponge, which was considered as the best ELD time for cracking-control conductive PU sponges, was attached to the arm part of the human body, as shown in Figure 7f. From Figure 7g, the resistance of the attached conductive sponge decreased during bending arms and the resistance signal showed a quick increase during releasing arms. This was because the bending/releasing induced more/less strain in the hollow structure, increasing/decreasing the contact area between Ni-coatings. Repetition of the arm movements leads to similar resistance responses for each cycle because the 20 min ELD Ni-coated PU sponge is very durable.

3. Conclusion

In conclusion, a novel, facile and universal strategy of preparing conductive flexible substrates by TA modification and electroless plating of metal with strong adhesion is introduced. The key innovation of this method is the use of TA as a solid bridge between all demonstrated surfaces and Pd\textsuperscript{2+} seeds, capturing Pd\textsuperscript{2+} and partially reducing Pd\textsuperscript{2+} into Pd nanoparticles. Subsequently, the site-selective ELD can be performed to yield high-quality metal coatings for flexible electronics at room temperature. This versatile approach has several unique advantages in the following aspects. First, the naturally abundant TA is very cheap and the TA modification solution can be reused for more than one month, holding great promises for large-scale production in the industry. Second, TA can covalently tether one end on virtually all material surfaces with strong adhesion, which is favorable for the assembly of flexible conductors. Third, this strategy shows superior compatibility with screen printing on textile substrates, offering great potential for the high-throughput fabrication of wearable electronics. Fourth, by understanding the mechanism of electroless plating with the aid of SEM, the cracking control can be achieved by varying ELD time to produce highly stretchable conductors and the high conductivity can be maintained after repeated stretching. Therefore, such a novel method can be anticipated to inspire remarkable applications in fields of robotic skins, fiber-shaped wearable devices, biomedical industries, etc. At last, in order to explore in depth, the relationship between conductivity and flexibility of surface-deposited metallic coating on flexible substrates, we introduce the Kelvin structure model to understand the mechanism of cluster growth, and to optimize conductivity and flexibility.

4. Experimental Section

Materials: Tannic acid, ammonium tetrachloropalladate (II) \((\text{NH}_4)_2\text{PdCl}_4\), and all other chemicals were purchased from Sigma-Aldrich. All flexible substrates were provided by the Dye House at the University of Manchester. All chemicals were used without further purification. Each substrate was ultrasonically cleaned in acetone and deionized (DI) water for 30 min, respectively, and dried with a N\textsubscript{2} gas stream.

Polymer Interface Molecular Engineering: Tannic acid was dissolved in DI water to prepare a tannic acid aqueous solution (5 g L\textsuperscript{−1}). After dipping cleaned substrates into the solution for 30 min, the tannic acid-coated surfaces were rinsed with DI water several times and then dried under a stream of N\textsubscript{2}.

Electroless Deposition: Catalysts were immobilized by immersing the modified samples into a 5 \times 10\textsuperscript{−2} m \((\text{NH}_4)_2\text{PdCl}_4\) aqueous solution and placed in a dark environment for 15 min. The physical absorption of catalysts was removed by thorough rinsing with DI water. The Ni electroless plating was performed in an ELD bath containing 4:1 mixture of freshly prepared solutions A and B at room temperature. Solution A consisted of 10 g L\textsuperscript{−1} lactic acid, 20 g L\textsuperscript{−1} sodium citrate, and 40 g L\textsuperscript{−1} nickel sulfate hexahydrate prepared in advance. Solution B was a freshly prepared reductant solution containing 1 g L\textsuperscript{−1} dimethylamine borane (DMAB) in DI water. After mixing, the solution was adjusted with ammonia to pH = 8. The Cu electroless deposition was performed in plating bath containing 1:1 volumetric proportion of nickel-to-reductant stocks at room temperature. A copper stock solution consisting of 12 g L\textsuperscript{−1} NaOH, 13 g L\textsuperscript{−1} CuSO\textsubscript{4}·5H\textsubscript{2}O, and 29 g L\textsuperscript{−1} KNaC\textsubscript{6}H\textsubscript{5}O\textsubscript{4}·4H\textsubscript{2}O was prepared in advance. A fresh reductant solution containing 9.5 mL L\textsuperscript{−1} HCHO in DI water was prepared separately. After ELD, all samples were washed several times and dried with compressed air.

Characterization: The coating of tannic acid on flexible substrates was tested by Fourier transform infrared spectroscopy (Nicolet iN10 MFTIR). The surface composition of catalyst-anchored substrates was analyzed by XPS Near Ambient Surface. The surface morphology of the samples was investigated by scanning electron microscopy (Zeiss Ultra-55 and TESCAN-LC Mira3). The size and the shape of the unit cell for metallic particles on the sample surface were characterized by X-ray diffraction (PANalytical X’Pert Pro X’Celerator difffractometer). A two-point probe method with a Keithley 2000 Multimeter was used to measure the resistance of flexible surfaces.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
Keywords
bending sensors, fibers, flexibility, Kelvin question, tannic acid
Supporting Information

A Nature Inspired, Flexible Substrate Strategy for Future Wearable Electronics

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<td>PEG (M&lt;sub&gt;w&lt;/sub&gt; = 8000 g/mol)</td>
<td>9 g</td>
<td>10 g</td>
</tr>
<tr>
<td>DI H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>4.6 g</td>
<td>5 g</td>
</tr>
<tr>
<td>(NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;PdCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.051 g</td>
<td>-</td>
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<td>Tannic acid</td>
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Supporting Movies

Supporting Movie S1, The coating mechanism of Ni nanoparticles on flexible substrates.
5.3 Publication Number Three

Ultraelastic Yarns from Curcumin-assisted ELD towards Wearable Human-Machine Interface Textiles
Ultraelastic Yarns from Curcumin-Assisted ELD toward Wearable Human–Machine Interface Textiles

Chuang Zhu, Ruohao Li, Xue Chen, Evelyn Chalmers, Xiaoteng Liu, Yuqi Wang, Ben Bin Xu,* and Xuqing Liu*

1. Introduction

Human–machine interfaces (HMIs), a frontier technology in electronic systems,[1–8] have great potentials in developing personal portable electronics and the Internet of Things (IoT) with high integrity and conformal fashion.[9–12] However, there are considerable gaps to achieve highly flexible units that can conformally fit to the curved substrate for gesture recognition and pressure sensing. The recent development of flexible and stretchable sensors has opened a new window to achieve high-performance wearable HMIs.[13–20] Gong et al. developed a stretchable strain sensor by doping polyaniline (PANI) microparticles into gold nanowires (AuNWs), which could be integrated with wireless circuitry to control robotic arms remotely.[21] Cao et al. utilized carbon nanotubes (CNTs) and screen printing technique to fabricate a patterned textile electrode[22] with good washability and self-powered touching/gesture sensing functions for the wireless smart home control. Jung et al. synthesized wearable porous pressure-sensitive rubbers (PPSRs)[23] and used the PPSRs-based HMIs to program the motion of a robot. Despite above attempts on realizing flexible sensing via structural design and/or microprocessing, challenges remain to be tackled such as relatively low conductivity, poor stretchability, and heavy devices, which prevent applications in a higher technology readiness level.

