Gold Nanoparticles: A Novel Dye for Synthetic Fabrics

Amy Watson

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Abstract

Fabric has always been prominent throughout history. In the last 70 years new synthetic fabrics have been developed which mimic the natural fibres but have increased strength, durability and stretchability. Common fibres include Polyester, Nylon and Lycra®. These fibres can be blended to incorporate the properties of both the individual fibre types.

Gold nanoparticles have been found to give the stable deep red colour found in stained glass but the science was not understood until the quantum mechanical work of Mie in 1908 on the interaction of electromagnetic radiation (visible light) with fine particles of matter. It is proposed that gold nanoparticles can be used as stable colourants bound to synthetic fibres and other textiles due to its chemical unreactivity. The most common formation method is the use of a reductant such as poly(ethylene imine), sodium citrate or tannic acid.

This thesis reports the research and development of new, novel hybrid materials created by combining the interesting properties of both the synthetic fabrics and gold nanoparticles.

Twenty five different methods (broken down into four general categories – pre-made colloids, in-situ reduction, use of external reductant after uptake of gold solution and growth of seed particles) were attempted resulting in fabrics that were a variety of shades and colours including pink, purple, tan and gold.

The synthetic fabric-gold nanoparticle hybrid samples were analysed by scanning electron microscopy, energy dispersive spectroscopy, infrared spectroscopy, ultraviolet/visible reflectance spectroscopy, x-ray photoelectron spectroscopy, fluorescence spectroscopy and ColourQuest measurements. A sample was also subjected to industry standard “abrasion” and colourfastness tests in which it gained the highest mark possible, showing no staining of other fabrics under dry rub conditions.

Atomic absorption measurements were performed on solutions after the fabric was removed in order to confirm the amount of gold uptake by the fabric samples.

Analysis showed that a range of nanoparticle sizes and shapes were produced which influenced the visual colour of the fabric. The purple samples produced are caused by small particles (<100nm) that have aggregated together. Samples that appear tan or gold in colour have mainly large particles (>500nm) that are either made up of small spheres fused together or are large plates (trigonal, hexagonal); therefore, Mie’s laws do not appear to apply. Light coloured samples generally have a few small particles (<100nm) that are spaced out over the fibre surface.

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Glossary

PEI	Poly(ethyleneimine)
UV/vis	Ultra Violet Visible
IR	Infra Red
XPS	X-ray Photoelectron Spectroscopy
SEM	Scanning Electron Microscopy
SEI	Secondary Electron imaging
EDS	Energy Dispersive Spectroscopy
AA	Atomic Absorption

1 Introduction/Background

Clothing is part of everyday life but the current method for dyeing uses organic dyes such as indigo (blue jeans, $C_{16}H_{10}N_2O_2$). These dyes only sit on the surface of the fabric so can leach out in the wash causing the fabric colour to fade as well as accidentally dyeing lighter coloured garments in the wash. The dyeing process produces vast quantities of carcinogenic wastewater which is harmful to the environment⁵⁻⁸. Washing powders have brighteners in them to improve the visual appearance of clothes but these are actually small pellets of blue dye. This means that over time the colour will alter slightly – blacks appear grey, bright yellows get darker etc.

It is proposed that gold nanoparticles can be used as stable colourants for natural and synthetic fabrics. Gold nanoparticles have size and shape tuneable colour emissions, due to the classical effect, Surface Plasmon Resonance^{9, 10}. This project focussed on the use of synthetic fabrics, mainly Polyester, Nylon, Polyester-Lycra® and Nylon-Lycra®. These fabrics have different functional groups that may bind directly to the gold nanoparticles giving a strong colour that is both stable and colourfast. This gives an environmentally friendly solution for the currently harmful dyeing process.

To date a wide variety of research has been done into the formation of gold nanoparticle colloids but little into their use as colourants. Some work has been done on the use of silver nanoparticles in fabric but only for its anti-microbial properties^{11, 12}. Our group (Professor Johnston, Dr Borrmann, Dr Richardson, Kirsten Burrridge

and Fern Kelly) has performed some research into the use of gold and silver nanoparticles as stable colourants and with anti-microbial properties on merino wool and cotton (see Figure 1.1) ^{13, 14}. This project is a continuation of some of that work using gold nanoparticles as stable colourants for synthetic clothing. No method currently exists for dyeing fabric with gold so they were developed as the project progressed.

1.1 Gold

Gold is a soft dense yellow metal, the most malleable and ductile metal known to man. It can be alloyed and is a good conductor of heat and electricity. One of the most important properties is that gold is chemically unreactive meaning that its appearance doesn't change with time¹⁵. It is only soluble in aqua regia (a mixture of concentrated hydrochloric acid and nitric acid) giving it high stability.

1.1.1 History

Historically gold has always been important to consumers. It is a sign of wealth; the more you have the richer you appear to the world¹⁶.

Gold trading first started after 3000BC when gold mines were discovered in Libya (part of the Egyptian empire at the time). Exact dates are not known but gold jewellery from the city of Ur has been found that dates back to 3500-2800BC. As the only gold source at the time was controlled by the Egyptians, it suggests that gold was an important source of trade. To the Egyptians gold was highly prized. It was referred to as 'the flesh of the gods' as it did not tarnish and shone like the sun god¹⁷. This meant it was only available to the pharaohs and priests but later on it was available to the wealthy nobles. King Tutankhamen's tomb is solid gold and weighs around 1.1 ton¹⁸.

Figure 1.2 Egyptian jewellery made from gold

Around 1500BC gold became the recognised standard medium of exchange for international trade. The first coin was also made at this time out of a naturally occurring alloy called electrum that was approximately $\frac{2}{3}$ gold and $\frac{1}{3}$ silver. This is very different to our currency today which is made out of paper or plastic¹⁹. Probably

the most famous gold coins are those of the Incans of South America or the Romans. Many wars have been started over gold. The Spanish invaded South America because of its rich deposits of gold and also cacao beans. Alexander the Great and also the Romans had campaigns that were to capture regions rich in gold (or had large amounts of gold coins). These regions were needed to fund further military campaigns.²⁰

Gold thread has been used for embroidery and incorporated into garments of the rich and powerful since ancient times (400BC-700AD)²¹. As it is extremely ductile, pure gold is able to be drawn out into thin wires or alloyed with silver or copper before being drawn in to threads. Gold embroidery is most commonly found in the clothing and furnishings of royalty and nobility throughout Europe, military and religious leaders.

1.1.2 Nanoparticles

A nanoparticle is a particle with at least one dimension in the range of 1 – 100 nm. They tend to display unique properties not seen in the corresponding bulk material²².

Gold nanoparticles have been found to give the stable deep red colour found in stained glass windows (example **Figure 1.3**) in churches and historical buildings for centuries but at the time the science was not understood. A famous example is the Lycurgus cup (see **Figure 1.4**) dating back to around 400AD.

Figure 1.3 Stained glass window of St Michael

Figure 1.4 Lycurgus cup under reflected (left) and transmitted light (right)

Small amounts of gold and silver metals were dissolved in molten glass so when the glass set the particles were trapped inside. Reflected light causes the cup to look

green but transmitted light turns the cup red²³. In 1857 Michael Faraday recognised that gold particles caused the colour of the stained glass due to differences in reflected and transmitted light, but it was not until the quantum mechanical work of Mie in 1908 on the interaction of electromagnetic radiation (visible light) with fine particles of matter, that the science was understood^{9, 10}. Mie solved Maxwell's equations for a metal sphere surrounded by a dielectric medium, using the dielectric function of the bulk metal. These theories gave rise to surface plasmon resonance, a classical effect in which the resonance interaction of the electromagnetic field of visible light promotes the coherent oscillation of conduction band electrons on the surface of noble metal particles. This effect causes the colours produced to be dependent on the size and shape of the metal nanoparticles. The composition of metals (e.g. addition of silver) can also determine the colour of the colloidal suspension. Smaller diameters generally exhibiting an absorbance at shorter wavelengths and reflection at longer wavelengths. Small spherical gold nanoparticles (7–20 nm) appear a deep wine red colour, while larger particles (including aggregates) appear blue/black or purple under visible light (see **Figure 1.5** and **Figure 1.6**).

Throughout history gold has always been highly prized as it is associated with wealth¹⁶. It is proposed that gold and silver nanoparticles can be used as stable colourants bound to wool fibres and other textiles due to its chemical unreactivity, but the colour changes between the nanoparticle colloid and the resulting fabric^{13, 14}.

Colloidal gold has been studied for a number of years and many formation methods exist. The most common are:

- use of a reductant (e.g. sodium citrate²⁴, tannic acid²⁵, poly(ethylenimine)^{4, 26, 27})

- photoreduction^{28, 29}
- electrochemical reduction³⁰
- a phase transfer catalyst in organic synthesis³¹
- sonolysis^{32, 33}
- laser ablation/gas deposition^{34, 35}.

These methods all transfer electrons to the gold causing it to go from a +3 state to 0. For example the proposed redox equation for trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) is:

Gas emissions (CO_2) could be analysed to check the validity of this equation ([1]).

Gold nanoparticles have a high surface energy which makes them very reactive, causing them to aggregate if they are not protected. Common methods include encapsulation in the aqueous pools of reverse microemulsions³⁶, dispersion in polymeric matrixes³⁷ and protection by self-assembled monolayers (citrate³⁸ and thiol-functionalised organic molecules³⁹)

1.1.3 Dye

Traditionally natural extracts from plants, animals or minerals have been used to dye fabrics⁴⁰. These organic dyes are not stable over time and may contribute to the degradation of the base material. Madder was a popular source of red dye for thousands of years until 1871 when German chemists Graebe and Liebermann synthesised artificial alizarin and started to produce it industrially². The roots of the madder plants are dried and crushed to give a pale red powder. In order to dye fabric a mordant needed to be used – which one influenced the end colour of the fabric (pink, red, purple or black). The mordant is usually a polyvalent metal ion that forms an insoluble coordination

Figure 1.7 Silk dress dyed with Mauve in 1862²

complex with the dye which can then be attached to the fibre surface. Depending on the colour and shade desired the mordant can be applied before or after the dye or

mixed in with the dye before application to the fibres. Incorporation of the metal atom into the delocalised electron system of the dye lowers the overall energy therefore influencing the visual colour. Common mordants include tannic acid, sodium chloride, and certain salts of aluminium, chromium, copper, iron, iodine, potassium, sodium, and tin.

Since the 1950's synthetic dyes such as Mauveine (purple, 3-amino-2,±9-dimethyl-5-phenyl-7-(p-tolylamino)phenazinium acetate), Curcumin (yellow, $C_{21}H_{20}O_6$) and indigo (blue, $C_{16}H_{10}N_2O_2$) have become popular as a replacement for natural dyes.

Figure 1.8 Synthetic dyed garment on catwalk model².

The first synthetic dye Mauveine (3-amino-2,±9-dimethyl-5-phenyl-7-(p-tolylamino)phenazinium acetate) was discovered by William Perkin in 1856. Made from coal tar, this first aniline based dye soon became the in-fashion colour worn by Eugénie the Empress of France and Queen Victoria of England. It replaced Royal or Tyrian purple (6,6'-dibromoindigo) made by crushing thousands of molluscs, a very time consuming and expensive process. Over 50 years later there are over 2,000 artificial colours all stemming from Perkin's work and it also influenced other industries such as photography, perfume and cosmetics, food industry (food colouring, sweeteners e.g. saccharin) to name a few⁴⁰.

Synthetic dyes today are produced on the same principle but using crude oil and ammonia as well as coal tar⁴¹.

1.1.3.1 Methods for dyeing synthetic fabrics

Synthetic fibres/fabrics have very low surface porosity so cannot be dyed the same way as natural fabrics such as wool and cotton. Disperse dyeing is used to impart colour to a synthetic fibre. In this process tiny dye molecules are suspended in a solution (for natural fibres the dye is dissolved) before the synthetic fibres are added. To attach the dye particles to the fibre surface the solution and fibres are heated above 100°C and pressurised. This causes the tightly packed polymer structures to relax slightly and allow the dye in. As the fibres cool the structure closes up again and traps the dye molecules².

1.1.3.2 Significance of using gold nanoparticles as a dye

Gold nanoparticles can be used for dyeing fibres and fabric⁴ instead of the traditional organic or natural dyes. Gold is very stable in air and does not react with moisture, oxygen or most corrosive agents making it very useful for industry. Gold has a long history related to jewellery and decoration so one assumes that clothing dyed with gold nanoparticles would be perceived as something of wealth. If colloids of gold nanoparticles can be made as dyes they will provide fabric with a colourfastness that is not available in clothing today. Consumers would be able to wash items of clothing as many times as they like without having to worry about the dye leaching out or reacting with chemicals present in the detergent.

Garments or items that have personal or historical importance would last longer so could be preserved for generations to come.

By using gold nanoparticles as a dye another industry could be weaned off its dependence on crude oil. It would make gold-fabric composites more environmentally friendly and provide consumers with an alternative option.

1.2 Fabric and Textiles

Fabric has always been prominent throughout history. Since the earliest civilisations natural materials such as cotton, silk, linen (woven flax) and wool have been to make a wide variety of useful items⁴². Objects such as clothes, tapestries, mats/rugs, carpets, drapes, sails, bedding and bandages (e.g. found on ancient Egyptian mummies⁴³) have been discovered over the years.

The development of synthetic fibres and fabric in the last 70 years has revolutionised the clothing industry. Synthetic fibres are designed to mimic properties of natural fibres but are easier to produce, have increased strength, durability and stretchability and their structure can be tailored to suit. Common fibres include Nylon and Polyester. In recent years Lycra® has been blended with these fibres to give added flexibility and stretchability. Sometimes these fibres are also combined with natural fibres to make use of properties of both the individual fibre types. In this research project samples of Nylon, Nylon-Lycra®, Polyester and Polyester-Lycra® will be dyed with gold to determine its feasibility as an alternate dye.

Industry standard tests will be done to test the durability, stability and colourfastness of the fabrics dyed with gold nanoparticles.

1.2.1 Nylon

Nylon was the first truly synthetic fibre to be introduced commercially by DuPont (1938) as a substitute for silk. Originally developed by Wallace Carothers in 1935, Nylon is a condensation copolymer formed by reacting equal molar amounts of a diamine and a dicarboxylic acid, with a catalyst so that peptide bonds form at both ends of each monomer⁴⁴. Previous research suggests that this functional group may bind to gold nanoparticles through the lone pair on the nitrogen²⁷.

Nylon has a creamy white colour but is translucent when thin. It is used as a fibre and in solid block form due to its properties of lightness, toughness and elasticity. These properties make it an important material for making small engineering components such as bearings and gears which need to be hard wearing and easy to machine⁴⁵. Nylon fibres can be spun and woven and can be coloured with pigments and dyes⁴⁶.

1.2.2 Polyester

Polyester was developed around 1940 and has rapidly become a leading product worldwide. Like Nylon, Polyester is also a condensation polymer formed by reacting equal molar amounts of a dialcohol with a dicarboxylic acid so an ester functional group results in the main chain. Polyesters can have many structural forms based on the starting products. As there are no nitrogen groups this fabric may not work; however gold nanoparticles may bind to Polyester through the lone pair on the oxygen.

Polyester fibres and fabric are used in the clothing industry due to favourable properties such as strength and resistance to stretching, shrinking, most chemicals and wrinkles. The fabric is also easy to wash and dries quickly.⁴⁷

Apart from clothing Polyester is widely used to make thermosetting plastic bottles (e.g. soft drink bottles, see **Figure 1.11**), sails for boats and thermal insulation for the International Space Station¹⁵. Plastic Polyester bottles can be recycled to make polar fleece which is also used in the clothing industry for making hats, scarves, jumpers etc.

1.2.3 Lycra®

Lycra® has exceptional elasticity and was designed as a replacement for rubber fibres. Since its invention in 1959 by DuPont scientist Joseph C. Shivers the structure of this revolutionary fibre has been kept closely guarded by the company. It is thought that the structure must have a soft rubbery segment to allow stretching to occur but a rigid segment to allow tensile strength (see **Figure 1.12**).⁴⁸

Lycra® and its competitor Spandex are used for lingerie, wetsuits, swimsuits, hosiery, surgical hose, cycling shorts, one piece rowing suits and motion capture suits. However, due to its elasticity Lycra® cannot be used in garments on its own and is generally blended with other fibres such as Nylon and Polyester. For example

cycling shorts are traditionally 80% Nylon and 20% Lycra® but this is enough to provide compression and stability to the wearers muscles.

Like the other fibres mentioned, Lycra® has lone pairs on oxygen and nitrogen (peptide bonds) that may bind to gold nanoparticles. Comparisons will be able to be made between Nylon and Polyester fibres with and without Lycra® fibres added. This will determine the best fabric and also the functional groups needed for successful dyeing with gold. Previous work by the group²⁷ suggests that most likely the lone pairs on nitrogen will be the only place that binds.

1.3 Methods of bonding

Gold is a fairly unreactive element but research has shown that it is able to bond to nitrogen, sulphur, oxygen and possibly to hydrogen (through hydrogen bonding). It is thought that fabrics containing one or more of these elements will be suitable for use with gold nanoparticles. Gold nanoparticles bonded to elements in the fabric should provide a colourfastness not shown by current organic dyes. This will allow the fabrics to be laundered frequently without the colour washing off or fading. The proposed methods of bonding are shown in **Figure 1.13**.⁴

Gold nanoparticles will be prepared and attached to the synthetic fibres, hopefully through one of the modes mentioned above. A linker may be needed for fabrics not containing nitrogen (i.e. Polyester). Capping agents may also be needed to stop aggregation of particles which will affect the colour of the fabric. If this method is unsuccessful in producing attractive colours then gold nanoparticles will be made in-situ i.e. formed on the fabric surface. Details of both methods are outlined later in the experimental section.

1.4 Research Objectives

The main aim of this research is to develop the use of gold nanoparticles as stable colourants for synthetic fabrics such as Nylon, Polyester and Lycra®. It is hoped that a variety of attractive colours will be produced to generate interest from industry. The fabric colours should be colourfast and stable with the environmental impact of the leftover solutions minimal. Optimally the gold will be spread evenly over the surface of the fabric so as to minimise cost.

Fabrics used are Nylon and Nylon-Lycra® composites mainly as previous work suggests gold binds effectively to the lone pair on the nitrogen²⁷. Polyester and Polyester-Lycra® composites will also be investigated to confirm that nitrogen is needed to bind to the gold nanoparticles.

2 Experimental Details

Two main approaches were attempted to provide colour the fabric substrates reproducibly with gold nanoparticles. First to produce gold nanoparticle colloids using methods from the literature (see Introduction), then attaching the gold nanoparticles to the fibre surface. Secondly to produce and attach the gold nanoparticles in-situ on the fabric surface in a single step synthesis. Details of both experimental procedures are outlined below.