The general methods to achieve flexible sensors with excellent conductivity and durability at low cost are to deposit metals, such as Ni and Cu, on substrates such as textiles,[24–26] plastic films,[27–29] fluorine rubbers,[30,31] and poly(dimethylsiloxane) (PDMS).[32,33] The exercised metallization strategies including sputtering,[34] electrochemical deposition,[35] and chemical vapor deposition[36] to physically or chemically plate metal thin films on flexible substrates have been studied. Compared with those methods, electroless deposition (ELD)[37,38] holds promising potentials at a scale-up level for its cost-effective nature—no need for expensive instruments and user-friendly operation conditions, as it can be performed at ambient environment. Polymer-assisted metal deposition (PAMD) has been regarded as a good complement to ELD,[39,40] where a full-solution process offers a desired anchoring layer to create flexible conductors with enhanced mechanical and electrical features. Zheng
and co-workers previously practiced the above concept by using poly[2-(methacryloyloxy)ethyl trimethylammonium chloride] brushes to graft onto the fiber surface and immobilize $[\text{PdCl}_2]^2^−$ species for site-selective ELD of Cu and Ni on textiles. The resulted yarns had conductivity values from 0.28 to 1 S cm$^{-1}$ while showing a high sensitivity to strain changes. Some other approaches offered alternatives to deal with these issues via doping dopamine and tannic acid to facilitate highly conductive and durable textiles. Nevertheless, it is less feasible in practical applications because the dopamine is expensive and tannic acid is unstable in aqueous solution during long-term storage due to the macromolecular aggregation and self-precipitation. The attempts are still ongoing for achieving high-quality and ultralight textile-based sensors for wearable HMIs.

In this paper, we describe a nature-inspired strategy to coat a thin metal layer on the elastic core-spun yarns through solution-process ELD, to achieve stretchable strain sensing yarns (SSSYs). The key-enabling feature of this strategy is to introduce curcumin, a natural dye to color textiles in the traditional textile dyeing process, as the polymer interface to adhere to elastic fibers via $\pi–\pi$ stacking and also capture catalysts through cation-$\pi$ interaction for the subsequent ELD. The curcumin-assisted ELD offers isotropic metallization to helical nylon strands in the outer layer of yarns to fulfill the electronic conductivity. The obtained helical bangled fiber with sheath–core structure contains the metal-coated wrapping helices that can respond to small stretching and bending stresses with significant changes in conductivity. We demonstrate the real-time wireless control of robotic hand by integrating the sensors into a smart glove with signal processing circuit. Moreover, the smart glove system shows potential applications in IoT by programming the color change of light with gesture controls.

2. Results and Discussion

The structure design of SSSYs is illustrated in Figure 1. In brief, curcumin was applied to promote the adhesion on the fiber surface via intermolecular hydrogen bonds and $\pi–\pi$ stacking to nest catalysts, leading to the successful ELD metallization of Cu or Ni on the surface of wrapping filaments at ambient conditions. These as-prepared SSSYs with conductive outer layers and the elastic core present superior flexibility to be conformally attached to the inner side of gloves via Ecoflex filtration in room temperature.

The surface chemical and physical properties of elastic yarns were assessed for each process to reveal the molecular interplays.
The Fourier transform infrared (FTIR) spectroscopy technique was applied to confirm the successful coating of curcumin on fibers. As shown in Figure 2a, compared with the FTIR spectrum of raw samples and pure curcumin from ref. [45], the FTIR spectrum of curcumin-coated samples shows an intense band at 1024 cm⁻¹ attributed to stretching vibrations of C–O groups in curcumin. X-ray photoelectron spectroscopy (XPS) was used to characterize the catalytic fibers to study the surface chemical composition, where a uniform distribution of elements was captured in Pd/curcumin yarns (Figure S1, Supporting Information). As shown in Figure 2b, the complex spectrum of Pd 3d electrons for a palladium loaded specimen is decomposed into two spin–orbit doublets, which are accounted for two electronic states of palladium: Pd (0) (binding energy 335.7 and 341.4 eV) and Pd (II) (337.2 and 342.5 eV). This indicates both reduction and chelation of palladium cations are accumulated in the curcumin-modified surface. The stronger Pd(II) doublet peaks demonstrate that more palladium ions were chelated by curcumin, which would enhance the catalytic activity in ELD because the catalytic performance of reduced Pd atoms is very poor, especially when metal particles are large and nonuniform. We noticed that, compared with the reported values, [47–50] Pd (II) peaks are negatively shifted by 1 eV, which could be attributed to that the curcumin layer gives a bigger electron-donating effect toward palladium cations, which may also facilitate the catalytic activity through altering their adsorption properties toward poisonous species such as CO.

After the catalytic activation, ELD-assisted metallization was performed to coat conformal layers of nanoparticles on the fiber surface. The morphological observation of coated layers from scanning electron microscope (SEM) suggests a significant change of surface from smooth state for the raw core-spun yarn (Figure 2d–g), to homogeneous and conformal Cu layers for the Cu-coated yarn (Figure 2e–h). After Ni ELD, the nickel coating on the surface of elastic yarns is also very uniform, continuous, and dense (Figure S2, Supporting Information). X-ray diffraction (XRD) was performed to ascertain the crystalline structure and size of metal deposits. As shown in Figure 2c, the XRD pattern of Ni-deposited yarns shows a broad diffraction peak at the 2θ value of 44.90 corresponding to the (111) plane of face-centered cubic (FCC) phase nickel (JCPDS Card No. 45-1027), which implies good conductivity of as-prepared conductive yarns. For the XRD pattern of Cu-coated samples, three distinct characteristic peaks at 2θ values of 43.90, 51.00, and 74.70 are assigned to the Cu (111), Cu (200), and Cu (220) planes, respectively. This diffraction pattern of Cu-coated yarns matches exactly with the standard pattern of cooper (JCPDS File No. 04-0836), and no diffraction peaks corresponding to copper oxide are observed, suggesting the excellent stability of metal coating. According to the Scherrer
equation, the average sizes of nickel and copper deposits were calculated to be 17.3 and 31.3 nm, respectively. Based on scale bars in SEM images of metal-coated surfaces under a low-voltage SEM at 2.5 keV (Figure 2f–i), it can be clearly seen that the sizes of grains are around 15–20 nm for Ni coating layers \((n = 5)\) and 20–40 nm for Cu films \((n = 5)\), which are in reasonable agreements with the theoretical values.