2.1 Materials

A very wide range of fibres and fabrics exist in the world today. They can be divided into two categories – natural fibres from animals and plants (e.g. wool, cotton) and manmade/synthetic fibres (e.g. Nylon, Polyester). This project focuses on synthetic fibres namely Nylon and Polyester and also Nylon-Lycra® and Polyester-Lycra® composites.

Fabric was obtained from Du Pont, Switzerland and was used as received or acid/base treated (submerged in 0.1M HCl or 0.1M NaOH for 10 minutes, removed then left to dry overnight). Acid/base treatment was performed in order to study the effect of protonating or deprotonating amine groups on the reducing properties of the fabric in relation to the reduction of gold.

For the preparation of the gold solution, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was obtained from Sigma-Aldrich in solid form. This was made into a 4% w/w gold solution by dissolving the solid with 0.1M HCl. Typically 0.8g $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was weighed into a glass jar and made up to 10g with 0.1M HCl to obtain the desired concentration.

Distilled water – Prepared by heating water to boiling point then collecting the water vapour by condensing it on a condenser with cold water flowing through it. However, contaminants with boiling points lower than 100°C will also be transferred to the distillate.

Millipore water – In comparison (to distilled water), Millipore water is purified by a number of ultrafiltration steps. Generally distilled water is passed through a number of microporous filters (varied pore size) which remove all contaminants larger than

the specified pore size i.e. purity of the water can be tuned based on its intended use (e.g. 0.22 μm Millipore membrane filters retain all bacteria so they can be used in medical applications such as sterilizing antibiotics). Frequently ion exchange is used as a final step to remove and dissolved contaminants that have made it through the filters. This involves passing the water through deionization bead which exchange hydrogen for cations or hydroxyl ions for anions. Overall the water is purer than achieved by just distillation so there is less chance of undesired interactions with the gold nanoparticles produced.

PEI – Polyethylene imine $((\text{CH}_2\text{CH}_2\text{NH})_n)$ was obtained from Sigma-Aldrich in liquid form. As it has a mass weight $\sim 25,000$ it is too viscous to use directly so an 18% w/w solution was made up by dissolving 9g of PEI in 41g of Millipore water.

Trisodium citrate – $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ was obtained from Sigma-Aldrich in solid form. This was made into a 10% w/w of trisodium citrate solution by dissolving the solid in Millipore water.

Tannic acid – $\text{C}_{76}\text{H}_{52}\text{O}_{46}$ was obtained from ProSciTech in solid form. This was made into a 10% w/w of tannic acid solution by dissolving the solid in Millipore water.

2.2 Preparation

2.2.1 Preparation of pre-made gold colloids

Gold colloids were prepared by adding an appropriate amount of gold solution to Millipore water in a glass sample vial. The solutions were stirred rapidly for 1 minute before the reductant (PEI or trisodium citrate or tannic acid) was added. The vials were then heated to reduce the Au^{3+} to Au^0 .

Samples of each fabric (Nylon, Polyester, Nylon-Lycra® or Polyester-Lycra®) were cut into squares weighing approximately 0.4g each. Untreated, acid treated and base treated samples were either:

a) Clamped inside a 35mm plastic slide frame measuring 5 x 5cm with a 2.3 x 3.5cm hole in the middle. The slide was placed in a plastic Petri dish before the pre made colloids were poured over the top (depth ~1cm) to fully immerse the fabric.

Or b) Placed inside the glass sample vial containing the pre made colloid and fully immersed.

Figure 2.1 (Left) Fabric sample in plastic slide frame submerged in pre made gold nanoparticle colloid. (Right) Fabric sample in glass sample vial immersed in pre made gold nanoparticle colloid.

Samples were then left overnight (unless otherwise stated) on the bench at room temperature or in a water bath at 50°C or 80°C during which time the gold nanoparticles attached to the fibre surface.

After soaking all gold-fabric samples were removed from solution, rinsed with distilled water and patted dry with paper towels.

A number of different methods were developed using the general approach above. These are detailed below.

Method 1: Based on literature methods by M. J. Richardson and J. H Johnston⁴, gold colloids were prepared by adding 80µL gold solution to 10mL Millipore water in glass sample vials. To this 20µL Polyethylene imine was added and shaken lightly to mix. The sample vials were placed in a water bath at 80°C for 5 minutes to form the gold nanoparticles and develop the colour. Resulting colloid was cooled to room temperature before samples of fabric were added to the glass vials and maintained at room temperature, 50°C or 80°C for 6 hours or overnight (**Table 2.1**).

Table 2.1 Method 1-Effect of changing fabric type and temperature/time after fabric added to glass sample vial.

Sample ID	Gold solution (4%)	Polyethylene imine	Temperature/Time of colloid	Fabric	Temperature/Time after fabric added
AW901A	80µL	20µL	80°C for 5 minutes	Nylon	RT overnight
AW901B	80µL	20µL	80°C for 5 minutes	Nylon-Lycra	RT overnight
AW901C	80µL	20µL	80°C for 5 minutes	Polyester	RT overnight
AW901D	80µL	20µL	80°C for 5 minutes	Polyester-Lycra	RT overnight
AW901E	80µL	20µL	80°C for 5 minutes	Nylon	80°C overnight
AW901F	80µL	20µL	80°C for 5 minutes	Nylon-Lycra	80°C overnight
AW901G	80µL	20µL	80°C for 5 minutes	Polyester	80°C overnight
AW901H	80µL	20µL	80°C for 5 minutes	Polyester-Lycra	80°C overnight
AW904A	80µL	20µL	80°C for 5 minutes	Nylon	50°C for 6 hours
AW904B	80µL	20µL	80°C for 5 minutes	Nylon-Lycra	50°C for 6 hours
AW904C	80µL	20µL	80°C for 5 minutes	Polyester	50°C for 6 hours
AW904D	80µL	20µL	80°C for 5 minutes	Polyester-Lycra	50°C for 6 hours

Method 2: The same gold colloid as **Method 1** was prepared but was placed into Petri dishes. Again the type of fabric and time/temperature after fabric added was varied.

6 samples of AW915E were made up using a total of 480 μL gold solution and 60mL Millipore water. They were heated in a water bath at 50°C for approximately 10 minutes to form the gold colloids and develop colour before being split into 4 Petri dishes and samples of fabric were submerged in the colloid. One sample was heated at 80°C overnight while the remaining samples were left on the bench at room temperature overnight (**Table 2.2**).

Table 2.2 Method 2-Effect of changing fabric type and temperature/time after fabric added to Petri dish

Sample ID	Millipore water	Gold solution (4%)	Polyethylene imine	Fabric	Temperature /Time after fabric added
AW915E x6	10mL	80 μL	20 μL		
	15mL	120 μL	30 μL	Nylon	80°C overnight
	15mL	120 μL	30 μL	Nylon	RT overnight
	15mL	120 μL	30 μL	Nylon-Lycra	RT overnight
	15mL	120 μL	30 μL	Polyester-Lycra	RT overnight

Method 3: The effect of trisodium citrate as a reductant was observed.

Gold colloids were prepared by adding 80 μL gold solution to 10mL Millipore water in glass sample vials. To this 20 μL trisodium citrate was added and shaken lightly to mix. The sample vials were placed in a water bath at 80°C for 5 minutes until the gold colloid and colour develop. Fabric samples were added to the colloid and either left on the bench at room temperature overnight or heated in the water bath at 50°C for 6 hours (**Table 2.3**).

Table 2.3 Method 3-Effect of changing reductant, fabric type and temperature/time after fabric added.

Sample ID	Gold solution (4%)	Trisodium citrate (10%)	Fabric	Temperature/Time after fabric added
AW903A	80 μL	20 μL	Nylon	RT overnight
AW903B	80 μL	20 μL	Nylon-Lycra	RT overnight

Table 2.3 cont Method 3-Effect of changing reductant, fabric type and temperature/time after fabric added.

Sample ID	Gold solution (4%)	Trisodium citrate (10%)	Fabric	Temperature/Time after fabric added
AW903C	80µL	20µL	Polyester	RT overnight
AW903D	80µL	20µL	Polyester-Lycra	RT overnight
AW904E	80µL	20µL	Nylon	50°C for 6 hours
AW904F	80µL	20µL	Nylon-Lycra	50°C for 6 hours
AW904G	80µL	20µL	Polyester	50°C for 6 hours
AW904H	80µL	20µL	Polyester-Lycra	50°C for 6 hours

Method 4: The volume of gold solution and trisodium citrate was varied along with the development time of the gold colloid to see if new colours could be observed.

Gold colloids were prepared by adding gold solution to 10mL Millipore water in glass sample vials. To this trisodium citrate was added and shaken lightly to mix. The sample vials were placed in a water bath at 50°C until the gold colloid and colour developed (see **Table 2.4** below). Resulting colloid was cooled to room temperature before Nylon samples were added and left on the bench at room temperature overnight.

Table 2.4 Method 4-Effect of varying the volume of gold solution, volume of trisodium citrate and development time of the gold colloid.

Sample ID	Gold solution (4%)	Trisodium citrate (10%)	Time in water bath at 50°C
AW905A	80µL	20µL	30 minutes
AW905B	80µL	40µL	10 minutes
AW905C	80µL	60µL	10 minutes
AW906A	80µL	80µL	10 minutes
AW906B	80µL	100µL	10 minutes
AW906C	80µL	200µL	10 minutes
AW906D	20µL	20µL	10 minutes
AW906E	20µL	40µL	20 minutes
AW907A	20µL	60µL	30 minutes

Table 2.4 cont Method 4-Effect of varying the volume of gold solution, volume of trisodium citrate and development time of the gold colloid.

Sample ID	Gold solution (4%)	Trisodium citrate (10%)	Time in water bath at 50°C
AW907B	20µL	80µL	30 minutes
AW907C	20µL	100µL	30 minutes
AW907D	20µL	200µL	30 minutes

Method 5: Similar to **Method 4**, the gold volume and reductant volume was varied but most importantly the development temperature was increased to 80°C to see if the colour is different or if the development time can be decreased.

Gold colloids were prepared by adding gold solution to 10mL Millipore water in glass sample vials. To this trisodium citrate was added and shaken lightly to mix. The sample vials were placed in a water bath at 80°C until the colour developed (see **Table 2.5** below). Resulting colloid was cooled to room temperature before Nylon samples were added and left on the bench at room temperature overnight.

Table 2.5 Method 5-Effect of varying the volume of gold solution, volume of trisodium citrate and development time of the gold colloid.

Sample ID	Gold solution (4%)	Trisodium citrate (10%)	Time in water bath at 80°C
AW907E	80µL	30µL	10 minutes
AW907F	80µL	90µL	10 minutes
AW908A	80µL	120µL	10 minutes
AW913A	150µL	20µL	30 minutes
AW913B	150µL	40µL	30 minutes
AW913C	150µL	60µL	30 minutes
AW913D	150µL	80µL	30 minutes
AW913E	150µL	100µL	30 minutes
AW913F	150µL	200µL	30 minutes

Method 6: Effect of tannic acid as a reductant.

Gold colloids were prepared by adding gold solution (see **Table 2.6**) to 10mL Millipore water in glass sample vials. To this tannic acid was added and shaken lightly to mix. The sample vials were placed in a water bath at 80°C for approximately

10 minutes until the gold colloid and colour developed. Resulting colloid was cooled to room temperature before samples of Nylon were added and left overnight on the bench at room temperature.

Table 2.6 Method 6-Effect of changing reductant, volume of gold solution and volume of tannic acid.

Sample ID	Gold solution (4%)	Tannic Acid (10%)	Sample ID	Gold solution (4%)	Tannic Acid (10%)
AW917A	20µL	20µL	AW918D	80µL	80µL
AW917B	20µL	40µL	AW918E	80µL	100µL
AW917C	20µL	60µL	AW918F	80µL	200µL
AW917D	20µL	80µL	AW920E	150µL	20µL
AW917E	20µL	100µL	AW920F	150µL	40µL
AW917F	20µL	200µL	AW920G	150µL	60µL
AW918A	80µL	20µL	AW921A	150µL	80µL
AW918B	80µL	40µL	AW921B	150µL	100µL
AW918C	80µL	60µL	AW921C	150µL	200µL

2.2.2 In-Situ preparation of gold nanoparticles on fibre surface

After preparing gold nanoparticles separately and attaching them to the fabric samples the next method was to prepare them in the presence of the fabric i.e. where the gold nanoparticles form directly on the fabric surface.

Fabric samples were clamped inside plastic slide frames and placed inside plastic Petri dishes or placed inside glass sample vials with Millipore water and gold solution. The samples were left to develop on the bench at room temperature or heated in a water bath (50-80°C) to develop colour. After soaking the fabric samples were removed from solution, rinsed with distilled water and patted dry with paper towels.

Method 7: In **Methods 1-6** a small range of gold solution volumes was used (20-150µL). This method looks at the effect of increasing the amount of gold present in the sample.

In glass sample vials 20mL Millipore water was added to the volume of gold specified in **Table 2.7**. The solutions were heated in a water bath at 50°C for approximately 10 minutes to see if any colour developed. Samples of Nylon were clamped inside 35mm plastic slide frames measuring 5 x 5cm with a 2.3 x 3.5cm hole in the middle. The slides were placed in plastic Petri dishes (see **Figure 2.1**) and the solutions from the glass sample vials were poured over the top to submerge the fabric. Samples were left on the bench at room temperature overnight.

Table 2.7 Method 7-Effect of varying the volume of gold solution without reductant present.

Sample ID	Gold solution (4%)	Temperature/Time of gold solution	Temperature/Time after fabric added
AW914A	40µL	50°C ~10 minutes	RT overnight
AW914B	100µL	50°C ~10 minutes	RT overnight
AW914C	200µL	50°C ~10 minutes	RT overnight
AW914D	400µL	50°C ~10 minutes	RT overnight

Method 8: In this batch of experiments **Method 7** was repeated but the fabric samples were added to the glass sample vials for development and the time varied. Samples of Nylon were cut 3 x 4cm and placed in glass sample vials containing 20mL Millipore water and the volume of gold specified in **Table 2.8** below. The samples were heated in a water bath at 50°C for 1-68 hours.

Table 2.8 Method 8-Effect of varying volume of gold solution and time in water bath.

Sample ID	Gold solution (4%)	Time in water bath at 50°C	Sample ID	Gold solution (4%)	Time in water bath at 50°C
AW923B	40µL	68 hours	AW923B (3)	40µL	5 hours
AW923C	100µL	68 hours	AW923C (3)	100µL	5 hours
AW923D	200µL	68 hours	AW923D (3)	200µL	5 hours
AW923E	300µL	68 hours	AW923E (3)	300µL	5 hours
AW923F	400µL	68 hours	AW923F (3)	400µL	5 hours
AW923B (2)	40µL	1 hour	AW923B (4)	40µL	18 hours
AW923C (2)	100µL	1 hour	AW923C (4)	100µL	18 hours
AW923D (2)	200µL	1 hour	AW923D (4)	200µL	18 hours

Table 2.8 cont Method 8-Effect of varying volume of gold solution and time in water bath.

Sample ID	Gold solution (4%)	Time in water bath at 50°C	Sample ID	Gold solution (4%)	Time in water bath at 50°C
AW923E (2)	300µL	1 hour	AW923E (4)	300µL	18 hours
AW923F (2)	400µL	1 hour	AW923F (4)	400µL	18 hours

Method 9: Quantitative uptake measurements were then performed to determine out the optimum volume of gold solution and uptake time.

Samples of fabric (untreated, acid treated (0.1M HCl) and base treated (0.1M NaOH)) were cut to ~0.4g and placed in glass sample vials containing 9.96mL Millipore water. To this 40µL gold solution was added and stirred with a plastic rod to disperse the gold. Samples were heated in a water bath at 50°C for specified time. After soaking the fabric samples were removed from solution and placed in new glass sample vials containing 10mL Millipore water. These were heated in the water bath to develop colour (AW445B-456C developed overnight at 50°C, all remaining samples 2 hours at 80°C).

Table 2.9a Method 9-Untreated fabric uptake (effect of changing time in water bath)

Sample ID	Fabric	Weight (g)	Time in water bath at 50°C	Sample ID	Fabric	Weight (g)	Time in water bath at 50°C
AW933A	Polyester	0.3990	10 minutes	AW937C	Polyester-Lycra	0.3970	18 hours
AW933B	Nylon	0.4085	10 minutes	AW937D	Nylon-Lycra	0.4048	18 hours
AW933C	Polyester-Lycra	0.4079	10 minutes	AW455F	Polyester	0.3678	2 hours
AW933D	Nylon-Lycra	0.4056	10 minutes	AW456A	Nylon	0.3902	2 hours
AW933E	Polyester	0.4084	30 minutes	AW456B	Polyester-Lycra	0.4039	2 hours
AW933F	Nylon	0.4009	30 minutes	AW456C	Nylon-Lycra	0.3996	2 hours
AW933G	Polyester-Lycra	0.3878	30 minutes	AW457A	Polyester	0.4099	10 minutes
AW933H	Nylon-Lycra	0.4123	30 minutes	AW457B	Nylon	0.3920	10 minutes
AW934A	Polyester	0.3979	1 hour	AW458A	Polyester-Lycra	0.4070	10 minutes

Table 2.9a cont Method 9-Untreated fabric uptake (effect of changing time in water bath)

Sample ID	Fabric	Weight (g)	Time in water bath at 50°C	Sample ID	Fabric	Weight (g)	Time in water bath at 50°C
AW934B	Nylon	0.4029	1 hour	AW458B	Nylon-Lycra	0.3998	10 minutes
AW934C	Polyester-Lycra	0.4096	1 hour	AW458C	Polyester	0.4047	40 minutes
AW934D	Nylon-Lycra	0.4119	1 hour	AW458D	Nylon	0.4002	40 minutes
AW934E	Polyester	0.4059	3 hours	AW458E	Polyester-Lycra	0.3989	40 minutes
AW934F	Nylon	0.4051	3 hours	AW458F	Nylon-Lycra	0.4058	40 minutes
AW934G	Polyester-Lycra	0.3980	3 hours	AW458G	Polyester	0.4054	100 minutes
AW935A	Nylon-Lycra	0.3920	3 hours	AW458H	Nylon	0.4086	100 minutes
AW935B	Polyester	0.3739	6 hours	AW459A	Polyester-Lycra	0.4070	100 minutes
AW935C	Nylon	0.3870	6 hours	AW459B	Nylon-Lycra	0.4082	100 minutes
AW935D	Polyester-Lycra	0.4005	6 hours	AW459C	Polyester	0.4090	3 hours
AW935E	Nylon-Lycra	0.3990	6 hours	AW459D	Nylon	0.4051	3 hours
AW937A	Polyester	0.4029	18 hours	AW459E	Polyester-Lycra	0.4077	3 hours
AW937B	Nylon	0.4001	18 hours	AW459F	Nylon-Lycra	0.4082	3 hours

Table 2.9b Method 9-Acid treated fabric uptakeN.B All samples developed for 2 hours at 80°C

Sample ID	Fabric	Weight (g)	Time in water bath at 50°C	Sample ID	Fabric	Weight (g)	Time in water bath at 50°C
AW462B	Polyester	0.4117	overnight	AW470C	Polyester	0.4180	1 hour
AW462C	Nylon	0.3793	overnight	AW470D	Nylon	0.3862	1 hour
AW462D	Polyester-Lycra	0.3999	overnight	AW470E	Polyester-Lycra	0.4137	1 hour
AW462E	Nylon-Lycra	0.4118	overnight	AW470F	Nylon-Lycra	0.4118	1 hour
AW469A	Polyester	0.4177	6 hours	AW470G	Polyester	0.4116	30 minutes
AW469B	Nylon	0.3989	6 hours	AW471A	Nylon	0.3883	30 minutes
AW469C	Polyester-Lycra	0.4076	6 hours	AW471B	Polyester-Lycra	0.3963	30 minutes
AW469D	Nylon-Lycra	0.4130	6 hours	AW471C	Nylon-Lycra	0.4093	30 minutes
AW469E	Polyester	0.3958	3 hours	AW471D	Polyester	0.4096	10 minutes
AW469F	Nylon	0.3924	3 hours	AW471E	Nylon	0.3892	10 minutes
AW470A	Polyester-Lycra	0.4156	3 hours	AW471F	Polyester-Lycra	0.4061	10 minutes
AW470B	Nylon-Lycra	0.4146	3 hours	AW471G	Nylon-Lycra	0.4142	10 minutes

Table 2.9c Method 9-Base treated fabric uptakeN.B All samples developed for 2 hours at 80°C

Sample ID	Fabric	Weight (g)	Time in water bath at 50°C	Sample ID	Fabric	Weight (g)	Time in water bath at 50°C
AW461A	Polyester	0.4037	overnight	AW463G	Polyester	0.4187	1 hour
AW461B	Nylon	0.3847	overnight	AW463H	Nylon	0.3807	1 hour
AW461C	Polyester-Lycra	0.4191	overnight	AW464A	Polyester-Lycra	0.3953	1 hour
AW462A	Nylon-Lycra	0.4014	overnight	AW464B	Nylon-Lycra	0.4150	1 hour
AW462F	Polyester	0.4179	6 hours	AW464C	Polyester	0.3994	30 minutes
AW462G	Nylon	0.3884	6 hours	AW464D	Nylon	0.3906	30 minutes

Table 2.9c cont Method 9-Base treated fabric uptake

N.B All samples developed for 2 hours at 80°C

Sample ID	Fabric	Weight (g)	Time in water bath at 50°C	Sample ID	Fabric	Weight (g)	Time in water bath at 50°C
AW463A	Polyester-Lycra	0.4172	6 hours	AW464E	Polyester-Lycra	0.4167	30 minutes
AW463B	Nylon-Lycra	0.4103	6 hours	AW464F	Nylon-Lycra	0.4180	30 minutes
AW463C	Polyester	0.3878	3 hours	AW464G	Polyester	0.4022	10 minutes
AW463D	Nylon	0.4079	3 hours	AW464H	Nylon	0.3775	10 minutes
AW463E	Polyester-Lycra	0.4095	3 hours	AW465A	Polyester-Lycra	0.4174	10 minutes
AW463F	Nylon-Lycra	0.4083	3 hours	AW465B	Nylon-Lycra	0.4165	10 minutes

Method 10: Once the quantitative uptake at 50°C was completed (**Method 9**), a similar uptake was performed at 80°C.

Samples of fabric were cut to ~0.4g and placed in glass sample vials containing 9.96mL Millipore water and 40µL gold solution. Samples were heated in a water bath at 80°C for the time specified in **Table 2.10** below. After soaking the fabric samples were removed from solution, rinsed with distilled water and placed in a new glass sample vials containing 20mL Millipore water. Samples were placed back in the water bath at 80°C and left to see if any colour developed on the fabric.

Table 2.10 Method 10-Quantitative uptake at 80°C.

Sample ID	Fabric	Weight (g)	Time in water bath at 80°C	Development Temperature/Time
AW946D	Nylon	0.4079	10 minutes	80°C overnight
AW946E	Nylon-Lycra	0.4101	10 minutes	80°C overnight
AW946F	Nylon	0.4057	30 minutes	80°C overnight
AW946G	Nylon-Lycra	0.4116	30 minutes	80°C overnight
AW947A	Nylon	0.4160	1 hour	80°C overnight
AW947B	Nylon-Lycra	0.4180	1 hour	80°C overnight
AW947C	Nylon	0.4028	2 hours	80°C overnight
AW947D	Nylon-Lycra	0.4086	2 hours	80°C overnight

Table 2.10 cont Method 10-Quantitative uptake at 80°C.

Sample ID	Fabric	Weight (g)	Time in water bath at 80°C	Development Temperature/Time
AW950C	Polyester	0.4097	30 minutes	80°C for 1 hour
AW950D	Nylon	0.3965	30 minutes	80°C for 1 hour
AW950E	Polyester-Lycra	0.4088	30 minutes	80°C for 1 hour
AW950F	Nylon-Lycra	0.4092	30 minutes	80°C for 1 hour
AW451B	Polyester	0.3898	30 minutes	80°C for 1 hour
AW451C	Polyester-Lycra	0.4051	30 minutes	80°C for 1 hour

Method 11: Final uptake was performed at room temperature, using only Nylon (untreated, acid treated (0.1M HCl), base treated (0.1M NaOH)) samples.

Samples of fabric were cut to ~0.4g and placed in glass sample vials containing 9.96mL Millipore water and 40µL gold solution. Once the samples were made up they were placed in a Sonicator for 3 minutes to remove any bubbles in the solution. Samples were left on the bench at room temperature for the time specified in **Table 2.11** before being removed from solution, squeezed and placed in a new glass sample vial containing 10mL Millipore water. Samples were placed in the water bath at 50°C and left for 2 days to see if any colour developed on the fabric.

Table 2.11 Method 11-Quantitative uptake at room temperature.

Sample ID	Weight (g)	Treatment	Time at room temperature
AW486A	0.4094	-	18 hours
AW486B	0.4096	-	24 hours
AW486C	0.3936	0.1M HCl	18 hours
AW486D	0.3930	0.1M HCl	24 hours
AW486E	0.3980	0.1M NaOH	18 hours
AW486F	0.4011	0.1M NaOH	24 hours
AW487A	0.4144	-	30 minutes
AW487B	0.3962	-	2 hours
AW487C	0.4182	-	6 hours
AW487D	0.3940	0.1M HCl	30 minutes

Table 2.11 cont Method 11-Quantitative uptake at room temperature.

Sample ID	Weight (g)	Treatment	Time at room temperature
AW487E	0.3950	0.1M HCl	2 hours
AW487F	0.3935	0.1M HCl	6 hours
AW487G	0.4072	0.1M NaOH	30 minutes
AW488A	0.3980	0.1M NaOH	2 hours
AW488B	0.3970	0.1M NaOH	6 hours

Results from Method 7 suggest that chloride ions are needed in the solution to help encourage the reduction of gold to Au⁰. They increase ionic conductivity of solutions to facilitate electron transfer required for the redox process. Therefore, the following samples were made for comparisons (**Method 12** and **13**).

Method 12: Fabric samples developed in the presence of chloride ions.

Samples of Nylon were cut to ~0.4g and placed in glass sample vials containing 9.96mL Millipore water. To this 40μL gold solution was added and stirred with a plastic rod to disperse the gold. Samples were left at room temperature (RT) or heated in a water bath at 50°C for the time specified in **Table 2.12**.

Table 2.12 Method 12-Fabric samples developed in the presence of chloride ions.

Sample ID	Weight (g)	Treatment	Temperature	Time
AW493A	0.4080	-	RT	3 days
AW493B	0.4109	-	RT	7 days
AW493C	0.4094	-	RT	14 days
AW493D	0.4091	0.1M HCl	RT	3 days
AW493E	0.3917	0.1M HCl	RT	7 days
AW493F	0.4067	0.1M HCl	RT	14 days
AW493G	0.4044	0.1M NaOH	RT	3 days
AW493H	0.4034	0.1M NaOH	RT	7 days
AW493I	0.4001	0.1M NaOH	RT	14 days
AW494A	0.4044	-	50°C	3 days
AW494B	0.4071	-	50°C	7 days

Table 2.12 cont Method 12-Fabric samples developed in the presence of chloride ions.

Sample ID	Weight (g)	Treatment	Temperature	Time
AW494C	0.4044	-	50°C	14 days
AW494D	0.4071	0.1M HCl	50°C	3 days
AW494E	0.3977	0.1M HCl	50°C	7 days
AW494F	0.4077	0.1M HCl	50°C	14 days
AW494G	0.4036	0.1M NaOH	50°C	3 days
AW494H	0.4060	0.1M NaOH	50°C	7 days
AW494I	0.4066	0.1M NaOH	50°C	14 days

Method 13: Fabric samples developed in the absence of chloride ions.

The same procedure as **Method 12** was performed but after the first 24 hours the Nylon samples were removed from solution, squeezed and placed in a new glass sample vials containing 10mL Millipore water.

Table 2.13 Method 13-Fabric samples developed in the absence of chloride ions.

Sample ID	Weight (g)	Treatment	Temperature (first 24 hours)	New Solution Time/Temperature
AW494J	0.4102	-	RT	6 days at RT
AW494K	0.3957	-	RT	13 days at RT
AW494L	0.4038	0.1M HCl	RT	6 days at RT
AW494M	0.4135	0.1M HCl	RT	13 days at RT
AW494N	0.4144	0.1M NaOH	RT	6 days at RT
AW494O	0.3885	0.1M NaOH	RT	13 days at RT
AW494P	0.4015	-	50°C	6 days at 50°C
AW494Q	0.3960	-	50°C	13 days at 50°C
AW495A	0.4095	0.1M HCl	50°C	6 days at 50°C
AW495B	0.4040	0.1M HCl	50°C	13 days at 50°C
AW495C	0.3946	0.1M NaOH	50°C	6 days at 50°C

Table 2.13 cont Method 13-Fabric samples developed in the absence of chloride ions.

Sample ID	Weight (g)	Treatment	Temperature (first 24 hours)	New Solution Time/Temperature
AW495D	0.4132	0.1M NaOH	50°C	13 days at 50°C
AW496A	0.3881	-	RT	2 days at RT
AW496B	0.4137	0.1M HCl	RT	2 days at RT
AW496C	0.4160	0.1M NaOH	RT	2 days at RT
AW496D	0.3980	-	50°C	2 days at 50°C
AW496E	0.4117	0.1M HCl	50°C	2 days at 50°C
AW496F	0.3965	0.1M NaOH	50°C	2 days at 50°C

As the previous samples had large quantities of gold solution added to them it was decided to decrease the volume of gold solution to see if there is a minimum volume needed to give colour to the fabric samples. The procedures are given in **Methods 14-17**.

Method 14: Effect of decreasing gold concentration.

All samples contain ~0.4g fabric placed in glass sample vials containing 10µL gold solution and 9.99mL Millipore water. These were heated in a water bath at 50°C for the time specified in **Table 2.14**. Samples AW445B-E were removed, squeezed and placed in new glass sample vials containing 10mL Millipore water and returned to the water bath overnight to develop any colour.

Table 2.14 Method 14-Effect of decreasing gold solution volume to 10µL and varying development time.

Sample ID	Fabric	Weight (g)	Treatment	Time in water bath at 50°C
AW455B	Polyester	0.3808	-	2 hours
AW455C	Nylon	0.3966	-	2 hours
AW455D	Polyester-Lycra	0.4063	-	2 hours
AW455E	Nylon-Lycra	0.4152	-	2 hours
AW203D	Nylon	0.4174	-	14 days
AW203E	Nylon	0.3836	0.1M HCl	14 days

Table 2.14 cont Method 14-Effect of decreasing gold solution volume to 10 μ L and varying development time.

Sample ID	Fabric	Weight (g)	Treatment	Time in water bath at 50°C
AW203F	Nylon	0.3871	0.1M NaOH	14 days
AW205G	Nylon	0.4045	-	3 days
AW205H	Nylon	0.3820	0.1M HCl	3 days
AW205I	Nylon	0.3853	0.1M NaOH	3 days
AW205J	Nylon	0.4177	-	7 days
AW205K	Nylon	0.3829	0.1M HCl	7 days
AW205L	Nylon	0.3751	0.1M NaOH	7 days
AW210B	Nylon	0.3611	0.1M NaOH	14 days

Method 15: Effect of decreasing gold concentration by increasing water volume.

Nylon samples were cut to ~0.4g and placed in glass sample vials with 10 μ L gold solution and 19.99mL Millipore water as specified in **Table 2.15** below. The samples were heated in a water bath at 50°C for 3-15 days to develop colour.

Table 2.15 Method 15-Effect of decreasing gold concentration by increasing water volume.

Sample ID	Weight (g)	Treatment	Time in water bath at 50°C
AW205M	0.3903	-	7 days
AW205N	0.3825	0.1M HCl	7 days
AW205O	0.3821	0.1M NaOH	7 days
AW206A	0.3925	-	3 days
AW206B	0.3828	0.1M HCl	3 days
AW206C	0.3734	0.1M NaOH	3 days
AW206D	0.3948	-	15 days
AW206E	0.3800	0.1M HCl	15 days
AW206F	0.3930	0.1M NaOH	15 days

Method 16: Again small volumes of gold solution were used to see if changes in colour can be observed.

Samples of Nylon were cut to ~0.4g and placed in glass sample vials with 20 μ L gold solution and 9.98mL Millipore water. The samples were heated in a water bath at 50°C for the time specified in **Table 2.16** below.

Table 2.16 Method 16-Effect of 20 μ L gold solution.

Sample ID	Weight (g)	Treatment	Time in water bath at 50°C
AW203A	0.4046	-	14 days
AW203B	0.4032	0.1M HCl	14 days
AW203C	0.3906	0.1M NaOH	14 days
AW205A	0.4110	-	3 days
AW205B	0.3820	0.1M HCl	3 days
AW205C	0.3912	0.1M NaOH	3 days
AW205D	0.4091	-	7 days
AW205E	0.3888	0.1M HCl	7 days
AW205F	0.3960	0.1M NaOH	7 days
AW210A	0.3933	-	14 days

Method 17: As all previous samples had been heated or left at room temperature to develop colour it was decided to study the effect of lowering the temperature during development time.

Nylon samples were cut to ~0.4g and placed in glass sample vials with 10 μ L gold solution and 9.99mL Millipore water. The samples were placed in the fridge at ~4°C for 7-21 days (**Table 2.17**). N.B AW207G-I were left to develop on the bench at room temperature for ~16 weeks.

Table 2.17 Method 17-Effect of lowering temperature during development time.

Sample ID	Weight (g)	Treatment	Time in fridge at ~4°C
AW207A	0.4023	-	7 days
AW207B	0.3908	0.1M HCl	7 days
AW207C	0.4066	0.1M NaOH	7 days

Table 2.17 cont Method 17-Effect of lowering temperature during development time.

Sample ID	Weight (g)	Treatment	Time in fridge at ~4°C
AW207D	0.4033	-	14 days
AW207E	0.3885	0.1M HCl	14 days
AW207F	0.3849	0.1M NaOH	14 days
AW207G	0.3849	-	21 days
AW207H	0.4025	0.1M HCl	21 days
AW207I	0.3905	0.1M NaOH	21 days

Method 18: Instead of acid or base treating the fabric before it was added to the gold solution, the pH of the solution was adjusted after the gold solution was added using dilute HCl and NaOH before the fabric was added.

In glass sample vials, 20µL gold solution and 10mL distilled water were placed. Each sample was adjusted to pH 2-12 (one pH unit increments i.e. pH 3, pH 4 etc) using small volumes of 0.1M HCl and NaOH. Once the desired pH was reached Nylon or Nylon-Lycra® samples were added to the solution before the samples were placed in a water bath at 80°C for 7 days. After soaking fabric samples were removed from solution, then put into a small beaker with distilled water and placed in a Sonicator for 3 minutes before they were patted dry with paper towels

Table 2.18 Method 18-Effect of adjusting the pH of solution before fabric is added.

Sample ID	Fabric	Weight (g)	pH	Sample ID	Fabric	Weight (g)	pH
AW222A	Nylon	0.4133	2.1	AW224J	Nylon	0.4123	7.1
AW222B	Nylon	0.4116	3.0	AW224K	Nylon-Lycra	0.4270	8.2
AW224A	Nylon-Lycra	0.4212	2.1	AW224L	Nylon	0.4182	8.1
AW224B	Nylon-Lycra	0.4229	3.0	AW224M	Nylon-Lycra	0.4200	9.2
AW224C	Nylon-Lycra	0.4206	4.1	AW224N	Nylon	0.4114	9.0
AW224D	Nylon	0.4163	4.3	AW224O	Nylon-Lycra	0.4046	10.2
AW224E	Nylon-Lycra	0.4021	5.1	AW224P	Nylon	0.4122	10.3
AW224F	Nylon	0.4153	5.0	AW225A	Nylon-Lycra	0.4180	11.1
AW224G	Nylon-Lycra	0.4275	6.0	AW225B	Nylon	0.4257	11.1

Table 2.18 cont Method 18-Effect of adjusting the pH of solution before fabric is added.

Sample ID	Fabric	Weight (g)	pH	Sample ID	Fabric	Weight (g)	pH
AW224H	Nylon	0.4109	6.1	AW225C	Nylon-Lycra	0.4250	12.0
AW224I	Nylon-Lycra	0.4172	7.0	AW225D	Nylon	0.4062	12.0

Method 19: Larger samples were prepared to see if the colour stays the same during scale up. Parafilm was placed over the top of all samples to minimise vapour loss. Two large Nylon samples were cut 7 x 7cm and 9 x 9cm. They were placed in conical flasks with gold solution and Millipore water (**Figure 2.2**). They were heated for 7 days in a water bath at 50°C.

Figure 2.2 (Left) Large Nylon sample in a conical flask with gold solution and Millipore water. (Right) Conical flask and glass sample vial in water bath.

Table 2.19 Method 19-Scale up.

Sample ID	Weight (g)	Millipore Water	Gold Solution (4%)
AW212A	0.8338	50mL	50µL
AW212B	1.4179	100mL	100µL

Method 20: As the colour was successfully replicated in both samples of **Method 19**, it was decided to try an even larger scale up to simulate an industrial process.