Compared with insulated textiles, the as-prepared SSSYs are electrically conductive. The electrical surface resistance of metal-coated core-spun yarns decreased with extending depositing time due to more metal nanoparticles deposited on fiber surface, as shown in Figure 3a. The resistance of nickel-coated samples and copper-plated yarns can reach as low as 5 and 0.2 \(\Omega\) cm\(^{-1}\) at 90 min, respectively. The resistance of copper-coated yarns is much lower than that of nickel-deposited samples because of the higher intrinsic conductivity of bulk Cu. Upon stretching, the helical structure wrapped yarns elongated in the longitudinal direction, where the detachment of the adjacent metal-deposited nylon yarns occurred, leading to an increase in resistance of SSSYs due to the loss of direct contacted area, as shown in Figure 3b,c for the nickel-coated nylon warping on the PU core under strain from 0% to 50%. This strain-dependent conductivity is further investigated on Ni-coated elastic yarns (Figure 3d). By applying 5% elongation, we found that the electrical resistance of as-prepared yarns witnessed a small increase from 6 to 9 \(\Omega\) and fully resumed from 9 to 6 \(\Omega\) once the external load was withdrawn because the nickel-coated nylon shell was brought into contact. The elasticity-enabled reversibility was then examined at higher elongation strains, e.g., 10%, 20%, 30%, and 50%, where the resistance of conductive yarns increased from 6 to 12.3, 15.2, 18.1, and 25.5 \(\Omega\), respectively, and recovered to the original values after unloading tensile forces.

In order to understand the electrical resistance evolution for the ELD-coated yarn at high elongation, we measured the strain–resistance response of the Ni-coated yarn under uniaxially stretching till it breaks. As shown in Figure 3e, the resistance...
of the nickel-based elastic yarns increased gradually to 25.5 Ω at 50% strain. When further increasing elongation, the resistance of as-made conductive fibers showed a dramatic increase due to the cracking and peeling off of nickel coating layers (Figure S3, Supporting Information), which could lead to the failure of local electrical network. We also found that the tensile performance of composite yarns is enhanced (Figure 3g), where the Ni-coated nylon yarns showed the same tensile property as Ni-deposited composite yarns. This is due to the homogeneous metal coating on nylon fiber surface, decreasing the frictional force between fibers. We next assessed the durability of metal-coated yarn by cyclic stretching at a fixed strain of 50%. A robust strain–resistance relationship was discovered for Ni-coated yarns after long-term stretching-releasing cycles (up to 5000, Figure 3f). Moreover, only a small increase in resistance was found for Cu-based elastic yarns after being exposed to the natural environment for 30 d (Figure 3h) or several washing cycles (Figure 3i), which shows the potential applications of Cu-coated yarns in harsh environment.

To further investigate the working mechanism of SSSYs, we conducted the theoretical study on resistance responses of metal-coated core-spun yarns under releasing, uniaxial stretching and bending. As shown in Figure 4a, SSSYs are decomposed as: PU core fiber, nylon yarns bangling around the core, and metal (Cu or Ni) film conformally deposited on the surface of nylon helices. At the initial state (0% strain), the adjacent metal-coated nylon rims are in contact with each other (Figure 4b). Under stretching, the winding angle (θ) and $N_{\text{detach}}$, detached windings appear with an average gap of $g$, as illustrated in Figure 4c. The full developments for scaling are given in the Supporting Information. Generally, the winding angle θ, the average gap $g$ of the detached nylon windings, and the resistance $R_{\text{detach}}$ will increase during the stretching. Therefore, the normalized resistance change, $\Delta \bar{R}$, can be expressed as a function of tensile strain $\varepsilon$, $\theta(e)$ ($\theta$ as a function of $e$), $g(e)$ ($g$ as a function of $e$), and $R_{\text{detach}}(e)$ ($R_{\text{detach}}$ as a function of $e$). It should be noted that $\theta$ changes very limited for the SSSYs when the applied strain is less than 50% (see Figure 3b,c). Thus, we can obtain the following scaling equation for the yarn under stretching.

\[
\Delta \bar{R} = \left( \frac{R_{\text{detach}}^{(0)}}{\rho_{\text{metal}} t_{\text{nylon}}/\tau_{\text{PU}}} - \frac{1}{1 - \nu \varepsilon} \right) \left( \frac{r_{\text{nylon}}/\cos \theta_0}{g_0} \right) 
\times \varepsilon + \left( \frac{1}{1 - \nu \varepsilon} - 1 \right)
\]

(1)

where $\rho_{\text{metal}}$ and $t$ are the electrical resistivity and thickness of metal film (Ni or Cu), respectively, $\nu$ is the Poisson’s ratio of PU, $r_{\text{nylon}}$ is the radius of nylon yarn, $r_{\text{PU}}$ is the radius of PU core (see Figure 4b), $\theta_0$ is the winding angle at initial state, $g_0$ is the assumed constant gap of detaching winding, and $R_{\text{detach}}^{(0)}$ is the assumed constant resistance of the detached winding. In addition to the tensile strain $\varepsilon$, $\Delta \bar{R}$ is found with dependencies on other two dimensionless parameters: relative resistance increase of one
detached winding $\Delta \hat{R}_{d} \left( = \frac{R_{d}^{(0)}}{r_{metal}/r_{nylon} - 1} \right)$ and the relative detached gap $\hat{g} \left( = \frac{g}{r_{nylon}/\cos \theta_{0}} \right)$. We can obtain $r_{PU} = 155 \mu m$, $r_{nylon} = 11 \mu m$ from Figure 2 and $\theta_{0} = 3^\circ$ and $g_{0} = 8 \mu m$ from Figure 3, and take $t = 17.3 \mu m$, $\rho_{0} = 6.99 \times 10^{-8} \Omega m$, $v = 0.5$ and $R_{d}^{(0)} = 0.41 \Omega$. Given by those data, this scaling relationship under stretching can be calculated as shown in Figure 4d, where the theoretical results are in good agreement with the experimental results of Ni-coated core-spun yarns.

From the perspective of bending in the following HMI system, a simplified model is created by assuming structural fiber as a beam (substrate) with metal-coated core-spun yarn attached to its top surface (Figure 4e). Under bending, we then can obtain the scaling equation for bending as follows (please see full derivations in the Supporting Information)

$$\Delta R = \left( \frac{R_{d}^{(0)}}{\rho_{metal}/r_{nylon}} \right) - \frac{1}{\left( 1 - v \cdot \frac{c}{L} \cdot \alpha \right)} \frac{r_{nylon}/\cos \theta_{0}}{g_{0}/L} \times \alpha + \left( \frac{1}{1 - v \cdot \frac{c}{L} \cdot \alpha} - 1 \right)$$

(2)

where $L$ is the initial length of the beam, $c$ is the distance between the top surface of the beam and its neutral surface (i.e., the surface at which the tensile strain is 0%), and $\alpha$ is the bending angle of the beam (see Figure 4e). With $\alpha = 0.07$ (index finger as the substrate beam) and other parameter values given in the above discussion, Equation (2) is plotted in Figure 4f, which shows that $\Delta R$ under bending is nearly proportional to $\alpha$. The experimental results of Ni-based composite yarns under bending also highly agree with the theoretical model.