Large Nylon and Nylon-Lyrcra® samples were cut and placed in a glass reactor tube (see **Figure 2.3**) with gold solution and ~3.5L distilled water. They were left with the water circulating for 3 days at 15°C. After the 3 days the fabric was taken out of solution, squeezed and cut in half. Half was returned to the reactor tube and left to develop for 7 days at 50°C. The other half was placed in a 500mL conical flask with 300mL distilled water. This was placed in a water bath for 9 days at 50°C. Fabric samples were removed from solution, then put into a small beaker with distilled water and placed in a Sonicator for 3 minutes before they were patted dry with paper towels.

Figure 2.3 Large scale set up

Table 2.20 Method 20-Glass reactor tube scale up.

Sample ID	Fabric	Weight (g)	Gold Solution (4%)
AW213A	Nylon	16.2216	400µL
AW218A	Nylon-Lycra	23.1195	580µL

2.2.3 Preparation of gold nanoparticles using a reductant after gold uptake

Experiments were carried out to see if the addition of a reductant after the gold solution is absorbed on to a fabric surface changes the colour of the resulting fabric.

Method 21: Effect of reductant after initial gold uptake onto the fabric surface.

Samples of acid and base treated fabric (Polyester, Nylon, Polyester-Lycra® and Nylon-Lycra®) were cut to approximately 0.4g and placed in glass sample vials containing 40µL gold solution and 9.96mL Millipore water. Samples were heated in a water bath at 50°C for time specified in **Table 2.21** below (30 minutes-2 hours). After this time the fabric was removed, squeezed and placed in a new sample vial containing 10mL trisodium citrate (1%) before returning samples to the water bath at either 50°C overnight or 80°C for 5-10 minutes. After the development time the fabric samples were removed from solution, rinsed with distilled water and patted dry with paper towels.

Table 2.21 Method 21-Effect of reductant after initial gold uptake.

Sample ID	Fabric	Weight (g)	Treatment	Time in water bath at 50°C	1% trisodium citrate
AW481A	Polyester	0.3893	0.1M HCl	30 minutes	50°C overnight
AW482A	Nylon	0.3945	0.1M HCl	30 minutes	50°C overnight
AW482B	Polyester-Lycra	0.4145	0.1M HCl	30 minutes	50°C overnight
AW482C	Nylon-Lycra	0.4134	0.1M HCl	30 minutes	50°C overnight
AW483A	Polyester	0.4014	0.1M NaOH	2 hours	80°C for 10 minutes
AW483B	Nylon	0.3928	0.1M NaOH	2 hours	80°C for 10 minutes
AW483C	Polyester-Lycra	0.4105	0.1M NaOH	2 hours	80°C for 10 minutes
AW483D	Nylon-Lycra	0.4056	0.1M NaOH	2 hours	80°C for 10 minutes
AW483E	Polyester	0.4113	0.1M NaOH	2 hours	80°C for 5 minutes
AW483F	Nylon	0.3873	0.1M NaOH	2 hours	80°C for 5 minutes
AW484A	Nylon-Lycra	0.4174	0.1M NaOH	2 hours	80°C for 5 minutes
AW484B	Polyester	0.4136	0.1M HCl	2 hours	80°C for 10 minutes
AW484C	Polyester-Lycra	0.4070	0.1M HCl	2 hours	80°C for 10 minutes
AW484D	Nylon-Lycra	0.4160	0.1M HCl	2 hours	80°C for 10 minutes

Table 2.21 cont Method 21-Effect of reductant after initial gold uptake.

Sample ID	Fabric	Weight (g)	Treatment	Time in water bath at 50°C	1% trisodium citrate
AW484E	Polyester	0.4144	0.1M HCl	2 hours	80°C for 5 minutes
AW484F	Nylon-Lycra	0.4140	0.1M HCl	2 hours	80°C for 5 minutes

2.2.4 Preparation of gold nanoparticles by growth of seed particles.

The previous method (**Method 21**) did not produce a noticeable change in fabric colour so it was decided to try and grow particles on the fabric surface from small seed particles. Particle size and shape influences the colour of the gold nanoparticles so small additions of gold solution were made to grow the particles to the desired size. **Methods 22-25** have samples with a minimum of 2 separate gold additions and a maximum of 9 additions.

Fabric samples were placed in glass sample vials with Millipore water and a small volume of gold solution. They were then heated in a water bath to develop colour before further additions of gold solution were added and returned to the water bath.

At the end of the development time all fabric samples were removed from solution, then put into a small beaker with distilled water and placed in a Sonicator for 3 minutes before they were removed and patted dry with paper towels.

Method 22: Effect of 2 or 3 small additions of gold solution over time.

Samples of Nylon were cut to ~0.4g and placed in glass sample vials containing Millipore water and the first volume of gold solution (4%). The vials were placed in a water bath at 50°C for the specified time before additional gold solution was added and stirred in.

Table 2.22 Method 22-Effect of 2 or 3 small additions of gold solution.

Sample ID	Weight (g)	Millipore water	Gold solution (4%)	Respective time of addition
AW215A	0.3993	19.98mL	20µL + 40µL	2 hours + 2 days
AW215B	0.4099	19.96mL	40µL + 20µL	2 hours + 2 days
AW215C	0.4003	10mL	20µL + 20µL + 20µL	2 hours + 2 hours + 4 days

Table 2.22 cont Method 22-Effect of 2 or 3 small additions of gold solution.

Sample ID	Weight (g)	Millipore water	Gold solution (4%)	Respective time of addition
AW215D	0.3916	10mL	10 μ L + 10 μ L + 10 μ L	2 hours + 2 hours + 4 days
AW215E	0.3979	10mL	20 μ L + 10 μ L + 10 μ L	2 hours + 2 hours + 4 days
AW216A	0.3936	10mL	10 μ L + 20 μ L + 20 μ L	2 hours + 2 hours + 4 days
AW216B	0.4066	10mL	10 μ L + 20 μ L + 10 μ L	2 hours + 2 hours + 4 days
AW216C	0.3959	10mL	20 μ L + 10 μ L + 20 μ L	2 hours + 2 hours + 4 days

Method 23: Effect of 2-7 small additions of gold solution over time.

Nylon samples were cut to ~0.4g and placed in glass sample vials containing 10mL Millipore water and the first volume of gold solution (4%). The vials were placed in a water bath at 80°C for the time specified in **Table 2.23** below before additional gold solution was added and stirred in. Samples were left in the water bath at 80°C for 1-7 days.

Table 2.23 Method 23-Effect of 2-7 small additions of gold solution.

Sample ID	Fabric	Weight (g)	Gold solution (4%)	Respective time of addition
AW219A	Nylon	0.3919	20 μ L + 20 μ L	Overnight + 5 days
AW219B	Nylon	0.3940	10 μ L + 10 μ L	Overnight + 5 days
AW219C	Nylon	0.4190	20 μ L + 20 μ L + 20 μ L + 20 μ L	1 hour + 1 hour + 1 hour + overnight
AW220A	Nylon	0.4018	10 μ L + 10 μ L + 10 μ L + 10 μ L + 10 μ L + 10 μ L + 10 μ L	1 hour + 2 hours + 1 hour + 1 hour + 1 hour + 1.5 hours + 7 days
AW220B	Nylon	0.3971	20 μ L + 20 μ L + 20 μ L + 20 μ L + 20 μ L + 20 μ L + 20 μ L	1 hour + 2 hours + 1 hour + 1 hour + 1 hour + 1.5 hours + 7 days

Method 24: Effect of adding small additions of gold solution over time in new sample vials.

Nylon and Nylon-Lycra® samples were cut to ~0.4g and placed in glass sample vials containing 10mL Millipore water and the first volume of gold solution (4%). The vials were placed in a water bath at 80°C for the time specified in **Table 2.24** before fabric samples were removed, squeezed and placed in new sample vials containing the additional gold solution (method repeated an additional 3-7 times). Samples were left in the water bath at 80°C for 4 days.

Table 2.24 Method 24-Effect of adding small additions of gold solution over time in new sample vials.

Sample ID	Fabric	Weight (g)	Gold solution (4%)	Respective time of addition
AW227A	Nylon	0.4079	20 μ L + 20 μ L + 20 μ L + 20 μ L + 20 μ L + 20 μ L + 20 μ L + 20 μ L + 20 μ L	1 hour + 1 hour + 1 hour + 1 hour + 1 hour + 1 hour + 1 hour + 1 hour + 4 days
AW227B	Nylon-Lycra	0.4170	20 μ L + 20 μ L + 20 μ L + 20 μ L + 20 μ L + 20 μ L + 20 μ L + 20 μ L + 20 μ L	1 hour + 1 hour + 1 hour + 1 hour + 1 hour + 1 hour + 1 hour + 1 hour + 4 days
AW227C	Nylon	0.4179	40 μ L + 40 μ L + 40 μ L + 40 μ L + 40 μ L	2 hours + 2 hours + 2 hours + 2 hours + 4 days
AW227D	Nylon-Lycra	0.4172	40 μ L + 40 μ L + 40 μ L + 40 μ L + 40 μ L	2 hours + 2 hours + 2 hours + 2 hours + 4 days

Method 25: Large sample scale up of 9 small additions of gold solution to observe if the colour is the same as the small samples with fewer additions.

A large nylon sample was placed in a 600mL conical flask with 40 μ L gold solution and 400mL distilled water. It was heated for an hour in a water bath at 80°C (Parafilm was placed over the top to minimise vapour loss). Further additions of gold solution were added every hour and the solution stirred. This procedure was repeated another 7 times (9 total, 360 μ L gold solution) before the flask was left in the water bath for 4 days at 80°C.

Table 2.25 Method 25-Large sample scale up of 9 small additions of gold solution.

Sample ID	Weight (g)	Gold solution (4%)	Respective time of addition
AW227E	1.6867	40 μ L + 40 μ L + 40 μ L + 40 μ L + 40 μ L + 40 μ L + 40 μ L + 40 μ L + 40 μ L	1 hour + 1 hour + 1 hour + 1 hour + 1 hour + 1 hour + 1 hour + 1 hour + 4 days

2.3 Characterisation

Fabric samples and gold colloids were characterised by a variety of methods to determine their chemical and optical properties.

2.3.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was carried out on a JEOL 6500 F field emission scanning electron microscope. This technique was used to look at the distribution of gold nanoparticles on fibre surface and to assess the size and shape of gold nanoparticles present. Surface morphology of the gold-fabric hybrid materials is important in determining the overall colour of the fabric. Images were taken at various positions on the fabric surface in order to assess the uniformity of the sample. Samples were prepared by separating individual fibres from the bulk dyed fabric under an optical microscope. The individual fibres were pressed into carbon tape on an aluminium stub. Cross sections were prepared in a similar manner but the fibres were wrapped in carbon tape and placed in liquid nitrogen before slicing at right angles to the fibres with a sharp razor blade to expose the fresh fibre cross section. These were placed on aluminium L-stubs.

Energy dispersive spectroscopy (EDS) was used to determine the distribution of different elements on the fabric surface. In particular it was used to confirm elements present in a fabric sample and to map the distribution of elements on the fabric surface. Gold, Nitrogen, Oxygen, Chlorine and Carbon were the main elements mapped to observe correlations between the gold nanoparticles and the fabric surface.

2.3.2 Infra Red Spectroscopy

Infra red (IR) spectroscopy was carried out using a PerkinElmer Spectrum One FT-IR Spectrometer. By measuring the vibrations and other bond movements in the original fabrics and the gold-fabric composites any changes in structural form can be identified.

Water has a strong absorption $3200 - 3600\text{ cm}^{-1}$ so may mask other signals present. Oxidation can also cause overlapping signals. Therefore the colloidal gold suspensions can not be analysed¹⁶.

Samples were prepared by pulling individual fibres from the fabric samples and cutting them as small as possible. These were added to KBr powder and pressed into disks. Gold nanoparticles bonded to the nitrogen or oxygen's present in the fabric should show a shift in peak position or decrease in peak intensity should be seen e.g. N-H peak at $\sim 3400\text{ cm}^{-1}$.

2.3.3 Ultra Violet Visible Spectroscopy

Reflectance Ultra violet visible spectroscopy (UV/vis), incorporating Kubelka-Munk transformations was carried out on a Varian Cary 100 scan spectrometer.

The gold-fabric composites were placed directly into the instrument and reflected light was measured as a percent reflectance (compared to a white standard of 100% reflectance) and also converted to absorption²³.

Colloidal gold suspensions were measured under absorbance mode to see if there is any correlation between the dyed fabric and the original colloid.

2.3.4 Colour Measurements

Ultra violet visible spectroscopy gives a spectrum that shows the wavelengths of light absorbed but is too complicated to give an indication of the visual colour of the object being analysed. The ColourQuest instrument works on the same principles as reflectance spectroscopy but simplifies the result to three coordinates that can be mapped to give the overall colour. The three coordinates are given the symbols L^* , a^* and b^* .

L^* is the measure of lightness with $L^*=0$ black and $L^*=100$ white. Positive a^* is red and negative a^* is green. Lastly positive b^* is yellow and negative b^* is blue (see

Figure 2.4). The tappi brightness at 457 nm and the iso-brightness at 577 nm can also be measured. These brightness factors are international measurements important when dealing with paper (Tappi) and pigment (Iso) samples ²². Brightness measurements as useful as a quantitative measurement of colour and the quality of the colouring process e.g. the difference between dull or bright red.

For each sample a set of values are given for each of the coordinates meaning that even the slightest change in colour or shade can be detected. This is important if colours are being matched, for example producing multiple batches of fabric for industry. These values are referred to as ColourQuest measurements in the results section.

Fabric samples are easily measured but solutions are difficult. An indication of colour change can be given by placing a cuvette filled with sample behind a piece of black cardboard with a slit cut in it. In this case the instrument will measure the difference between the solution and the cardboard.

2.3.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a non-destructive surface sensitive technique that provides information about the electronic state and composition of the surface region of a sample. It is a useful analysis tool for understanding the interactions between the fabric surface and the gold nanoparticles. If the particles are bonded to the surface then the spectra will change. XPS spectra are obtained by irradiating a clean sample (handled as little as possible to prevent surface contamination), under vacuum, with a beam of aluminium or magnesium x-rays whilst simultaneously measuring the kinetic energy and number of core electrons that are resultantly emitted from the top 10 nm of sample. Each atomic orbital (for every element) has a characteristic binding energy associated with it so shifts in binding energy peaks in an XPS spectra provide information about the chemical environment of the sample surface. XPS analysis was undertaken at the Surface Science department, University of Auckland.

2.3.6 Fluorescence Spectroscopy

Fluorescence spectroscopy measures the quantity/intensity of light emitted by a sample after it has been hit with various photons of light (usually 300-750 nm). Molecules in the sample absorb light at wavelengths characteristic to the individual particle or molecule. When a photon of light is absorbed an electron in the molecule can be promoted up to a higher level (if enough energy is present). As the electron drops down the energy is released as another photon. Generally the incident (absorbed-excitation) and emission (released) photons have different wavelengths so are able to be measured. The spectrofluorimeter can measure excitation and emission spectra as they are mirror images of each other. Measuring over different wavelength ranges can help identify molecules present. If a peak shifts when a different range is used then the peak is most likely due to Raman vibrations and not individual particles or molecules.

The basic instrument layout is below:

The monochromators choose the wavelengths of light that can pass through. Slits can also be set so the sample and detector are not flooded with light.

Fluorescence spectroscopy can be used to identify molecules present in a sample and changes in fabric structure. It is a non destructive technique and has the advantage of being able to analyse both solid and liquid samples⁴⁹. This means both the fabric (structural changes) and colloidal gold suspensions were able to be analysed during the dyeing process.

Fabric samples were run with excitation wavelength of 300nm over an emission range of 300-750nm (scan speed 250nm/minute). Filter slits were set at 5nm with a filter after the sample of 435nm to eliminate second order scattering peaks.

2.3.7 Atomic Absorption

Atomic absorption (AA) is a useful technique used for analysing the concentration of metal element left in a solution. The liquid sample is sucked into the instrument and atomised. A specified wavelength of light is passed through the flame to excite the electrons in the desired element. Using the Beer-Lambert law, the number of transitions can be calculated from the amount of light that reaches the detector on the other side of the flame. This signal is proportional to the concentration of the metal element being measured.

In this research atomic absorption has been used to analyse the amount of gold remaining after the fabric samples have been removed to give an indication of how much gold was transferred to each fabric sample.

Gold can be measured over two concentration ranges relating to separate wavelengths. At 242.8nm a range of 3.5-14ppm can be analysed and at 267.6nm the range is 7.0-30ppm. As long as the solutions are dilute enough samples can be measured at one or both of these ranges.

Due to the overlapping working ranges 8 standards (3, 5, 7, 10, 12, 14, 20, 25 and 30ppm) were made up by diluting Gold Atomic Absorption Standard Solution from Aldrich with 5% by mass HCl.

Liquid samples to be measured were filtered through a glass crucible (rinsed with a few drops of aqua regia and distilled water between each sample to dissolve any trapped gold) to remove any fibres that would block the instrument. Each sample was measured at the lower working range first (3.5-14ppm), if the concentration value came up as an error (i.e. too high a concentration) then the sample was measured again at the higher working range (7.0-30ppm). If the concentration was still too high then the sample was quantitatively diluted until a reading was obtained.

2.3.8 Testing of colourfastness and durability of fabrics

A Nylon-gold composite sample (AW212B) was produced and sent to Ag Research Ltd, Textiles Division, Lincoln Research Centre, Christchurch for industry standard "abrasion" and colourfastness tests.

The sample was subjected to The Woolmark Company™ 165 August 2002 colourfastness to rubbing (textile materials and dyed sheepskins) tests. The test assessed staining onto a white cloth when the fabric is rubbed, wet and dry under standard conditions. The stained cloths are then assessed both wet and dry and graded against a set of Standard Grey Scales. Grading is on a scale of 1 to 5 with 1 being excessive staining and 5 being no staining at all.

These results are used to determine whether or not these materials are suitable as consumer products.

3 Results and Discussion

3.1 Original fabrics

The original undyed fabrics (Polyester, Nylon, Polyester-Lycra®, Nylon-Lycra®) were characterised by SEM, IR spectroscopy, UV/vis reflectance spectroscopy, XPS, Fluorescence spectroscopy and ColourQuest measurements to allow comparisons with the gold nanoparticle – fabric composites.

Visually the starting fabrics appear bright white suggesting that they may have been treated with bleach or whiteners before they were obtained for this project. The original, undyed fabrics can be seen in **Figure 3.1** below.

ColourQuest measurements were performed to provide a numerical result for comparison with the optical colour of the dyed fabrics. The results can be seen in **Figure 3.2**.

These measurements are supported by the results obtained from the UV/vis reflectance (see **Figure 3.3** and **Figure 3.4**). All undyed fabrics have an L^* value around 95 (on a scale of 0 being black and 100 being white) and a^* and b^* values close to 0 showing that the fabrics are fairly close to pure white. Iso Brightness (577nm) and Tappi Brightness (457nm) are both over 80.

UV/vis reflectance spectra were obtained and can be seen in **Figure 3.3** and Figure **3.4**. They show that for all original fabric samples, over the range of 425-900nm a fairly constant reflectance ~95% is achieved giving the fabric a white appearance. Below 425nm (down to 190nm) there are small absorption peaks (i.e. less reflectance) with percentage reflectance as low as 70% but as this is below the visible region it will not affect the colour of the fabric.

SEM images of the original undyed Nylon were taken at 70, 200 and 2,500 times magnification and can be seen in **Figure 3.5** below. Under the microscope the fabric appears like bunches of noodles – the fibres are very smooth and wrapped around each other. The packed synthetic fibres do not provide a high surface area or porosity suggesting that once the gold solution is introduced the gold will only sit on the surface of the fibres allowing smaller amounts of gold to be used.

IR spectra (**Figures 3.6-3.9**) were obtained for the four original undyed fabrics. The Polyester IR spectrum (**Figure 3.6**) shows the peaks expected including terminal OH groups at $\sim 3400\text{ cm}^{-1}$, C-H stretch at $3000\text{-}2900\text{ cm}^{-1}$, C=O $\sim 1700\text{ cm}^{-1}$, C-H bend $\sim 1400\text{ cm}^{-1}$ and C-O $\sim 1250\text{ cm}^{-1}$.⁵⁰

In the case of Nylon (**Figure 3.7**) there are no OH groups, instead the peak $\sim 3400\text{ cm}^{-1}$ is due to the stretching of N-H groups present in the fabric. The N-H bend peak is also observed $\sim 1630\text{ cm}^{-1}$. The C=O peak is hidden by this peak (N-H bend) and appears as a slight shoulder. Again the C-H stretch ($3000\text{-}2900\text{ cm}^{-1}$) C-H bend ($\sim 1400\text{ cm}^{-1}$) and C-O ($\sim 1250\text{ cm}^{-1}$) are also observed.⁵⁰

As Polyester-Lycra® is a blend of fibres, the IR spectrum (**Figure 3.8**) shows peaks corresponding to the functional groups of both individual fibre types. The OH (terminal polyester) and C=O peaks ($\sim 3400\text{ cm}^{-1}$ and $\sim 1700\text{ cm}^{-1}$) are visible but show a decrease in intensity. The amine groups are observed as shoulders on these peaks with the N-H stretch and bend at $\sim 3300\text{ cm}^{-1}$ and $\sim 1630\text{ cm}^{-1}$ respectively. The C-H stretch at $3000\text{--}2900\text{ cm}^{-1}$, C-H bend at $\sim 1400\text{ cm}^{-1}$ and C-O at $\sim 1250\text{ cm}^{-1}$ are also observed.⁵⁰

The Nylon-Lycra® spectrum (**Figure 3.9**) is similar to that of Nylon (**Figure 3.7**) but the main peak most likely contains an O-H peak at $\sim 3400\text{ cm}^{-1}$ as well as the expected N-H (stretch) peak at $\sim 3300\text{ cm}^{-1}$ due to terminal OH groups in the Lycra®. Other groups of importance are C-H stretch at $3000\text{--}2900\text{ cm}^{-1}$, C=O (observed as a shoulder) $\sim 1700\text{ cm}^{-1}$, N-H bend $\sim 1630\text{ cm}^{-1}$, C-H bend $\sim 1400\text{ cm}^{-1}$ and C-O $\sim 1250\text{ cm}^{-1}$.⁵⁰

Once the gold is added to these fabrics a decrease in the N-H or C=O peaks should be seen, depending on the gold binding site.

XPS was performed at Auckland University. When the untreated fabrics are compared to those from the literature⁵¹, a few differences are observed. Polyester has three peaks in the carbon 1s spectrum (**Figure 3.10**) as expected but the third peak is shifted slightly upfield – this may be due to contaminants/impurities in the sample. In the oxygen 1s spectrum (**Figure 3.11**) there are two peaks as expected but they appear as one broad peak instead of two individual peaks (see Appendix A for reference spectra).

The untreated Nylon spectra were closer to the reference spectra for Nylon 6-6, only the oxygen 1s (**Figure 3.13**) was different showing two peaks (under the broad peak) when only one was expected. Carbon 1s spectrum (**Figure 3.12**) shows that four peaks can be fitted (as given by the reference spectrum – Appendix A) but the peak intensities are different causing a shift in the second highest peak from 288 eV to 286.2 eV, a new shoulder on this peak is also observed. Again this is most likely due to contaminants/impurities. As gold nanoparticles are added to the fabric it is

expected that it will mainly be the nitrogen 1s peak (**Figure 3.14**) that will change due to the change in nitrogen environment caused by the bonding of gold nanoparticles to the fibre surface.

Figure 3.12 Carbon 1s XPS spectrum of original, undyed Nylon

Figure 3.13 Oxygen 1s XPS spectrum of original, undyed Nylon

Untreated Polyester-Lycra®, acid treated Nylon, acid treated Polyester-Lycra®, base treated Nylon and base treated Polyester-Lycra® spectra and analysis can be found in Appendix A.

Fluorescence spectroscopy showed large asymmetric emission peaks starting at approximately 420nm and trailing off close to 750nm (see **Figure 3.15**). Gold is known to have its own fluorescence so a new peak in the spectrum may be observed in the fabric-gold composites.

Figure 3.15 Fluorescence spectra of original, undyed fabrics.
(From top) Polyester, Nylon, Nylon-Lycra®, Polyester-Lycra®

3.2 Results and characterisation of pre made colloids transferred to fabric surface

3.2.1 Effect of PEI as a reductant

Method 1: Wine red coloured gold nanoparticle colloids were produced and successfully transferred to untreated samples of Polyester, Nylon, Polyester-Lycra® and Nylon-Lycra®. Unfortunately the colour changes upon transfer. The dyed fabric samples are patchy purple, some with dark spots (see **Table 3.1** and **Figure 3.16**).

Table 3.1 Fabric type and resulting colour for Method 1 samples.

Sample ID	Fabric	Colour after development
AW901A	Nylon	Patchy pink & purple
AW901B	Nylon-Lycra	White with pink spots
AW901C	Polyester	Pink with some darker patches
AW901D	Polyester-Lycra	White with dark pink spots
AW901E	Nylon	Dark patchy purple
AW901F	Nylon-Lycra	Dark patchy purple (almost black)
AW901G	Polyester	Dark & light purple bands
AW901H	Polyester-Lycra	Dark red/purple with pink patches
AW904A	Nylon	Patchy pink & purple with black spots
AW904B	Nylon-Lycra	Pale pink with dark spots
AW904C	Polyester	Patchy pink & purple
AW904D	Polyester-Lycra	Patchy pink, white & purple with black spots

Method 2: The same wine red gold nanoparticle colloid as Method 1 was produced. As the last method had samples placed in glass sample tubes that resulted in patchy fabrics, this method studied the effect of temperature on samples that were held flat by plastic slides. The samples show two separate colour areas – the inside of the fabrics that were directly exposed to the gold nanoparticle colloids are pale pink with dark spots or bands and the outer areas which were inside the plastic slides show dirty purple/pink colours. This shows that there is a difference in diffusion rates into the fabric that is clamped inside the slide (see **Table 3.2** and **Figure 3.17**).

In the Polyester-Lycra sample (AW916D), it appears that the lines are due to the way the fabric is woven and not from the dyeing process.

Table 3.2 Fabric type and resulting colour for Method 2 samples.

Sample ID	Fabric	Colour after development
AW915E x6		Wine red (Colloid)
	Nylon (AW916A)	Pale pink/peach with some dark purple spots
	Nylon (AW916B)	Pale pink/purple with lots of dark purple spots
	Nylon-Lycra (AW916C)	Uneven pale pink/purple, few dark spots
	Polyester-Lycra (AW916D)	Pale pink/purple with dark pink bands

ColourQuest analysis was performed on all samples from Method 1 and Method 2 (see **Figure 3.18** and **Figure 3.19**). The measurements show that the darker the samples the lower the L^* value (which was expected).

AW901B and D are visibly lighter and this is reflected in the high L^* values (>80). The fabric samples are pink/purple in colour shown by the positive a^* values ($+a^*$ =red) and negative b^* values ($-b^*$ =blue). There is little difference in the a^* and b^* values suggesting that it is the L^* value that influences the shade of the fabric the most. It is the difference between a light pink/purple sample and one that looks almost black.

Iso brightness and Tappi brightness follows the same pattern as the L^* values – the samples that appear black have values lower than 20.

In Method 2 the measurements show that three out of the four samples (AW916B-D) have approximately the same a^* and b^* values which is a confirmation of the visual observation. The L^* value gradually increases over the three sample which explains the visual greying of the fabric. The fourth sample (AW916A) is pink/peach in the

centre due to +a* (red) and +b* (yellow) values. Interestingly it is the b* value that changes the colour of the fabric the most as the a* value is almost identical to the other three samples.

Further analysis was performed on samples AW901E from Method 1 and AW916A-D from Method 2.

UV/vis reflectance spectroscopy spectra of the samples show a significant decrease in reflectance percentage from the original fabrics. In the case of AW901E (**Figure 3.20**), when it is compared to the original Nylon fabric a decrease of almost 50% is observed.

Also for this sample the reflectance percentage is reasonably constant at just under 40% with a small absorption peak between 190-230nm. This backs up the ColourQuest measurements as if the sample was for example, red or green then large absorption peaks would be expected around 700nm (red) or 550nm (green). Black however gives a constant line as it absorbs all wavelengths evenly.

For Method 2 the UV/vis reflectance spectra (**Figure 3.21**) are very different from the sample in Method 1 (AW901E). Instead of a constant reflectance ~35% there is a series of absorption peaks and reflection peaks. The absorption peak occurring at ~525nm corresponds to the absorption of cyan/green in the visible spectrum. This absorption combined with the reflectance of red light above 625nm (~80%R) gives the pink colour observed in the fabric. Sample AW916A has a shallower absorption peak in this region that appears more as two small absorption peaks merged together – this may account for the slight difference in the sample colour (pink/peach instead of pink/purple).

Below 400nm each sample shows a slight variation in peak shape but as this is not in the visible region of the spectrum, the effect is not seen in the fabric colours.

Figure 3.21 UV/vis reflectance spectra of samples from Method 2

SEM was performed under both SEI and backscatter conditions at varied magnifications on Samples AW901E and AW916A.

AW901E (see **Figure 3.22**) – At a magnification of 10,000 times it can be seen that there is an uneven distribution of various size particles. When observed under backscatter conditions these particles show up white indicating that they are a heavy element such as gold. At this magnification it is hard to tell if the larger particles are bigger nanoparticles or smaller ones bunched together. Upon further magnification (20,000 times) it can be seen that the particles are indeed smaller but bunched suggesting that the nanoparticles may be bonding over multiple binding sites. At 60,000 times magnification the particles are clearly bunched and arranged randomly. The nanoparticles however appear to have a relatively constant size ~30nm and shape – spherical. When bunched the group particles measure up to 200nm.

EDS performed on the sample at 60,000 times magnification proves that the particles are gold. The map shows a direct correlation between gold and the particles on the elemental map (bright red spots). Other elements such as oxygen, nitrogen and chlorine (from the starting solution $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in HCl) were mapped to try and determine binding sites but they show an even, constant distribution.

AW916A (see **Figure 3.24**) – A cross section was observed at 4,000 times magnification which showed the cylindrical shape of the synthetic Nylon fibres. A few gold nanoparticles are observed on the surface of the cross section but this is most likely from particles being dragged across the surface during the preparation process (cutting) rather than the particles being bonded to the surface.

The side-on images show patches of gold nanoparticles similar to those observed in AW901E. However, some of these particles appear to be larger in diameter instead of being small particles close together. Distribution is still irregular and the size of particles present range from approximately 30nm to 100nm.

EDS was performed on the backscatter images of AW916A at 3,500 and 70,000 times magnification. Like Method 1 it confirms that the bright white areas observed under backscatter conditions are gold. Nitrogen is present only where the fibres are, but chlorine (at very low concentrations) is spread evenly over the entire map.

Fluorescence spectroscopy was performed on samples AW901E, AW916A, AW916B, AW916C and AW916D.

AW901E (**Figure 3.26**) shows an almost identical plot to that of untreated Nylon (see **Figure 3.15**). The peak is similar with the only difference being the decrease in intensity – untreated Nylon ~7 compared to just under 4 in AW901E. This suggests that the fluorescence of the fabric may be due to added brighteners.

When compared to the Nylon spectrum, AW916A (**Figure 3.27**) has a very different shape – a large broad asymmetric hump vs. the original sharp jagged peak. It appears to have two peaks (that have merged) and intensity over two times the original peak indicating that the gold is fluorescing therefore producing a second peak in the spectrum.

The remaining samples (**Figure 3.27**) are similar to the original fabrics, only showing changes in intensity. AW916B has a similar shape to Nylon but slightly lower intensity, AW916C has a similar shape to Nylon-Lycra® but almost three times the intensity and AW916D has the same shape as Polyester-Lycra® but over twice the intensity. The increase in intensity is unexpected and suggests that attaching the gold nanoparticles to the fabric surface in the case of Lycra® blends enhances the fluorescence that was already present in the original fabrics.

3.2.2 Effect of trisodium citrate as a reductant

Method 3: In this method the effect of changing the type of reductant was observed. A murky yellow colloid was produced and transferred to the fabric surfaces. The Polyester samples show no change in colour with the Lycra® blend only marginally better with off white/yellow/grey colours.

Nylon and Nylon-Lycra® samples dyed with this colloid came out patchy yellow and light purple which is not significantly different from the previous methods.

Table 3.3 Fabric type and resulting colour for Method 3 samples.

Sample ID	Fabric	Colour after development
AW903A	Nylon	Patchy yellow & light purple
AW903B	Nylon-Lycra	Patchy yellow, pink & light purple
AW903C	Polyester	White
AW903D	Polyester-Lycra	Very pale yellow
AW904E	Nylon	Patchy yellow & light purple
AW904F	Nylon-Lycra	Patchy yellow & light purple
AW904G	Polyester	White
AW904H	Polyester-Lycra	Slightly off white/yellow-grey

Method 4: A range of gold nanoparticle colloids were produced by varying the amount of gold solution and trisodium citrate added. Their colours ranged from orange to purple but surprisingly there is not a lot of difference in the final dyed fabrics. More evenly dyed fabrics were produced though. As Nylon was showing the greatest affinity for the gold nanoparticles in the previous methods it was the only fabric used in this method. This provides a better platform for comparison of samples.

Table 3.4 Colloid colour and resulting colour on Nylon fabric for Method 4 samples.

Sample ID	Colloid Colour	Fabric	Colour after development
AW905A	Murky orange	Nylon (AW909A)	Patchy pink, purple & grey
AW905B	Murky orange/purple	Nylon (AW909B)	Fairly even pastel pink
AW905C	Murky red	Nylon (AW909C)	Dark pink/rose
AW906A	Dark red/purple	Nylon (AW909D)	Patchy dark purple, darker around the edge
AW906B	Dark red/purple	Nylon (AW909E)	Patchy dark purple
AW906C	Dark red/purple	Nylon (AW909F)	Dark purple/blue
AW906D	Clear red	Nylon (AW910A)	Faint purple with pink edging, few dark purple spots
AW906E	Dark purple/red	Nylon (AW910B)	Faint grey
AW907A	Deep purple	Nylon (AW910C)	Very faint pink
AW907B	Deep purple/red	Nylon (AW910D)	Patchy pastel purple with some lighter spots
AW907C	Deep purple/red	Nylon (AW910E)	Light purple
AW907D	Deep purple/red	Nylon (AW910F)	Patchy purple with dark purple edges

Figure 3.29 Photographs of samples dyed with trisodium citrate reduced gold nanoparticle colloids (Method 4)

Method 5: A variety of different coloured gold nanoparticle colloids were produced as can be seen in Table 3.5 below. Once transferred to the Nylon fabrics they were either light brown/gold or dark purple coloured.

Table 3.5 Colloid colour and resulting colour on Nylon fabric for Method 5 samples.

Sample ID	Colloid Colour	Fabric	Colour before development	Colour after development
AW907E	Murky orange			
AW907F	Deep red	Nylon (AW911A)	Dark purple/grey edges, pink/purple middle	
AW908A	Dark red/purple	Nylon (AW911B)	Dark purple with odd light patch	
AW913A	Yellow with metallic particles	Nylon (AW922C)	Pale lemon yellow, slightly darker around edge	Light brown, gold/brown edges

Table 3.5 cont Colloid colour and resulting colour on Nylon fabric for Method 5 samples.

Sample ID	Colloid Colour	Fabric	Colour before development	Colour after development
AW913B	Medium yellow with metallic particles	Nylon (AW922D)	Pale lemon yellow, slightly darker around edge	Light brown, gold/brown edges
AW913C	Medium yellow with metallic particles	Nylon (AW922E)	Pale lemon yellow, dark strip around edge	Light brown, gold/brown edges
AW913D	Dark yellow with large metallic particles	Nylon (AW922F)	One edge yellow strip, rest beige	Light brown, gold/brown edges
AW913E	Dark yellow with large metallic particles	Nylon (AW922G)	Pale beige/tan	
AW913F	Murky pink/purple	Nylon (AW923A)	Dark purple with one light spot	Black with a red spot

ColourQuest measurements were performed on all samples from Methods 3-5 (**Figures 3.31-3.33**). They appear to show a trend based on fabric type.

In Method 3 Polyester (AW903C and AW904G) has almost identical values to the original fabric with L^* values over 90, a^* and b^* values close to zero backing up the visual observations.

Polyester-Lycra® samples (AW903D and AW904H) show a slight variation – +a* (red) and +b* (yellow) values just above zero combined with high L* values (>80%R) gives the off-white appearance of the fabric.

AW903A (Nylon) and AW903B (Nylon-Lycra®) show similar values except on the brightness scales (L*, Iso brightness and Tappi brightness) indicating that they are just two different shades of the same colour. AW904E (Nylon) and AW904F (Nylon-Lycra®) are close to the colour of AW903A and AW903B, however all points are lower resulting in a darker/dirtier colour.

At first glance there appears to be no correlation between samples from Method 4 but there are a few cases where two or more samples can be grouped. The most obvious of these is AW910B and C which are almost identical to the original Nylon sample. AW910D-F are all approximately the same colour but differ in shade due to their L* values. Likewise AW909D-F are all dark purple in colour and only have differences in their shades. The remaining three samples (AW909A-C) are pinks. They have the most positive a* (red) values from this method and the type of pink (i.e. rose, pale pink etc) comes from this increased value combined with the neutral/slightly -b* (blue) and various L* values.