On the basis of the excellent strain–resistance response discussed above, our as-fabricated conductive core-spun yarns were demonstrated to monitor the motion of human fingers and realize the remote control of the robotic hand. In detail, Ecoflex was used to adhere Ni-based sensor materials to the inner side of cotton gloves by mixing A and B solutions with weight ratio 1:1. Importantly, the Ecoflex encapsulation layer, as a skin-safe product, not only prevents the direct contact from nickel to human skin but also protects the nickel coating from oxidation. The weights of the smart glove and the built-in sensor materials are only 8.5 and 0.1g, respectively, because of the lightweight nature of fiber assemblies. With the as-fabricated nickel-coated core-spun yarns.

Apart from controlling the robotic palm, as-prepared smart gloves also have potential applications in IoT by using If This, Then That (IFTTT) protocol through WiFi modules. To realize this, the Philips Hue lightbulb which supports the IFTTT protocol was used in the IoT system. The core idea of IoT is to assign unique identifiers (UIDs) to the interrelated computing devices, machines, objects, animals, or people and transfer data over a network with automatic control. The IFTTT protocol is a platform which triggers actions on the hardware if the received signals reach the threshold. From Figure S7 (Supporting Information), the WiFi module enhanced Arduino board collected resistance values when bending/releasing fingers. Subsequently, the built-in DSP in the WiFi module boosted Arduino board would analyze the value of resistance based on designed algorithm above and then posted a trigger to IFTTT. In the final step, the lights executed the action based on different triggers. In Figure 5d, we coded the gestures to control the bulb such as showing palm or “fist” to turn off the light, hand signal of “one” for orange color, and hand signal of “two” for pink light. More triggers based on different finger combinations were designed and demonstrated in Movie S2 (Supporting Information).
3. Conclusion

In summary, highly reliable and stretchable strain sensors based on metal-coated core-spun yarns were developed via a low-cost, facile, and scalable method. The unique structure of covered elastic yarns endowed sensor materials with excellent stretchability (>1100%) and high durability during 5000 continuous stretching–releasing cycles under 50% strain without obvious damage. The superb cyclic performance should be assigned to the predecorated curcumin interface, which significantly increases the adhesion between metal nanoparticles and flexible substrates. The highly sensitive and durable nature of as-prepared conductive yarns equipped them as promising wearable strain sensors with excellent integration and adaptivity. Moreover, the theoretical model study was conducted to explore the working mechanism of SSSYs. By integrating these SSSY sensors with commercial cotton gloves, the real-time wireless control of the robotic palm could be successfully implemented by using the signal processing circuit. More interestingly, the concept of smart glove was advanced into the application in IoT to manipulate the colors of light based on a gesture controlling mechanism. We expected that this approach would open a new window in designing wearable devices for applications in HMIs and IoT such as smart home controlling, healthcare, and industrial automation.

4. Experimental Section

Materials: Curcumin, ammonium tetrachloropalladate (II) \([\text{(NH}_4\text{)}_2\text{PdCl}_4]\), ethanol absolute, and all other chemicals were purchased from Sigma-Aldrich. Core-spun elastic yarns were obtained from the Dye House at the University of Manchester. Cotton glove, robotic hand, Philips Hue lightbulb, and signal processing units were purchased from the market. Each substrate was ultrasonically cleaned in acetone and distilled (DI) water for 30 min, respectively and dried with a N\(_2\) gas stream.

Polymer Interface Design: Curcumin was dissolved in ethanol absolute to prepare a curcumin solution (5 g L\(^{-1}\)). Cleaned samples were then immersed into the solution for 30 min and the curcumin-coated samples were rinsed with DI water for several times, followed by N\(_2\) drying.

Electroless Deposition: Catalyst species were captured by dipping curcumin-grafted samples into a 5 \(\times\) 10\(^{-2}\) M \([\text{(NH}_4\text{)}_2\text{PdCl}_4]\) aqueous solution and then placed in a dark environment for 15 min. DI water rinsing was applied to remove the physical absorption of catalysts. The Ni ELD was conducted in a plating bath containing 4:1 mixture of solution A and B at ambient environment. Solution A made of 10 g L\(^{-1}\) lactic acid, 20 g L\(^{-1}\) sodium citrate, and 40 g L\(^{-1}\) nickel sulfate hexahydrate in DI water was
prepared in advance. Solution B containing 1 g L⁻¹ dimethylamine borane (DMAB) in DI water was freshly prepared. The pH of mixed solutions was adjusted to ≈8 before immersing catalytic samples. The Cu ELD was conducted in plating bath composed of 1:1 mixture of the Cu stock solution and freshly prepared 9.5 mL L⁻¹ HCHO in DI water. The copper stock containing 12 g L⁻¹ NaOH, 13 g L⁻¹ CuSO₄·5H₂O, and 29 g L⁻¹ KNH₄C₂H₃O₂·4H₂O in DI water was prepared in advance. After ELD, all samples were washed for several times and subsequently dried with compressed air.

Characterization: The modification of curcumin on elastic yarns was tested by Fourier transform infrared spectroscopy (NICOLET 5700 FTIR). The tensile property of metal-coated yarns was tested by tensile machine Instron 3345. A two-point probe method with a Keithley 2000 Multimeter was used to measure the resistance of metal-coated stretchable yarns.

Statistical Analysis: Statistical analysis was compiled on the means of the data obtained from at least three independent experiments using Origin software. All values were expressed as the mean ± standard deviation (SD) of individual sample. The sample size (n) numbers for each experiment were indicated in the figure legends.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

curcumin, electrodeless deposition, human–machine interfaces, textiles, wearable electronics

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Supporting Information

Ultraelastic Yarns from Curcumin-assisted ELD towards Wearable Human-Machine Interface Textiles

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**Table S1.** The highest threshold and the lowest threshold of different fingers

<table>
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<th>Finger</th>
<th>The lowest threshold (releasing) (ohm)</th>
<th>The highest threshold (bending) (ohm)</th>
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<td>Little finger</td>
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Supporting Movies

Supporting Movie S1. The robotic hand accurately reflected the user’s real hand gestures.

Supporting Movie S2. As-made smart gloves changed the color of light based on different hand gestures.
Theoretical study on resistance responses of metal-coated core-spun yarns under tension and bending

In this supporting document, the detailed theoretical studies on the resistance responses of metal-coated core-spun yarns under tension and bending are presented. As shown in Figure 4a, SSSYs are composed of three parts: PU core fibers, nylon yarns wrapped around the core, and metal (Cu or Ni) film coated on the surface of nylon fibers. Therefore, the resistance \( R_{SSSY} \) is equal to \( R_{PU} \), \( R_{nylon} \) and \( R_{metal} \) in parallel. Then \( R \) can be calculated as:

\[
R = \frac{1}{\frac{1}{R_{PU}} + \frac{1}{R_{nylon}} + \frac{1}{R_{metal}}} \quad (1)
\]

Since raw PU and nylon are isolators, \( R_{PU} \) and \( R_{nylon} \) are much larger than that \( R_{metal} \) of metals (Cu, Ni), which leads to \( \frac{1}{R_{PU}} \) and \( \frac{1}{R_{nylon}} \ll \frac{1}{R_{metal}} \). By neglecting \( \frac{1}{R_{PU}} \) and \( \frac{1}{R_{nylon}} \) in equation (1), we can obtain:

\[
R = R_{metal} \quad (2)
\]

The resistance \( R_{metal} \) can be calculated by using the following formula:

\[
R_{metal} = \rho_{metal} \frac{L_{metal}}{S_{metal}} \quad (3)
\]

where \( \rho_{metal} \) is the electrical resistivity of the metal, \( L_{metal} \) is the effective length of the metal resistor and \( S_{metal} \) is effective cross-sectional area of the metal coating. Before applying the tensile force on the PU core, the adjacent metal-coated nylon yarns are in contact with each other, as illustrated in Figure 3b. Therefore, the electric current can directly pass through the metal film on the adjacent nylon fibers. Considering only one nylon winding, its effective length \( L_{metal} \) and cross-sectional area \( S_{metal} \) can be calculated as:

\[
L_{metal} = \pi r_{nylon} \quad (4a)
\]

\[
S_{metal} = 2\pi (r_{PU} + 2r_{nylon}) \times t \approx 2\pi r_{PU} t \quad (4b)
\]
where $r_{nylon}$ is the radius of the nylon yarn, $r_{PU}$ is the radius of the PU core, and $t$ is the thickness of the metal film, as shown in Figure 4b. Because of $r_{nylon} \ll r_{PU}$, $r_{nylon}$ can be neglected in equation (4b) and by introducing equation (4) into equation (3), we can obtain:

$$R_{contact,1} = \frac{\rho_{metal} r_{nylon}}{2t} r_{PU}$$  \hspace{1cm} (5)

Equation (5) estimates the resistance of the metal film coated on the upper surface of the nylon winding at contacting state. In fact, the electric current can also pass through the metal film on the lower part, as illustrated in Figure 4b. As the conductive path of the lower metal film is in parallel to that of the upper metal coating and theoretically, they have the same resistance, the total resistance of one metal-coated nylon winding at contacting state can be estimated as:

$$R_{contact} = \frac{1}{R_{contact,1}} \times 2 = \frac{\rho_{metal} r_{nylon}}{4t} r_{PU}$$  \hspace{1cm} (6)

We suppose that there are $N_{total}$ nylon windings and since all windings are in series, the total resistance $R_{0,layer}$ can be calculated as:

$$R_{0,layer} = N_{total} \times R_{contact} = N_{total} \times \left( \frac{\rho_{metal} r_{nylon}}{4t} r_{PU} \right)$$  \hspace{1cm} (7)

Equation (7) estimates the resistance of one single layer of metal-coated nylon yarns. We suppose that there are $n$ layers of nylon yarns wrapped around the PU core. Because all layers are in parallel, the total resistance $R_0$ in the initial state (before stretching) can be estimated as:

$$R_0 = \frac{1}{R_{0,layer}} \times n = \frac{1}{n} \times N_{total} \left( \frac{\rho_{metal} r_{nylon}}{4t} r_{PU} \right)$$  \hspace{1cm} (8)

When stretching the PU core to a tensile strain $\varepsilon$, several adjacent nylon windings would detach, as shown in Figure 3c. Considering one detached winding, the electric current would skip this detached winding and pass through the contacted windings on other adjacent layers with smaller resistance, as depicted in Figure 4c. We suppose that $R_{detach}$ is the resistance of one detached winding and there are $N_{detach}$ detached windings in each layer (assuming all layers have the same number of detached windings). Therefore, the total resistance $R$ under tension can be estimated with the aid of equations (7) and (8) as:

$$S-10$$
where \( r_{P_U} \) is the radius of the PU core under tension, which can be calculated as:

\[
r_{P_U} = (1 - \nu)e_{P_U}
\]  

with \( \nu \) being the Poisson’s ratio of PU. Introducing equation (10) into equation (9), we have:

\[
R = \frac{1}{n} \left( N_{\text{total}} - N_{\text{detach}} \right) \times \left( \frac{\rho_{\text{metal}} r_{\text{nylon}}}{4t} \right) + N_{\text{detach}} \times R_{\text{detach}} 
\]  

Moreover, by using equations (8) and (11), we can further calculate the relative variation of the resistance \( \Delta R \) as:

\[
\Delta R = \frac{R - R_0}{R_0} = \frac{N_{\text{detach}}}{N_{\text{total}}} \left( R_{\text{detach}} \left( \frac{\rho_{\text{metal}} r_{\text{nylon}}}{4t(1-\nu)} \right)^{-1} - \frac{1}{1-\nu} \right) + \left( \frac{1}{1-\nu} - 1 \right)
\]

In equation (12), \( \rho_{\text{metal}} \) (electrical resistivity of the metal) is an intrinsic material parameter; \( t \) (thickness of the metal film), \( r_{P_U} \) (radius of the PU core) and \( r_{\text{nylon}} \) (radius of the nylon yarn before stretching) are the geometric parameters of the metal-coated core-spun yarns, which are supposed to be unchanged during the tension loading. The term \( N_{\text{detach}}/N_{\text{total}} \) in equation (12) would increase by stretching the PU core to a larger strain (i.e. more nylon windings would detach), leading to the increase of the resistance with increasing strain.

In the initial state (i.e. strain of 0), the adjacent metal-coated nylon windings are in contact with each other. By supposing that the nylon windings cover the whole surface of the PU core, we can calculate the initial length \( L^{(0)}_{P_U} \) of the PU core as:

\[
L^{(0)}_{P_U} = N_{\text{total}} \frac{2r_{\text{nylon}}}{\cos \theta_0}
\]

where \( \theta_0 \) is the initial winding angle, as shown in Figure 4a (assuming all windings have the same winding angle). When stretching the PU core, the winding angle changes to \( \theta \) and \( N_{\text{detach}} \) detached windings appear with an average gap of \( g \), as illustrated in Figure 4c. Then the length \( L_{P_U} \) of the PU core after stretching can be estimated as:

\[
L_{P_U} = N_{\text{total}} \frac{2r_{\text{nylon}}}{\cos \theta} + N_{\text{detach}} \times 2g
\]
From equations (13) and (14), the normal tensile strain \( \varepsilon \) can be calculated as:

\[
\varepsilon = \frac{L_{PU} - L_{PU}^{(0)}}{L_{PU}^{(0)}} = \left( \frac{\cos \theta_0}{\cos \theta} - 1 \right) + \frac{\cos \theta_0}{r_{nylon}} \times g \times \frac{N_{detach}}{N_{total}}
\]

(15)

From equation (15), we can further derive the formula as:

\[
\frac{N_{detach}}{N_{total}} = \frac{r_{nylon} \cos \theta_0}{g} \left( \varepsilon + 1 - \frac{\cos \theta_0}{\cos \theta} \right)
\]

(16)

By introducing equation (16) into equation (12), we can finally obtain the strain–resistance relation under stretching as:

\[
\Delta R = \left( \frac{R_{detach}^{(0)}}{\rho_{metal} r_{nylon}} - \frac{1}{1 - \nu} \right) \frac{r_{nylon} \cos \theta_0}{g(\varepsilon)} \left( \varepsilon + 1 - \frac{\cos \theta_0}{\cos \theta(\varepsilon)} \right) + \left( \frac{1}{1 - \nu} - 1 \right)
\]