There are two groups of samples from Method 5 – light brown/gold coloured fabric (AW922C-F and to some extent AW922G) and dark purple coloured fabric (AW911A-B and AW923A). The dark purple fabrics have similar ColourQuest measurements to the results obtained for AW909D-F in Method 4. This can be confirmed by visual observation as well. All values for AW922C-F are positive resulting in a light brown colour (mixture of yellow and red) but as the samples are tremendously uneven the readings may not reflect the true colour. ColourQuest takes a reading over the whole sample so the light and dark areas will appear as average calculations e.g. ~60-70%. Therefore it is hard to compare the values of these samples to that of other methods.

Further analysis was performed on samples AW909B-C and AW910E from Method 4 and AW911B, AW922C and AW923A from Method 5.

UV/vis reflectance spectra for AW909B-C and AW910E are similar to those from Method 2. Again a small absorption peak is observed ~525nm corresponding to the absorption of cyan/green. In AW910E there is a large percentage reflectance in the blue/indigo range of the spectrum (400-500nm) which backs up the ColourQuest measurements of -b* (blue). AW909B has a large reflectance percentage in the red range (>600nm) which gives rise to the pink colour observed in the fabric. AW909C does not quite have the expected spectrum – as it is visibly pink a stronger reflectance would be expected in the red region. It is a reasonably dirty colour though so the spectrum may be a result of the mix of colours.

From Method 5 AW911B and AW923A have similar spectra but surprisingly they look very different to AW910E even though they are all shades of purple. Both have almost a flat reflectance under 40% in the 250-900nm range similar to that of AW901E from Method 1. This backs up the visual observation of very dark purple as the samples absorb across all wavelengths of the visible spectrum.

AW922C has a similar spectrum to that of AW909B but the absorption peak is not as pronounced at ~590nm meaning that more yellow light is reflected, therefore giving it a tan versus pink appearance.

Figure 3.34 UV/vis reflectance spectra of samples from Method 4 and Method 5

SEM was performed under both SEI and backscatter conditions at varied magnifications on Samples AW909C and AW910E.

AW909C (see **Figure 3.35**) – Just like samples from previous methods it can be seen that there is an uneven distribution of assorted particle sizes. At 4,000 times magnification there are particles scattered all over the fibre surface. There is a large particle just to the right of the centre image that is not observed under backscatter conditions suggesting that it is made up of lighter elements such as carbon, oxygen etc. There are many bright white particles visible which can be assumed to be gold, this was confirmed by EDS mapping (see **Figure 3.36**). Some of the larger particles appear to be smaller ones fused together. Upon further magnification (60,000 times) it can be seen that the particles are mainly spherical and between 20nm and 50nm in diameter. These particles are more evenly dispersed than in previous samples but there are still some areas with no nanoparticles present and other patches where they are clumped together. This may explain the unevenness of the colour in the sample.

Figure 3.35 SEM images of AW909C. (Left) Under SEI conditions at 4,000 and 60,000 times magnification. (Right) Corresponding images under backscatter conditions.

EDS was performed on the backscatter images of AW909C at 4,000 and 60,000 times magnification. As in previous methods it confirms that the bright white areas observed under backscatter conditions are gold. In **Figure 3.36** the gold is mapped as bright red patches making them easy to identify. Nitrogen is observed to be in areas where the fibres are and chlorine is spread evenly over the entire map.

AW910E (see **Figure 3.37**) – The cross section observed at 3,700 times magnification shows a few particles on the cut surface of the fibre but this is most likely due to transference from the cutting blade. If the gold was absorbing through the surface of the fibre then more particles should be observed, similar to that of the side-on image.

At 50,000 times magnification of the side-on view there are large particles visible that are uneven in size and distribution. Unlike AW909C there are not as many particles present and only a few areas have bunched particles; most are individual spheres. The size of particles present ranges from approximately 20nm to 60nm. Where AW909C (pink) has a large amount of smaller particles spread over the fibre surface these larger, more dispersed particles may give the sample its purple colour.

EDS was performed on the backscatter image of AW910E at 50,000 times magnification. The bright white patches observed under backscatter conditions are confirmed to be gold. In **Figure 3.38** the gold is shown as bright red patches but only the larger nanoparticles are easily identified. The smaller particles do not come through as strongly. Nitrogen and chlorine are spread evenly over the entire map except in the bottom left hand corner.

Fluorescence spectroscopy was performed on samples AW909B, AW909C, AW922C and AW923A.

In **Figure 3.39** the fluorescence spectra of AW909B, AW909C and AW923A show almost identical plots to that of untreated Nylon. The peaks of AW909B and AW909C show a decrease in intensity (2.5-3.5) compared to ~7 in untreated Nylon. AW923A has the same intensity as the untreated Nylon showing that in this sample, although there is clearly gold present (dark purple colouring) the gold is not fluorescing. Possibly a larger particle size of gold nanoparticles is needed for the fluorescence of the gold to be seen over the fabric's fluorescence.

This is not the case in AW922C. When compared to the Nylon spectrum a large broad asymmetric hump is observed, similar to that of AW916A from Method 2. Again it appears to have two merged peaks and intensity over five times the original peak indicating that the gold is fluorescing to produce this spectrum. As the only difference between the samples is colour and therefore particle size, the gold nanoparticles may need to reach a certain diameter before they produce fluorescence of their own.

Figure 3.39 Fluorescence spectra of samples from Method 4 and Method 5

3.2.3 Effect of tannic acid as a reductant

Method 6: Tannic acid was the last reductant used in an attempt to develop new colours. Results were less successful than the reductants used in the previous five methods. The first six samples have virtually no colour change; all are close to the starting nylon fabric samples – only a faint grey colour is observed. The remaining samples are all various shades of pink and purple like the samples from previous methods but the colours are dirtier. Only AW921D and AW922A are evenly coloured and reasonably attractive.

Table 3.6 Colloid colour and resulting colour on Nylon fabric for Method 6 samples.

Sample ID	Colloid Colour	Fabric	Colour after development
AW917A	Dark pink/rose	Nylon (AW919A)	Off white
AW917B	Dark pink/purple	Nylon (AW919B)	Off white
AW917C	Dark pink/purple	Nylon (AW919C)	Off white
AW917D	Dark pink/purple	Nylon (AW919D)	Off white

Table 3.6 cont Colloid colour and resulting colour on Nylon fabric for Method 6 samples.

Sample ID	Colloid Colour	Fabric	Colour after development
AW917E	Purple/pink	Nylon (AW919E)	Off white
AW917F	Dark purple	Nylon (AW919F)	Off white
AW918A	Murky orange/pink	Nylon (AW919G)	Very faint pale pink
AW918B	Deep red	Nylon (AW919H)	Faint pale purple, one corner darker, few dark spots
AW918C	Deep purple	Nylon (AW920A)	Faint purple/blue
AW918D	Deep purple	Nylon (AW920B)	Brown strip around edge, rest grey/pink/purple
AW918E	Deep purple	Nylon (AW920C)	Patchy grey/purple
AW918F	Black	Nylon (AW920D)	Green/grey
AW920E	Orange/pink	Nylon (AW921D)	Reddy purple
AW920F	Deep rose	Nylon (AW921E)	Dark purple with a lighter patch
AW920G	Dark red/purple	Nylon (AW921F)	Patchy purple, darker around the edges
AW921A	Purple/rose	Nylon (AW921G)	Purple/red, darker around the edges
AW921B	Deep purple/red	Nylon (AW922A)	Dark purple/red
AW921C	Dark green/black	Nylon (AW922B)	Green/grey with purple around the edge

Figure 3.40 Photographs of samples dyed with tannic acid reduced gold nanoparticle colloids (Method 6)

ColourQuest measurements were performed on all samples from Method 6. AW919A-F have similar values to the original fabric – L^* values over 90 and a^* values close to zero. The only difference is the b^* values which are all around approximately +10 (yellow). This value gives the samples their off-white appearance. From AW919G to AW922B the samples show a general trend of all values decreasing which results in darker, dirtier colours. These can be compared to the samples from previous methods as visually they appear the same.

The samples can be split into groups – pinks and purples. Slight variations in colour that cannot be easily detected by the naked eye can be picked up by the

ColourQuest in the form of differing a^* and b^* values. The pinks (AW919G, AW921D) have $+a^*$ (red) values and high L^* values (>70) compared to the purples with medium L^* values (40-70). Visually the purples do not appear very different from each other, only lighter or darker but the ColourQuest measurement show that there are some noticeable differences. AW919H-AW920D all have a^* and b^* values close to zero but AW921E-AW922A have $+a^*$ (red) values and $-b^*$ (blue) values.

AW920D and AW922B show similar values except on the brightness scales (L^* , Iso brightness and Tappi brightness) indicating that they are just two different shades of the same colour (purple). The only difference between these two samples was the amount of gold solution added (80 μ L vs. 150 μ L) indicating that the gold may play an important part in changing the shade of a sample.

These slight variations in colour would be important on an industrial scale as batches of fabric need to be dyed the same colour every time.

Further analysis was performed on samples AW921D and AW922A.

UV/vis reflectance spectra for AW921D and AW922A are similar to those from Method 4 and Method 5. AW921D is almost identical to AW909C from Method 4, again an absorption peak is observed ~525nm corresponding to the absorption of cyan/green. The reflectance percentage seen in the red range (>600nm) of the spectrum is not as large expected, again this may be due to the fact that it is a dirty colour so the spectrum may be a result of the mixing of colours.

AW922A can be compared to AW911B and AW923A from Method 5 and AW901E from Method 1. A relatively flat reflectance under 40% in the 190-900nm is observed, which is slightly different to the previous spectra that were only flat above 250nm. As this is in the UV range though it will not affect the visible colour therefore very dark purple coloured fabric is observed as the sample absorbs across all wavelengths of the visible spectrum.

Figure 3.42 UV/vis reflectance spectra of samples from Method 6

Fluorescence spectroscopy was performed on samples AW921D and AW922A.

In Figure 3.43 the fluorescence spectra of AW921D and AW922A show almost identical (slightly smoother) plots to that of untreated Nylon. Only an increase in intensity is observed, 13-16 compared to ~7 in untreated Nylon suggesting that the gold nanoparticles present are enhancing the fluorescence.

3.3 Results of gold nanoparticles prepared In-Situ on fibre surface

3.3.1 Effect of gold concentration and uptake/development time

Method 7: The colours obtained from this method are reasonably attractive and AW915C and AW915D are evenly coloured. Unfortunately these colours developed in a dark drawer over a period of a few weeks once the fabric was removed from solution and dried. This meant that the samples were difficult to reproduce as the effect of UV light on the samples was outside the scope of the thesis.

The samples all show a different colour around the outside edges where the plastic slide was clamped suggesting that diffusion rates may influence the colour outcome. Compared to the previous methods the colours are unique (peach and gold compared to pink and purple) and the method is simpler (amine groups in the fabric are used as the reductant) which would be more useful if this was to be upscaled for industry.

Table 3.7a Colour before and after development for Method 7 Nylon samples.

Sample ID	Fabric	Colour before development	Colour after development
AW914A	Nylon (AW915A)	Light yellow, darker around the edges	Yellow/grey middle, pink/purple edges
AW914B	Nylon (AW915B)	Pastel yellow	Gold middle, peach edges
AW914C	Nylon (AW915C)	Pastel/bright yellow	Gold middle, peach edges
AW914D	Nylon (AW915D)	Bright yellow	Gold middle, peach edges

Method 8: Samples for this method were very patchy due to the way they were folded into the glass sample vials. Darker areas are where the fabric was directly exposed to the gold solution. This proves that Nylon is non porous so in order to achieve even uptake the samples need to be as flat as possible. Again the colour developed over time in the dark drawer so they were hard to replicate. As the amount of gold present is increased the colour changes from purple (40 μ L) to tan brown (400 μ L).

AA analysis shows that 98-99% of gold in the solution is taken up by the fabric. The maximum amount of gold in solution was 1600ppm and of this only ~21ppm remains after the fabric is removed. Later methods (Method 12 and 13) show the uptake of gold over time and that the amount of gold that leaches back out of the fabric during development is minimal.

Table 3.8 Colour before and after development for Method 8 Nylon samples and Atomic Absorption results.

Sample ID	Fabric	Colour before development	Colour after development	Au ppm left in solution (AA)
AW923B	Nylon (AW924A)	Dark purple		0.34
AW923C	Nylon (AW924B)	Peach with a few purple spots	Peach with a few pink patches	0.21
AW923D	Nylon (AW924C)	Yellow/orange, few darker spots	Patchy cream/brown	3.42
AW923E	Nylon (AW924D)	Lemon yellow	Patchy cream, yellow & brown	14.71
AW923F	Nylon (AW924E)	Dark yellow/orange	Tan brown	17.65
AW923B (2)	Nylon (AW924F)	Pale cream/yellow	Light purple	1.31
AW923C (2)	Nylon (AW925A)	Pale yellow	Pale cream/brown	9.75

Table 3.8 cont Colour before and after development for Method 8 Nylon samples and Atomic Absorption results.

Sample ID	Fabric	Colour before development	Colour after development	Au ppm left in solution (AA)
AW923D (2)	Nylon (AW925B)	Yellow	Patchy cream/brown	16.41
AW923E (2)	Nylon (AW925C)	Lemon yellow	Patchy cream & tan brown	20.15
AW923F (2)	Nylon (AW925D)	Lemon yellow	Patchy cream & tan brown	21.24
AW923B (3)	Nylon (AW925E)	Pale cream/yellow	Patchy cream & light purple	0.20
AW923C (3)	Nylon (AW925F)	Peach	Patchy cream & light grey/purple	7.23
AW923D (3)	Nylon (AW925G)	Orange/yellow	Patchy cream/brown	14.84
AW923E (3)	Nylon (AW925H)	Yellow/orange	Patchy cream & tan brown	19.96
AW923F (3)	Nylon (AW925I)	Yellow/orange	Patchy cream & tan brown	21.75
AW923B (4)	Nylon (AW926A)	Pale cream/yellow	Patchy cream/grey & light purple	0.17
AW923C (4)	Nylon (AW926B)	Darker peach	Pale cream/brown	5.02
AW923D (4)	Nylon (AW926C)	Darker orange/yellow	Patchy cream & light brown	12.53
AW923E (4)	Nylon (AW926D)	Orange/yellow	Patchy yellow & tan brown	16.99
AW923F (4)	Nylon (AW926E)	Orange/yellow	Patchy yellow & tan brown	19.64

ColourQuest measurements were performed on all samples from Method 7 and Method 8.

In Method 7 AW915B-D have the same a^* and b^* values but slightly different L^* values indicating they are different shades of the same colour but this cannot be seen visually. AW915A is very different with yellow/grey and pink/purple coloured fabric. The ColourQuest measurements are very similar to those of AW909C from Method 4 with $+a^*$ (red) and neutral b^* values.

Method 8 samples can be grouped according to the amount of gold in the solution that the fabric was soaked in. The 40 μ L gold solution samples are all shades of purple with increasing $+a^*$ values as the development time is increased. AW924A (68

hours development) has a large decrease in L^* values which is expected as visually it is a darker sample. The remaining samples all show a general increasing trend in $+a^*$ and $+b^*$ values corresponding to the change in fabric colour from cream to tan brown. These values are similar to AW922C-F from Method 5 but the L^* values are much lower due to the fabric being a much darker shade of tan brown.

Further analysis was performed on samples AW915A and AW915D from Method 7 and AW924A, AW924E and AW925A from Method 8.

UV/vis reflectance spectra of AW915A and AW924A are similar to those observed in previous methods. Both have the absorption peak 525nm corresponding to the absorption of cyan/green light and large reflection percentages in the red range. AW915A has a reflection peak in the violet/blue range of the spectrum which is not observed in AW924A even though visually they are similar shades of purple.

AW925A is also purple but it has a completely different spectrum. A gradual increase in percentage reflection is seen in the visible region (400-700nm) which plateaus at 700-900nm. This high reflection may be due to the fact that it is a very light purple. The ColourQuest measurements back this up with an L^* value >80 .

AW915D and AW924E have relatively uninteresting spectra with a constant reflection of ~40% between 300 and 500nm which gradually increases to ~60% by 900nm. The mixture of reflection percentages gives rise to the tan brown colour seen in the fabric (backed up by the ColourQuest measurements).

Figure 3.48 UV/vis reflectance spectra of samples from Method 7 and Method 8

SEM was performed under both SEI and backscatter conditions at varied magnifications on samples AW915B, AW915D, AW924A and AW924E. Selected images and EDS maps can be seen below. Although AW915B and AW915D have similar visible colours, the particle sizes and distribution are different for each sample.

AW915B (**Figure 3.49**) under backscatter conditions shows that there are not many gold nanoparticles present on the fibre surface. A few large (>1 μ m), bright white particles can be seen along with some large clumps of lighter elements (later

determined by EDS, see **Figure 3.50** below). Some smaller spherical nanoparticles can be seen and like previous methods they are unevenly dispersed over the fibre surface. However compared to samples from other methods the particles appear to be individual spheres and not bunched together.

EDS performed on AW915B produced some interesting maps. As can be seen in **Figure 3.50** the large particles in the middle of the fibre are indeed gold and there is a large concentration of gold in the large clump attached to the bottom of the fibre. Sodium and sulphur are also present in high concentrations suggesting that some form of contaminant has managed to get into the sample. The clump visible on the top of the fibre is mainly chlorine which has most likely come from the gold solution (HAuCl_4 in HCl) but it is still unusual for it to appear as anything other than an even distribution over the fibre surface. These contaminants may have affected the colour of the fabric and produced the peach colour that is visible around the edges.

AW915D shows similar visible colours as AW915B so a sample was cut so that both the peach and gold coloured fabrics could be observed under the microscope. Corner 1 (peach coloured fabric) shows very similar results to those seen above in **Figure 3.49**. There are large blocks of chlorine present indicating that this may be needed to produce the attractive peach colour. Corner 2 (gold coloured fabric) shows large (>500nm) gold particles present in various shapes – spheres, rods, triangular and hexagonal plates. These large particles may be why the fabric has a gold appearance instead of the usual purple colour given by smaller nanoparticles.

EDS (**Figure 3.52**) confirms that the large blocks visible in the SEM image of Corner 1 (peach coloured fabric) are chlorine most likely present as NaCl. Most likely this is again from the starting gold solution. In the Corner 2 (gold coloured fabric) map the chlorine is back to being evenly distributed over the fibre surface. Large concentrations of gold are visible corresponding to the shapes visible in the SEM images (**Figure 3.51**). Like previous samples the particles are unevenly distributed. The variety of shapes formed may be due to the high concentration of gold present in the sample – the rods, triangular and hexagonal plates may be due to gold preferentially aggregating to form a more stable particle. The range of particle shapes for gold was not expected at first but after a literature search it was discovered that these shapes are quite common⁵².

AW924A has mainly spherical nanoparticles present that appear to be uniform in size - approximately 100nm in diameter. Only one small triangular plate is visible in **Figure 3.53** below. The nanoparticles are unevenly distributed but they do not seem to be bunched together. It is just visible in the EDS map that these are indeed gold nanoparticles. Nitrogen and chlorine are evenly distributed over the fibre surface.

Like AW915D, sample AW924E (**Figure 3.54**) has a variety of gold particle shapes. Only a few nanorods are visible this time, triangular and hexagonal plates dominate, some with diameters over 2µm. The spherical particles present are uniform in size and are more uniformly distributed than previous samples, only a few small patches show bunching. This bunching may be the first stage in the formation of the larger

plates – the triangular plates appear to be an intermediate stage in the hexagonal plate formation ⁵². As observed in **Figure 3.54** below the thin triangular plates appear to thicken as their points get truncated which eventually forms relatively thick hexagonal plates. These thicker plates are visibly brighter under SEM backscatter conditions as more electrons are bounced back to the detector. These plates most likely give the tan brown colour visibly observed - the particles are so large (no longer nanometer size) that it is unlikely that Surface Plasmon Resonance influences the colour.

EDS performed on AW924E (**Figure 3.55**) clearly shows that the large particles observed in the SEM images are elemental gold (appearing as bright red patches). Again nitrogen and chlorine are evenly distributed across the fibre surface. Interestingly where there are high concentrations of gold present there is a space in the nitrogen map (black areas) suggesting that the gold plates are thick enough to shield the nitrogens on the surface of the fibre from the electron beam.

XPS was performed on AW915D to try and identify the gold binding site/s. Both the peach and gold coloured fabrics were analysed and the results can be seen in **Figures 3.56-3.61** below.

When the oxygen 1s spectra are compared to the original Nylon spectrum (**Figure 3.13**) the main peak (C=O/C-O) has shifted from ~532.6 eV to ~531.9 eV. The peach coloured fabric has approximately the same fitted peak placements as the original fabric, only a minor deviation ~0.1 eV up field is observed but the peak heights are significantly different. Originally there is a tall fitted peak at ~532.6 eV and a much smaller one at ~531.2 eV, in the peach coloured fabric these peaks are approximately the same height leading to a broadening in the main peak. The gold coloured fabric has an identical shape of the main peak and fitted peaks to that of the peach coloured fabric but the fitted peaks are both moved upfield by approximately 0.5 eV. This suggests that there are stronger interactions between the gold particles and the oxygens in the Nylon substrate, possibly due to the increase in the amount of gold present.

Nitrogen 1s spectra of both the peach and gold coloured fabrics show similar changes to those observed in the oxygen 1s spectra. When compared to the nitrogen 1s spectrum of the original Nylon (**Figure 3.14**) the peach coloured fabric shows no change (in the N-H peak) but the gold coloured fabric has a new small but broad peak at ~401.2 eV (N⁰). The main peak has also moved slightly upfield from ~399.7

eV to ~400 eV. These results suggest that the amine groups are being oxidised to imine groups therefore causing the reduction of the Au³⁺ to gold nanoparticles on the surface of the fibre. Interactions are strong between the nitrogens in the Nylon substrate and the gold particles, possibly due to the increased availability of gold.

Gold 4f spectra can only be compared to each other and literature results (see Appendix A) as there was no gold trace in the original Nylon wide scan. In both the peach and gold coloured fabric spectra there are two main peaks observed at ~84.1 eV and ~87.9 eV. These correspond to the spin peaks 7/2 and 5/2 respectively. Gold nanoparticles prepared separately have these peaks slightly downfield at ~82.3 eV and ~86 eV⁴. In the gold coloured fabrics there is a second set of fitted peaks at ~85.2 eV and ~89.4 eV corresponding to the Au-Cl (and possibly Au-N) interactions (pink and blue lines in **Figure 3.60**).

The combination of the oxygen 1s, nitrogen 1s and gold 4f spectra shows that gold nanoparticles present on the fabric substrate surface do interact with both nitrogen and oxygen present in the fabric backbone providing a strong chemical bond which is not easily broken (ie gold does not rub off the surface-see colourfastness test, Section 3.5). This binding only seems to occur if both oxygen and nitrogen are present though as otherwise Polyester should have taken up the gold ions and formed nanoparticles.

Table 3.7b XPS-Oxygen 1s peak heights and positions

Sample ID	Fabric type	Peak 1		Peak 2	
		Binding energy (eV)	Height (counts)	Binding energy (eV)	Height (counts)
Undyed	Nylon	531.4	407	532.6	2556
AW915D (peach)	Nylon	531.6	673	532.8	709
AW915D (gold)	Nylon	531.6	927	532.8	795

Table 3.7c XPS-Nitrogen 1s peak heights and positions

Sample ID	Fabric type	Peak 1		Peak 2	
		Binding energy (eV)	Height (counts)	Binding energy (eV)	Height (counts)
Undyed	Nylon	399.8	312		
AW915D (peach)	Nylon	399.8	441		
AW915D (gold)	Nylon	399.8	410	401.2	34

Table 3.7d XPS-Gold 4f peak heights and positions

Sample ID	Fabric type	Peak 1		Peak 2		Peak 3		Peak 4	
		Binding energy (eV)	Height (counts)	Binding energy (eV)	Height (counts)	Binding energy (eV)	Height (counts)	Binding energy (eV)	Height (counts)
AW915D (peach)	Nylon	84.2	10	88.0	7				
AW915D (gold)	Nylon	84.4	100	85.2	83	88.2	96	89.2	33

Fluorescence spectroscopy was performed on samples AW915A, AW915D, AW924A, AW924E and AW925A (see **Figure 3.62**).

AW915A and AW924A show almost identical plots to that of untreated Nylon, the only difference being a large decrease in intensity (1.7-2.1) compared to ~7 in untreated Nylon.

AW915D, AW924E and AW925A show a similar large broad asymmetric hump to the ones observed in previous methods. Again it is thought that the gold is fluorescing causing a second peak and therefore the broadening. There is a change in intensity as well – AW915D is slightly greater (~11), AW924E is lower (~3) and AW925A has almost 7 times the intensity (~47). This may be due to varied amounts of gold present on the fabric surface.

Figure 3.62 Fluorescence spectra of samples from Method 7 and Method 8

3.3.2 Uptake of gold solution by fabric at room temperature, 50°C and 80°C

Method 9: Untreated Polyester, Nylon, Polyester-Lycra® and Nylon-Lycra® samples were all cut to approximately the same weight (0.4g) and added to glass sample vials containing exactly the same amount of gold solution in each one so that quantitative uptake could be performed. After the desired time the fabrics were removed from solution and the remaining solutions analysed by AA so that the uptake could be grouped (see **Figures 3.81-3.84** below). Samples were put into glass sample vials containing Millipore water but the resulting colours appear to be due to the vivid bleeding out and colouring the fabric. To check if this was the case a second uptake was performed and it was found that the colour is essentially the same, therefore it is the gold nanoparticles causing the colour not from the vivid bleeding as first thought.

Polyester had a lower uptake than the other fabrics (Nylon, Polyester-Lycra®, Nylon-Lycra®) and the fabric has obtained an off white/slightly grey colour. Of a 160ppm starting solution 91ppm (57%) was the maximum uptake. The Polyester-Lycra® samples are slightly darker grey in colour having obtained a maximum uptake of 132ppm (83%). This lack of colour development suggests that gold is present as Au^{3+} on the surface instead of reduced Au^0 therefore, nitrogen is needed in the fabric to produce the coloured gold nanoparticles (polyester only has oxygen but Lycra® has both oxygen and nitrogen).

Nylon and Nylon-Lycra® both have obtained a dark red/purple colour. Even though the uptake time is different the colour is the same for all samples. Uptake is much higher than the Polyester samples (due to amine groups being present in the fabric therefore reducing the gold) with almost all the gold removed from the solution by the fabric (0.27ppm remains = 99.8% removed).

The acid and base-treated fabric samples are similar to the untreated fabrics. This either suggests that protonating or deprotonating the amine groups in the fabric has little influence on the resulting colour OR that the treatment solutions were not strong/concentrated enough to change a significant number of amine groups in the fabric. The Polyester and Polyester-Lycra® samples show identical colours and the Nylon and Nylon-Lycra® samples are slightly redder. Both the acid and base-treated fabrics uptake less of the gold solution but the difference is small (0-10%).

Table 3.9a Results for Method 9 – Untreated fabric uptake of gold solution at 50°C (starting concentration 160 ppm Au).

Sample ID	Fabric	Colour before development	Colour after development	Au ppm left in solution (AA)	% Uptake
AW933A	Polyester	Off white (slightly)	Off white (slightly)	152	5
AW933B	Nylon	Patchy lemon yellow	Patchy red-purple	18	89
AW933C	Polyester-Lycra	Off white (slightly grey)	Off white/grey	128	20
AW933D	Nylon-Lycra	Patchy lemon yellow	Patchy red-purple	53	67
AW933E	Polyester	Off white	Off white	130	19
AW933F	Nylon	Patchy lemon yellow	Patchy red-purple	11	93
AW933G	Polyester-Lycra	Faint purple-grey	Off white/grey	126	21
AW933H	Nylon-Lycra	Patchy lemon yellow	Patchy red-purple	26	84
AW934A	Polyester	Off white	Off white	133	17
AW934B	Nylon	Patchy lemon yellow	Patchy red-purple	3	98
AW934C	Polyester-Lycra	Grey-pink	Off white/grey	110	31
AW934D	Nylon-Lycra	Patchy lemon yellow	Patchy red-purple	8	95
AW934E	Polyester	Off white	Off white	97	39
AW934F	Nylon	Patchy lemon yellow	Patchy red-purple	0	100
AW934G	Polyester-Lycra	Patchy grey-pink	Off white/grey	60	63
AW935A	Nylon-Lycra	Patchy lemon yellow	Patchy red-purple	0	100
AW935B	Polyester	Off white with pink spots	Off white with pink spots	72	55
AW935C	Nylon	Patchy lemon yellow	Patchy red-purple	0	100
AW935D	Polyester-Lycra	Pink-grey with some darker pink patches	Off white/grey	46	71
AW935E	Nylon-Lycra	Patchy lemon yellow	Patchy red-purple	0	100
AW937A	Polyester	Off white with pink/purple spots	Off white with pink/purple spots	69	57
AW937B	Nylon	Patchy yellow-grey	Patchy red-purple	0	100
AW937C	Polyester-Lycra	Patchy dark pink with a few dark spots	Off white/grey	28	83
AW937D	Nylon-Lycra	Yellow-grey with white spots	Patchy red-purple	0	100

Table 3.9b Results for Method 9 – Untreated fabric colour after the second uptake of gold solution at 50°C.

Sample ID	Fabric	Colour before development	Colour after development
AW455F	Polyester	No colour change	No colour change
AW456A	Nylon	Patchy yellow & purple/pink	Patchy light purple, red-orange & dark purple
AW456B	Polyester-Lycra	Faint pink/purple	Off white/grey
AW456C	Nylon-Lycra	Patchy yellow/grey & magenta	Patchy light purple, red-orange & dark purple
AW457A	Polyester	Very faint pale pink	White
AW457B	Nylon	Patchy light & dark purple	Patchy light & medium red/purple
AW458A	Polyester-Lycra	Light grey/purple	Off white/grey
AW458B	Nylon-Lycra	Dark purple/red with a few lighter patches	Dark purple/red with a few lighter patches
AW458C	Polyester	Very faint pale pink	Off white/grey
AW458D	Nylon	Dark purple/red with the odd darker patch	Dark purple/red with the odd darker patch
AW458E	Polyester-Lycra	Light grey with a hint of purple	Off white/grey
AW458F	Nylon-Lycra	Dark purple/red with a few yellow & lighter patches (creases)	Dark purple/red with a few yellow & lighter patches (creases)
AW458G	Polyester	Faint pale pink	Off white/grey
AW458H	Nylon	Patchy light & dark purple/red	Patchy light & dark purple/red
AW459A	Polyester-Lycra	Light grey/pink	Off white/grey
AW459B	Nylon-Lycra	Medium purple with the odd light or dark patch	Medium purple with the odd light or dark patch
AW459C	Polyester	No colour change	No colour change
AW459D	Nylon	Patchy light, medium & dark purple/red	Patchy light, medium & dark purple/red
AW459E	Polyester-Lycra	Light grey/purple	Off white/grey
AW459F	Nylon-Lycra	Patchy light & dark purple/red	Patchy light & dark purple/red

Table 3.9c Results for Method 9 – Acid-treated fabric uptake of gold solution at 50°C (starting concentration 160 ppm Au).

Sample ID	Fabric	Colour before development	Colour after development	Au ppm left in solution (AA)	% Uptake
AW462B	Polyester	Very faint yellow	(AW468E) Off white	127	21
AW462C	Nylon	Patchy lemon yellow	(AW468F) Patchy light & dark purple	2	99
AW462D	Polyester-Lycra	Peachy with the odd dark spot	(AW468G) Light grey	72	55
AW462E	Nylon-Lycra	Patchy lemon yellow	(AW468H) Patchy light & dark red/purple	1	99
AW469A	Polyester	No colour change	(AW473E) Off white	95	41
AW469B	Nylon	Patchy lemon yellow & white	(AW473F) Patchy light purple & dark red-purple	2	99
AW469C	Polyester-Lycra	Pale orange/purple	(AW473G) Pale grey with dark purple spots	70	56
AW469D	Nylon-Lycra	Patchy lemon yellow & white	(AW473H) Red-purple with light purple patches.	1	99
AW469E	Polyester	Very pale faint yellow	(AW473A) Pale yellow	99	38
AW469F	Nylon	Patchy lemon yellow & white	(AW473B) Patchy light & dark red-purple/grey	2	99
AW470A	Polyester-Lycra	Yellow grey with a few dark spots	(AW473C) Pale grey	77	52
AW470B	Nylon-Lycra	Patchy lemon yellow & white	(AW473D) Light red-purple with darker patches	3	98
AW470C	Polyester	No colour change except a few dark blue spots	(AW472I) Pale yellow with a light purple spot	97	39
AW470D	Nylon	Patchy lemon yellow & white	(AW472J) Patchy dark red-purple, medium & light purple	4	98
AW470E	Polyester-Lycra	Grey with purple patches & dark purple spots	(AW472K) Pale grey/purple with darker patches & spots	93	42
AW470F	Nylon-Lycra	Patchy lemon yellow & white	(AW472L) Patchy light purple & darker red-purple	9	94

Table 3.9c cont Results for Method 9 – Acid-treated fabric uptake of gold solution at 50°C (starting concentration 160 ppm Au).

Sample ID	Fabric	Colour before development	Colour after development	Au ppm left in solution (AA)	% Uptake
AW470G	Polyester	No colour change	(AW472E) Off white	120	25
AW471A	Nylon	Patchy lemon yellow & white	(AW472F) Patchy light purple & medium red-purple/grey	7	96
AW471B	Polyester-Lycra	Pale yellow with a few dark spots	(AW472G) Pale grey/purple	117	27
AW471C	Nylon-Lycra	Patchy bright yellow & white	(AW472H) Pale grey/purple with lighter patches	22	86
AW471D	Polyester	Very pale faint yellow	(AW472A) Pale yellow with a few darker patches	125	22
AW471E	Nylon	Patchy lemon yellow & white with purple spots	(AW472B) Patchy light & dark purple & red-purple	18	89
AW471F	Polyester-Lycra	Light yellow/grey	(AW472C) Pale grey/purple	104	35
AW471G	Nylon-Lycra	Patchy lemon & light yellow	(AW472D) Patchy light purple & dark red-purple	24	85

Table 3.9d Results for Method 9 – Base-treated fabric uptake of gold solution at 50°C (starting concentration 160 ppm Au).

Sample ID	Fabric	Colour before development	Colour after development	Au ppm left in solution (AA)	% Uptake
AW461A	Polyester	White with a few purple patches	(AW468A) Off white with a few light red/purple patches	130	19
AW461B	Nylon	Patchy light & dark purple	(AW468B) Dark red/purple with some light purple patches	2	99
AW461C	Polyester-Lycra	Light purple/grey	(AW468C) Light grey/purple with a few darker spots	86	46
AW462A	Nylon-Lycra	Patchy magenta & gold/grey	(AW468D) Dark purple with patches of red & light purple	2	99
AW462F	Polyester	White with a few purple spots	(AW467K) Off white with a few light purple spots/patches	146	9
AW462G	Nylon	Patchy light purple & grey/yellow/green	(AW467L) Dark red/purple with some lighter patches	4	98
AW463A	Polyester-Lycra	Even light purple/grey	(AW467M) Light purple/grey	126	21
AW463B	Nylon-Lycra	Patchy light purple & grey/yellow	(AW467N) Dark red/purple with light purple patches	2	99
AW463C	Polyester	No colour change	(AW467G) One dark blue spot	89	44
AW463D	Nylon	Patchy white & yellow/grey	(AW467H) Patchy red/purple & light purple	6	96
AW463E	Polyester-Lycra	Light purple with a few darker areas	(AW467I) Light grey/purple with a few darker spots	122	24
AW463F	Nylon-Lycra	Yellow/grey with a few white patches	(AW467J) Dark red/purple with a few light purple patches	8	95
AW463G	Polyester	No colour change	(AW467C) No colour change	130	19
AW463H	Nylon	Patchy yellow/grey and white with a dark spot in one corner	(AW467D) Patchy dark red/purple & light purple	7	96
AW464A	Polyester-Lycra	Fairly even light purple with the odd darker patch	(AW467E) Pale grey with patches of pink/light purple	113	29
AW464B	Nylon-Lycra	Patchy yellow grey, purple and white	(AW467F) Red/purple with a few light purple areas	7	96

Table 3.9d cont Results for Method 9 – Base-treated fabric uptake of gold solution at 50°C (starting concentration 160 ppm Au).