(17)

In general cases, the winding angle \( \theta \), the average gap \( g \) of the detached nylon windings, and the resistance \( R_{detach} \) of detached winding will increase with the tensile strain \( \varepsilon \). Therefore, before obtaining the analytical expression of \( \Delta R \) as a function of \( \varepsilon, \theta(\varepsilon) \) (\( \theta \) as a function of \( \varepsilon \)), \( g(\varepsilon) \) (\( g \) as a function of \( \varepsilon \)), and \( R_{detach}(\varepsilon) \) (\( R_{detach} \) as a function of \( \varepsilon \)) need to be determined first. For the core-spun yarns studied here, we found that the winding angle only changes a little when the recoverable strain range is below 50%, as shown in Figures 3b and 3c. By taking \( \theta(\varepsilon) = \theta_0 \), equation (17) can be simplified as:

\[
\Delta R = \left( \frac{R_{detach}^{(0)}}{\rho_{metal} r_{nylon}} - \frac{1}{1 - \nu} \right) \frac{r_{nylon} \cos \theta_0}{g(\varepsilon)} \varepsilon + \left( \frac{1}{1 - \nu} - 1 \right)
\]

(18)

Considering the simplest case, where \( g(\varepsilon) \) is constant (= \( g_0 \)) and \( R_{detach}(\varepsilon) \) is also constant (= \( R_d^{(0)} \)), equation (18) can be further simplified as:

\[
\Delta R = \left( \left( \frac{R_d^{(0)}}{\rho_{metal} r_{nylon}} - \frac{1}{1 - \nu} \right) \frac{r_{nylon} \cos \theta_0}{g_0} \right) \times \varepsilon + \left( \frac{1}{1 - \nu} - 1 \right)
\]

(19)

From the perspective of bending behaviour in the smart glove system, the whole heterogeneous structure can be simplified as a beam (substrate) with metal-coated core-spun yarn (functional component SSSYs) attached to its top surface, as shown in Figure 4e. When bending the
substrate beam, the top surface of the beam would elongate, causing the tensile force applied on the SSSYs. The resulted tensile strain will lead to an increase in the resistance of the core-spun yarns due to the detached windings (see Figure 3c), and an analytical relation between the tensile strain and the relative variation of resistance has already been derived (equation (19)). Under the assumption of pure bending, the tensile strain $\varepsilon$ of SSSYs can be estimated as:

$$\varepsilon = \frac{c}{\rho}$$

(20)

where $c$ is the distance between the top surface of the beam and its neutral surface (i.e. the surface at which the tensile strain is 0%), and $\rho$ is the radius of the deformed beam (see Figure 4e). The bending angle $\alpha$ is related to the curvature $\frac{1}{\rho}$ of the beam by the following formula:

$$\alpha = \frac{L}{\rho}$$

(21)

where $L$ is the initial length of the beam. With the aid of equations (19-21), we can obtain the bending angle–resistance relation as the following formula:

$$\Delta \overline{R} = \left( \frac{R_{d}^{(0)}}{\rho_{metal}} \frac{r_{nylon}}{r_{PU}} \frac{1}{1-\nu} \right) \frac{\cos \theta_0}{\theta_0} \frac{c}{L} \times \alpha + \left( \frac{1}{1-\nu} \frac{c}{L} \alpha - 1 \right)$$

(22)
Chapter 6. Discussions on the Papers
6.1 Dopamine-assisted ELD

The novelty of this publication is the use of an adhesive polydopamine (PDA) layer as the fibre interface for manufacturing different conductive fibres. PDA nanofilms were firstly grown on the fibre surface via π-π stacking in the dopamine-dissolved tris buffer. Afterwards, catalysts were anchored on the PDA-modified fibres via cation-π interaction in the catalytic solution. In the final step, Ni nanoparticles were deposited on the catalysed areas of fibres in the electroless deposition (ELD) bath. The Fourier-transform infrared spectroscopy (FTIR) results of PDA-modified fibres confirmed the successful coating of PDA on fibres. The Pd 3d region in the X-ray photoelectron spectroscopy (XPS) spectrum of catalytic samples revealed that Pd$^{2+}$ ions were chelated and reduced into Pd$^0$ nanoparticles by PDA via cation-π interaction. The stabilised Pd$^{2+}$ ions on the fibre surface enhanced the catalytic performance in the followed ELD process, leading to the good quality of metal coatings on fibres. The scanning electron microscope (SEM) images of Ni-coated yarns showed that Ni nanoparticles were homogeneously, compactly and continuously deposited on the fibre surface. Importantly, for the cotton fibre with hollow structure, Ni nanoparticles were fully covered not only on the upper surface of fibres, but also on the inner surface of fibres, causing the integral metal coatings. The X-ray diffraction (XRD) spectrum of Ni-coated cotton fibres demonstrated that the crystalline structure of Ni was face-centred cubic and the crystal plane of Ni was (111). According to the Scherer equation, the average size of Ni nanoparticles was about 16.6 nm. During the ELD process, the surface resistance of Ni-plated cotton yarns decreased when the plating time increased. The resistance of Ni-based cotton yarn was 0.05 Ω/cm at 60 min ELD. As-made Ni-deposited cotton yarns showed no obvious increase of surface resistance after 5 hand washing cycles or 2000 simple bending cycles (bending radius = 15 mm) due to the designed interface between the fibre substrate and metal nanoparticles. For demonstrations, a simple electrical circuit was built by connecting a 9 V alkaline battery with one electrical contact of the light-emitting diode (LED). When as-made Ni-coated cotton yarns contacted to the other contact of LED and the power source, the LED
switched on immediately and illuminated for more than 10 min until the contact was disconnected. In addition, these Ni-deposited yarns were sewn into a commercial cotton glove to monitor the finger motions. When human finger bent at different gestures including grasping and holding, these conductive yarns were stretched, resulting in the increased contact area between conductive fibres. This gave decreased surface resistance value of the Ni-deposited cotton yarns. During the releasing of fingers, the resistance recovered to its original value. By recording the resistance signal changes versus the hand gestures, the motions of different fingers could be successfully tracked.
6.2 TA-assisted ELD

The novelty of this publication is the introducing of the tannic acid (TA) layer as the binder between the fibre surface and the metal films for producing metal-coated 3D polyurethane (PU) sponges and metal patterns on cotton fabrics. In the first step, TA was grafted on the fibre surface via \( \pi-\pi \) stacking in the TA aqueous solution. Catalysts were then captured by TA-modified fibres through cation-\( \pi \) interaction in the (NH\(_4\))\(_2\)PdCl\(_4\) aqueous solution. Finally, metal nanoparticles were plated on the catalytic areas of fibres in the electroless deposition (ELD) solution. The successful grafting of TA on cotton sheets and 3D sponges was proved by observing the Fourier-transform infrared spectroscopy (FTIR) spectrum of TA-coated samples. The Pd 3d region in the X-ray photoelectron spectroscopy (XPS) spectrum of TA-modified samples demonstrated that two electronic states of palladium (Pd\(^{2+}\) and Pd\(^0\)) were presented in the catalytic surface because of the cation-\( \pi \) interaction between the TA layer and Pd\(^{2+}\) ions. The homogenous, compact and continuous deposition of metal nanoparticles on samples was revealed by using scanning electron microscope (SEM). According to the X-ray diffraction (XRD) results of Ni and Cu-coated samples, there are three crystal planes of Cu nanoparticles including (111), (200) and (220), while Ni nanoparticles only showed crystal plane of (111). By using Scherer equation, the particle size of Cu and Ni was calculated to be about 16.5 and 31.1 nm respectively. The fabric stiffness test and two-point probe method were applied to explore the bending length of Ni-coated cotton fabrics in the warp direction and the surface resistance of metallised samples, respectively. During the ELD process, the surface resistance of Ni-deposited fabrics decreased from 3230 to 1.02 \( \Omega/\text{sq} \), while the bending length of conductive fabrics in the warp direction increased from 1.925 to 3.925 cm, demonstrating the higher stiffness of Ni-based samples with the longer ELD time. Based on the SEM images of conductive fabrics at different ELD times, the growth of metal nanoparticles on fibres was divided into three steps: the nucleation period (loose coating), the growth of spherical nodules (multilayers shape) and the aggregating of nanoparticles (clusters). Because of the unfilled gaps between Ni nanoparticles on the fibre surface at 10 and 20
min ELD, only a small increase of surface resistance of conductive samples in the mechanical bending test was shown. However, the surface resistance of conductive samples at 30 and 60 min ELD experienced a dramatic increase after repeated bending cycles due to the cracking of Ni clusters on the fibre surface. Importantly, the Kelvin structure model was introduced to illustrate the formation of the honeycomb-like structure of metal clusters. Neighbour swapping and bubble disappearance were two primary reasons for the topological changes in ELD. From SEM image of the cross section of metal coatings, it was clear to see that metal clusters were small and incompact on the bottom of metal layers, while the top of metal layers owned big and dense metal aggregations. For practical applications, a Ni interdigital electrode was fabricated onto the flexible cotton fabric via screen printing. Two strategies including using catalytic source in the printing ink and using TA polymer in the printing gel were demonstrated in the screen printing. The feature of the conductive pad was that interlocking comb-shaped arrays were sensitive to external conductors. Thus, the human finger touching could be monitored by observing the illumination of light-emitting diode (LED) in a simple circuit that was made of keypad, conductive yarns and battery because human finger with residual body fluid was an electrical conductor. Besides, Ni-coated 3D sponges could be used as pressure sensors and arm bending sensors based on the change of contact areas between spongy conductors. In details, Ni-plated sponges at 10, 20, 30 and 60 min ELD were tested when placing different weights on the top of conductive sponges. The surface resistance of 10 and 20 min ELD metal-coated sponges was durable under repetitive loading of weights because of the high flexibility of these sponges. However, the surface resistance of 30 and 60 min ELD metallised sponges decreased in the two cycles of weight-loading test due to the brittle and stiff Ni films on the surface of PU sponges. The 20 min ELD Ni-deposited sponges were then attached to the human arm for tracking the arm bending because these samples were highly durable.
6.3 Curcumin-assisted ELD

The novelty of this publication is the use of curcumin as the glue between fibre surface and metal coatings for fabricating conductive core-spun yarns. In the fabrication process, curcumin was firstly coated on the elastic yarns via $\pi-\pi$ stacking in the curcumin ethanol solution. Catalysts were then immobilised on the curcumin-modified fibres via cation-$\pi$ interaction in the catalytic source. Cu or Ni nanoparticles were finally deposited on the catalytic areas of fibres in the electroless deposition (ELD) bath. The Fourier-transform infrared spectroscopy (FTIR) spectrum of curcumin-coated core-spun yarns demonstrated the successful coating of curcumin on the fibre surface. The Pd 3d region in the X-ray photoelectron spectroscopy (XPS) spectrum of curcumin-modified samples was decomposed into two spin-orbital doublets, indicating that both reduction and chelation of Pd$^{2+}$ were accumulated in the curcumin layer. The scanning electron microscope (SEM) images of metal-coated stretchable yarns revealed that metal nanoparticles were uniformly, densely and continuously plated on the fibre surface. The diffraction peaks in the X-ray diffraction (XRD) spectrum of metal-coated samples demonstrated that the crystal plane of Ni was (111) and Cu showed three crystal planes including (111), (200) and (220). Based on the Scherrer equation, the particle size of Cu and Ni was calculated to be about 17.3 and 31.3 nm respectively. The resistance of Cu-coated samples reached 0.2 $\Omega$/cm at 90 min ELD. Importantly, although the nylon wrapping of the core-spun yarns was coated with metal nanoparticles, the core part (elastic spandex) of the composite yarns remained uncoated. Upon stretching, the conductive helices of the composite yarns elongated in the longitudinal direction, causing the detachment of the adjacent metal-coated nylon yarns. This resulted in the increased resistance of conductive elastic yarns because of the decrease of contact area between conductive fibres. Compare with bare samples, the metal-coated elastic yarns showed much higher tolerable strain ($>>1100\%$) because the homogeneous metal nanoparticles on the fibre surface decreased the frictional forces between fibres. The normalised resistance of metal-coated core-spun yarns showed no obvious change when the repetitive stretching-releasing test was under 50% tensile
strain. When further increasing the tensile strain, the cracking of metal coatings occurred, leading to the failure of local electrical network. The metallised elastic yarns were durable when being exposed to the natural environment for 30 days and hand-washed for 10 cycles. A theoretical model was established to investigate the working mechanism of the strain sensing stretchable yarns (SSSYs). Both of bending and stretching models were studied and the experimental results highly agreed with these models. For practical applications, a wearable human-machine interface (HMI) textile was constructed based on SSSYs. In detail, SSSYs were firstly attached to cotton glove via Ecoflex filtration. Afterwards, the control system consisting of transmit circuit and receive circuit was designed for the signal processing. When human finger bent, the resistance changes due to the change of contact between metallised fibres were converted into digital signals by analog-to-digital converters (ADCs). By using wireless communication modules, these data were then collected by the robotic hand and digital-to-analog converters (DACs) were applied to convert the digital signals into analog servos for different robotic fingers. Finally, the operator’s real hand gestures were accurately reflected by the robotic hand because the individual analog angle input determined the specific position of each robotic finger. In addition, this smart glove could also control the colour of the Philips Hue lightbulb by using If This, Then That (IFTTT) protocols through WIFI modules.
Chapter 7. Conclusions and Future Work
7.1 Conclusions

This project explored the possibility of fabricating durable conductive fibres for textile-based wearable electronics via fibre interface molecular engineering (FIME). Polyphenols including dopamine, tannic acid (TA) and curcumin, were used to modify different fibres via one-step dip doping at room temperature without destructing the fibre structure. Afterwards, the polyphenol layer on the fibre surface served as the platform to anchor catalysts for the electroless deposition (ELD) of metals on the catalysed areas of fibres. The resultant conductive yarns were very durable because polyphenols introduced powerful adhesion forces between metal layers and fibres. Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were used to evaluate the chemical structures of polyphenols-modified fibres and catalysts-immobilised samples, respectively. Scanning electron microscope (SEM) and X-ray diffraction (XRD) were used to characterise the surface morphology and crystalline structure of metal-coated fibres, respectively. The physical properties of conductive yarns and fabrics were explored by using bending, hand washing and tensile test. The two-point probe method was used to demonstrate the electrical properties of metallised samples.

• To achieve the first objective in the section 1.2, dopamine was used to form an adhesive polydopamine (PDA) layer on the fibre surface by pH-induced polymerisation in the tris buffer. After the catalyst immobilisation and ELD of Ni, different Ni-coated yarns and fabrics were obtained. From the results of FTIR and XPS, it was found that PDA was successfully coated on the fibre surface and the Pd$^{2+}$ ions were absorbed on the PDA layers of the surface-modified fibres. The SEM images of Ni-coated fibres confirmed the homogeneous deposition of metal nanoparticles on fibres and the XRD spectrum of Ni-deposited samples demonstrated the crystalline structure and particle size of Ni coatings. The two-point probe method revealed that the resistance of Ni-plated cotton yarns was 0.05 $\Omega$/cm at 60 min ELD. Only a small increase in surface resistance of metallised yarns after hand washing and bending cycles, indicating the excellent durability of Ni-based samples. These conductive yarns could power the light-
emitting diode (LED) in a simple circuit and monitor the finger movements because the change of contact area between conductive fibres during the bending-releasing process of the finger caused the varied resistance signals.

- To achieve the second objective in the section 1.2, screen printing technology was used to print metal patterns on cotton fabrics. Two types of printing gels including TA ink and catalytic gel were prepared. For strategy A, TA was firstly coated on the fibre surface, followed by printing the catalytic source on the TA-modified fabric. Finally, metal patterns were formed on the catalyst-printed areas of the fabric in the ELD bath. For strategy B, in the first step, TA was screen-printed on the fabric. Afterwards, catalysts were captured on the TA-modified areas of cotton fabric. Metal nanoparticles were finally deposited on catalytic areas of the cotton fabric, forming the metal-patterned fabric. SEM images of the partially metallised fabric showed a clear boundary between metal-coated area and raw area, demonstrating the good quality of metal patterns. The conductive pad fabricated by printing the Ni interdigital electrode on the cotton fabric could be used to track human finger touching in a simple electrical circuit.

- To achieve the third objective in the section 1.2, TA-assisted ELD was used to yield conductive 3D sponges. The successful TA coating on sponges and the catalyst-absorption on the TA layers of surface-modified sponges were revealed by using FTIR and XPS, respectively. From the SEM images, it was found that metal nanoparticles were fully covered on the surface of 3D sponges. The resistance of 20 min ELD Ni-coated sponges showed an obvious change after two cycles of the loading of different weights, indicating the good durability of these samples. When weights were placed on the top of metallised 3D sponges, the contact area between conductive spongy units increased, leading to the decreased resistance. This indicated that Ni-plated 3D sponges could be used as pressure sensors. In addition, these sponges could be also used as arm-bending sensors to monitor the human arm movements because the bending-releasing process of human arm resulted in the resistance change of conductive sponges.

- To achieve the fourth objective in the section 1.2, curcumin was used to modify the core-spun yarns, followed by anchoring catalysts on the curcumin-modified fibres. In
the final step, metal nanoparticles were deposited on the nylon shell of the elastic yarns in the ELD bath. FTIR and XPS were used to confirm the grafting of curcumin on fibres surface and the immobilisation of Pd$^{2+}$ on the curcumin-modified stretchable yarns, respectively. SEM images of metal-coated elastic yarns revealed that metal nanoparticles were uniformly plated on the wrapping part of the stretchable yarns. Due to the inherent stretchability of the spandex core, these conductive core-spun yarns could maintain the resistance when the applied strain was less than 50%. However, further increasing the tensile strain would destroy the metal coatings. The strain-sensing properties of these conductive samples were characterised by collecting the surface resistance during stretching. A theoretical model was used to study the working mechanism when conductive elastic yarns were bent and stretched. The surface resistance of metal-plated elastic yarns increased when tensile strain was applied to these samples because of the decreased contact area between metallised nylon wrapping. These conductive compound yarns could be used as strain sensors in wearable human-machine interface (HMI) textiles to control the robotic hand and the colour of light by using signal processing units.

In conclusion, the use of polyphenols opens a new window for modifying the surface of fibres via $\pi$-$\pi$ stacking and absorbing catalysts via cation-$\pi$ interaction. Different conductive fibres with high durability were manufactured by using polyphenols-assisted ELD and textile-based human-body monitoring sensors were constructed based on metallised yarns and fabrics. This method will lead to broadened application of conductive fibres in the wearable electronics, composite industry and medical diagnostics.
7.2 Future Work

Although the successes achieved in this research provide potential ways for manufacturing metal-coated fibres, polyphenols assisted electroless deposition (ELD) is still at an early stage of development. Future work that can be done as a continuation of the project is as follows:

1. The discussion of stretchable conductors in this project were only about metal-coated core-spun yarns. Instead, intrinsically stretchable polydimethylsiloxane (PDMS) with buckled metal layers can be produced by polyphenols assisted ELD for electronic skins. PDMS is compatible with biological tissue and metal films are electrically conductive. Polyphenols can be used to modify PDMS surface and anchor catalyst salts. Subsequently, by pre-stretching catalytic PDMS in the ELD solution, wrinkled metal-deposited PDMS can be obtained after releasing. More importantly, PDMS with conductive patterns such as serpentine can be fabricated by using surface lithography techniques.

2. Cu or Ni-coated textiles with high conductivity and excellent durability can be used as soft electrodes for fibre-based supercapacitors (SCs). Due to fast charging and discharging capability, long life cycles and great safety, flexible SCs have become a good development direction. To fabricate the composite electrodes, active materials such as graphene and MnO$_2$ are required to be coated on metal-coated yarns and fabrics. For example, electrochemically electrolysing can be used to deposit graphene on metal-plated cotton yarns by immersing these yarns, as working electrodes, into graphene oxide aqueous suspension at an applied potential of -1.2 V for a certain time. To further improving the specific surface area of flexible electrodes, the morphology of metal coatings on the surface of fibres can be controlled by varying concentrations of ELD solutions to achieve high-performance SCs. The concept of flexible SCs with modified metal nanostructures provide a possible solution for energy storage.

3. Traditional textile-based composites have widespread applications such as automotive textiles, medical textiles, geotextiles and protective clothing. For example, Kevlar composites have high tensile strength and chemical stability at high
temperatures and Layer-up method is widely used to produce composites by vacuum pumping resin into laid-up preregs on a mould surface. By combining polyphenols-assisted ELD technique and conventional lay-up method, conductive Kevlar composites can be fabricated for electromagnetic shielding.
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