Sample ID	Fabric	Colour before development	Colour after development	Au ppm left in solution (AA)	% Uptake
AW464C	Polyester	No colour change	(AW466E) No colour change	158	1
AW464D	Nylon	Patchy white & lemon yellow	(AW466F) Patchy red/purple & light purple	30	81
AW464E	Polyester-Lycra	Patchy white & light purple	(AW467A) Patchy light purple/grey & pale pink/purple	159	1
AW464F	Nylon-Lycra	Patchy white & lemon yellow	(AW467B) Patchy dark red/purple & light purple	42	74
AW464G	Polyester	No colour change	(AW466A) No colour change	158	1
AW464H	Nylon	Patchy white & lemon yellow, patchy	(AW466B) Patchy dark purple, red & pale purple	65	59
AW465A	Polyester-Lycra	Very light purple/grey	(AW466C) Patchy light grey, pale purple & pink	160	0
AW465B	Nylon-Lycra	Patchy white & lemon yellow	(AW466D) Patchy red/purple, light purple & grey	160	0

Figure 3.66 Photographs of samples from quantitative uptake of gold solution and development at 50°C - Base-treated fabric (Method 9)

Method 10: The uptake and development of gold solution by fabric was repeated at 80°C to see if temperature changes control the colour imparted on the fabric. It was found that in the case of Polyester and Polyester-Lycra® that the colour is not affected as only a very light shade of grey is observed. The Nylon and Nylon-Lycra® however gain a darker shade of purple (bluer) when compared to the samples from Method 9 due to greater reduction and formation of gold nanoparticles (possibly larger nanoparticles). Development time also seems to play a part as the samples that were only developed in the water bath for 1 hour are lighter in colour and also patchier. AA analysis shows that an uptake of 80-99% is achieved for all samples.

Table 3.10a Results for Method 10 – Overnight development at 80°C (starting concentration 160 ppm Au).

Sample ID	Fabric	Colour before development	Colour after development	Au ppm left in solution (AA)	% Uptake
AW451B	Polyester	Three small purple spots			
AW451C	Polyester-Lycra	Pink	Off-white (grey) with pink streaks		
AW946D	Nylon	Yellow	Patchy purple	7	96
AW946E	Nylon-Lycra	Yellow	Patchy purple	32	80
AW946F	Nylon	Yellow	Patchy purple	4	98
AW946G	Nylon-Lycra	Pale yellow	Patchy purple	8	95
AW947A	Nylon	Yellow-grey	Patchy purple	1	99
AW947B	Nylon-Lycra	Yellow-grey	Patchy purple	3	98
AW947C	Nylon	Purple-lavender	Patchy purple	2	99
AW947D	Nylon-Lycra	Pale purple	Patchy purple	1	99

Table 3.10b Results for Method 10 – 1 hour development at 80°C .

Sample ID	Fabric	Colour before development	Colour after development
AW950C	Polyester	Faint purple with darker spots	Off white with purple spots
AW950D	Nylon	Patchy pink-purple	Patchy light & medium pink/purple
AW950E	Polyester-Lycra	Very light pink-purple	Off white, few pink/purple spots
AW950F	Nylon-Lycra	Patchy red-purple & white	Patchy red-purple & white

Method 11: Final uptake was performed only on Nylon at room temperature as it was the easiest to work with and gave the most consistent results. Again it was thought that if the temperature was controlled during the uptake of gold then the resulting colour would be different. Unfortunately this is not the case, since as found for previous methods another shade of purple was obtained. Visually acid and base-treating the fabric before the gold uptake does little to the resulting colour, the acid treated samples appearing to be only slightly lighter in the shade of purple obtained. Interestingly all the fabric samples have the same colour even though there is a wide range of gold uptake (62-99%) which suggests that it is the size of the gold particles present in the sample that determines the colour, not how much gold is absorbed and reduced onto the fibre surface.

Table 3.11 Results for Method 11 – Uptake of gold solution at room temperature, development at 50°C (starting concentration 160 ppm Au).

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA)	% Uptake
AW486A	Nylon	Very patchy light & medium purple	1	99
AW486B	Nylon	Patchy light & medium purple	1	99
AW486C	Nylon	Patchy white & light purple	1	99
AW486D	Nylon	Light purple with a few white patches	2	99
AW486E	Nylon	Fairly even dark purple	9	94
AW486F	Nylon	Even coloured dark purple/red	3	98
AW487A	Nylon	Patchy light & medium purple	11	93
AW487B	Nylon	Light purple with a few darker patches	11	93
AW487C	Nylon	Medium purple with large lighter patches	5	97
AW487D	Nylon	Patchy light purple & white	10	94
AW487E	Nylon	Patchy light purple with some darker patches & white areas	1	99
AW487F	Nylon	Patchy light & medium purple with white patches	1	99
AW487G	Nylon	Fairly even medium purple with the odd lighter patch	62	61
AW488A	Nylon	Fairly even medium purple with the odd light patch	62	61
AW488B	Nylon	Patchy medium purple with a few light patches	14	91

ColourQuest measurements were performed on all samples from Methods 9-11 and the results can be seen in Figures 3.70-3.76 below. As can be seen clearly on the graphs the samples are grouped by fabric type.

All the Polyester samples have very high L^* values (>80) and virtually neutral a^* and b^* values which gives rise to the off white appearance of the fabric. Polyester-Lycra® shows similar results with slightly lower L^* values (~ 80), neutral or slightly $+a^*$ values (red) and neutral or slightly $-b^*$ values (blue) giving the fabric a light grey colour.

Nylon and Nylon-Lycra® samples all show small variations in their ColourQuest values. L^* values are between 40 and 60 due to the fabric being darker shades of purple. This is backed up by the slightly $-b^*$ values (blue) and $+a^*$ values (red) of 10-20. These a^* values are higher than the ones obtained from the purple samples in all of the previous methods, this may be due to the colour being more uniform so the ColourQuest is measuring sharper colours rather than a mixture of colours as seen previously.

Figure 3.73 ColourQuest measurements of Method 9 – Base treated fabric samples

Figure 3.74 ColourQuest measurements of Method 10 fabric samples (overnight development)

Further analysis was only carried out on sample AW459D from the second uptake at 50°C (Method 9).

UV/vis reflectance spectroscopy performed on AW459D results in a spectrum (**Figure 3.77**) that is very similar to the other purple samples from previous methods (e.g. AW924A from Method 8). Again the absorption peak at 525nm corresponding to the absorption of cyan/green light is observed and there are moderate reflection percentages in the red range (>650nm).

SEM was performed under both SEI and backscatter conditions at varied magnifications on Sample AW459D. Selected images and EDS maps can be seen below in **Figure 3.78** and **Figure 3.79**.

Spherical gold nanoparticles have been formed with a diameter ranging from 10 to 80nm. Although their size varies the nanoparticles appear to be more evenly distributed than in previous samples. There are only a few small areas where the nanoparticles have bunched together in groups that are no larger than 100nm in diameter. Some lighter element contaminants are still visible on the surface of the fibre.

EDS mapping confirms again that the spherical nanoparticles are gold as shown by the bright red spots in **Figure 3.79**. The large particles (>50nm) are easily recognised but the smaller particles are harder to discern as they get masked by the nitrogen and chlorine maps which show even distribution over the fibre surface.

Fluorescence spectroscopy was performed on AW459D (**Figure 3.80**). It was found that only a small amount of fluorescence was present when compared to the original Nylon sample (**Figure 3.15**) – maximum intensity ~1 compared to ~7 in the original sample. The main peak has a slightly different shape, a new plateau is observed between 550 and 700nm which may be from the fluorescing of the gold nanoparticles.

Results of the quantitative uptakes were graphed by fabric type and can be seen in **Figures 3.81-3.84** below.

Polyester (Figure 3.81): Untreated Polyester has the best uptake with just over half the starting concentration of gold absorbed within 6 hours. From 6 hours to 18 hours the uptake concentration plateaus. The acid-treated Polyester has a maximum uptake of ~100ppm within 2 hours but after further time in the water bath the uptake

concentration has decreased again (35ppm absorbed onto the fibre surface) suggesting that the gold leaches back out of the fabric over time. Base-treated Polyester shows this same trend with a maximum uptake of ~70ppm after 6 hours which decreases to ~40ppm after 16 hours in the water bath at 50°C. The resulting fabric colour suggests that although AuCl_4^- is taken up by the fabric it is not reduced significantly, giving rise to the off-white colour observed.

Nylon (Figure 3.82): Almost all the quantitative uptakes performed at varied temperatures show nearly complete (<2ppm) uptake of the gold solution (and reduction due to the amine groups) by the Nylon fabric by 16 hours except for the base-treated Nylon with uptake performed at room temperature (complete uptake after 24 hours). Upon magnifying the lower quarter of the graph it can be seen that the maximum uptake of gold solution is achieved within 3 hours by untreated Nylon at 50°C, untreated Nylon at 80°C, acid-treated Nylon at room temperature and acid-treated Nylon at 50°C.

Previous methods have shown that there is little colour change caused in the fabric by acid or base treating the fabric, therefore plain untreated Nylon can be used in further methods as it gives a reasonable uptake time at 50°C and 80°C (complete uptake in 1-3 hours).

Polyester-Lycra® (Figure 3.83): Like Polyester, untreated Polyester-Lycra® has the best uptake with just under three quarters of the starting concentration of gold being

absorbed by the fabric within 6 hours. From 6 hours to 18 hours the uptake concentration slowly decreases to ~100ppm absorbed by the fabric suggesting that the gold leaches back out of the fabric over time. The acid-treated Polyester has a maximum uptake of ~90ppm within 6 hours but after further time in the water bath the uptake concentration has decreased slightly again. Base-treated Polyester undergoes multiple increases and decreases in the gold concentration uptake and finally shows a maximum uptake of ~80ppm after 16 hours. Polyester-Lycra® shows much larger uptakes of gold than Polyester suggesting that nitrogen (in the Lycra®) is needed in the substrate for the gold nanoparticles to bind to.

Nylon-Lycra® (Figure 3.84): The quantitative uptakes performed with Nylon-Lycra® all show that maximum uptake of gold by the fabric is achieved within 6 hours. From 6 to 18 hours the uptake plateaus and unlike Polyester and Polyester-Lycra® the gold does not appear to leach back out suggesting that it is chemically bound to the fibre surface.

Concentrations of less than 10ppm remaining in solution are achieved within the first hour; this is slightly better than the rate achieved by Nylon indicating that the extra nitrogens present (from Lycra®) are enhancing the uptake. If this is to be adapted for industry then a tailor-made synthetic fabric with a sufficient quantity of nitrogen in the structural backbone could improve the uptake time to less than one hour.

Again the base-treated fabric is slower to reach maximum uptake (by 6 hours) with a decrease in uptake concentration at 3 hours. This may be a one-off deviation but repetitive uptakes were not performed to test the consistency of the results.

3.3.3 Effect of the presence/absence of chloride ions

Method 12: Samples in this method were developed in the presence of chloride ions (i.e. developed in the same glass sample vial as the uptake was performed in) to see if chloride has any influence on the resulting fabric colour. Colours presented in

Table 3.12a were visible after development but the colour has continued developing over time in a dark drawer to give those seen in **Figure 3.85**.

The samples are all very patchy in colour especially the room temperature uptake and development samples. Untreated Nylon samples (room temperature uptake and development) look like they have been tie dyed – patches of yellow, pink, purple, grey and white are visible. It appears that the patchiness is due to the fabric being folded into the glass sample vials. Acid-treated Nylon samples (room temperature) show small patches of yellow, purple and grey but are mainly white. Base-treated Nylon samples (room temperature) are various shades of purple and grey.

Untreated, acid-treated and base-treated Nylon samples with gold uptake and development at 50°C are less patchy and various shades of purple.

AA analysis shows that almost complete uptake of the gold solution present was obtained by all samples.

Table 3.12a Results for Method 12 – Uptake and colour development at room temperature (starting concentration 160ppm Au).

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA)	% Uptake
AW493A	Nylon	Patchy pale yellow, white & purple/grey. Darker in creases	0	100
AW493B	Nylon	Pale yellow with purple patches, large purple spot on one edge	9	94
AW493C	Nylon	Pale yellow with white patches	2	99
AW493D	Nylon	Patchy white & yellow in the middle with darker lemon yellow around edges	0	100
AW493E	Nylon	Patchy white, pale & lemon yellow	0	100
AW493F	Nylon	Pale yellow in middle, lemon yellow patches around edges	0	100
AW493G	Nylon	Patchy lemon yellow & grey with white patches	0	100
AW493H	Nylon	Patchy white, lemon yellow & grey	0	100
AW493I	Nylon	Patchy purple, yellow & grey	0	100

Table 3.12b Results for Method 12 – Uptake and colour development at 50°C (starting concentration 160ppm Au).

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA)	% Uptake
AW494A	Nylon	Pale grey purple with three purple spots	0	100
AW494B	Nylon	Fairly even grey/red-purple with two lighter patches	0	100
AW494C	Nylon	Fairly even purple/red with lighter patches & two dark purple spots	0	100
AW494D	Nylon	White with very pale purple & grey patches. One purple spot	0	100
AW494E	Nylon	Patchy light purple & light grey	0	100
AW494F	Nylon	Light purple, lighter in creases	0	100
AW494G	Nylon	Dark red/purple. Lighter in creases	0	100
AW494H	Nylon	Fairly even dark red/purple with few lighter patches	0	100
AW494I	Nylon	Dark red/purple. Lighter in creases	0	100

Method 13: Samples in this method were developed in the absence of chloride ions but a significant change in colour is not observed. All samples are still very patchy in appearance. Like Method 12 the colour of the samples has continued developing over time in a dark drawer to give those seen in **Figure 3.87**.

The samples with uptake and development in the water bath at 50°C are slightly darker shades of purple than the corresponding samples developed in the presence of chloride ions.

Room temperature uptake and development samples also show a slight darkening in shade, the most obvious example being the acid-treated fabric samples which have a lot more visible colour (pink and purple) than the corresponding samples developed in the presence of chloride ions. The base-treated samples are identical visually and this can be seen in the ColourQuest measurements (see paragraph below).

AA analysis shows that almost all of the gold solution is taken up by the fabric (~152ppm). The second glass sample vials (ones the fabric was developed in) all have minimal amounts of gold present in the solution suggesting that there is no leaching after uptake and development. This in turn suggests that the gold nanoparticles bind to the fabric rather than sitting on the surface like traditional dyes.

Table 3.13a Results for Method 13 – Uptake and colour development at room temperature (starting concentration 160ppm Au).

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA) (separate sample vials)		% Uptake	
			1	2	1	2
AW494J	Nylon	Pale lemon yellow with purple around the edges & creases	0	0	100	100
AW494K	Nylon	Patchy pink, orange & purple	1	0	99	100
AW494L	Nylon	Patchy white, lemon yellow & purple	1	0	99	100
AW494M	Nylon	Patchy cream & pink, few dark spots	0	0	100	100
AW494N	Nylon	Patchy grey, yellow & purple (purple around edges & creases)	8	0	95	100
AW494O	Nylon	Patchy dark purple & pink/orange	2	0	99	100
AW496A	Nylon	Pale lemon yellow with white patches & purple spots in one corner	0	0	100	100
AW496B	Nylon	Patchy white & pale lemon yellow	0	0	100	100
AW496C	Nylon	Very patchy yellow, purple, grey, white & brown	1	0	99	100

Table 3.13b Results for Method 13 – Uptake and colour development at 50°C (starting concentration 160ppm Au).

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA) (separate sample vials)		% Uptake	
			1	2	1	2
AW494P	Nylon	Even dark purple/red with a few lighter patches	0	0	100	100
AW494Q	Nylon	Patchy light & dark purple	0	0	100	100
AW495A	Nylon	Patchy red & purple with a few light purple patches	0	0	100	100
AW495B	Nylon	Patchy pink & dark purple	0	0	100	100
AW495C	Nylon	Dark purple (hint of red) with lighter patches	0	0	100	100
AW495D	Nylon	Patchy light & dark purple	0	0	100	100
AW496D	Nylon	Patchy dark purple/red, light purple/grey & medium purple	0	1	100	99
AW496E	Nylon	Patchy light, medium & dark purple. Lighter in creases	0	0	100	100
AW496F	Nylon	Dark red/purple with light purple in the creases	0	0	100	100

ColourQuest measurements were performed on all samples from Method 12 and Method 13, the results can be seen in **Figures 3.89-3.92** below. As the samples are all Nylon fabric they are grouped by treatment type on the graphs.

As was seen visibly the acid-treated Nylon samples from Method 12 (uptake and development at room temperature) show no change from the original undyed fabric. The corresponding samples from Method 13 show +a*, neutral b* and moderate L* (>70) values which gives the fabric its pink colour.

ColourQuest values of the base-treated samples (room temperature and 50°C) from Method 12, the acid treated samples (50°C) from Method 12, the untreated and base-treated samples (room temperature) from Method 13 and all Nylon samples (50°C) from Method 13 show that they are all slightly different shades of the same colour (purple) with little or no variation in their a* and b* values.

The remaining samples are very patchy in appearance and this is reflected in their measured values which have no correlation with each other.

Further analysis was carried out on samples AW494P, AW495A and AW495C from development at 50°C in the absence of chloride ions (Method 13).

UV/vis reflectance spectroscopy performed on samples AW494P, AW495A and AW495C results in spectra (**Figure 3.93**) that are very similar to the other purple samples from previous methods (e.g. AW459D from Method 9). Once again an absorption peak is observed at 525nm corresponding to the absorption of cyan/green light but the reflection percentages in the red range (>650nm) vary slightly between the samples.

SEM was performed under both SEI and backscatter conditions at varied magnifications on samples AW494P, AW495A and AW495C. Selected images and EDS maps can be seen below in **Figures 3.94-3.99**. Although the samples have similar visible colours, there is a considerable spread in particle size, shape and distribution for each sample so the overall colours observed are similar and represent an average Surface Plasmon Resonance.

Cross section images of AW494P were obtained and can be seen in **Figure 3.94** and **Figure 3.95**. Like previous cross sections there are a few gold nanoparticles observed on the surface of the cross section, most likely this is from particles being dragged across the surface when the fibre was cut. The backscatter image clearly shows that there are a large number of gold nanoparticles on the uncut surfaces of the fibre. Spherical particles 20-100nm in diameter are observed with some particles aggregating to form clumps up to 500nm in diameter.

The side on-image shows much of the same with some areas showing large bunches made up of smaller nanoparticles. Like sample AW909C from Method 4 there is a

much larger concentration of nanoparticles on the fibre surface when compared to other samples.

Figure 3.95 shows a close up of the cross section edge at 10,000 times magnification under SEI and backscatter conditions. The corresponding EDS map is also shown on the right hand side. Again it appears that the nanoparticles are only on the uncut surface of the fibre and are various sizes of spherical particles. The EDS map confirms that these particles are gold with plenty of red patches visible on the map. In areas of high gold concentration the nitrogen map shows black spots as the gold is masking the nitrogen atoms from the electron beam. Chlorine appears to have an even distribution over the whole fibre surface.

SEM images of AW495A (**Figure 3.96**) show that there are fewer nanoparticles present on the fibre surface than in the previous sample. These particles are uneven in distribution and particle size. A backscatter image at 5,500 times magnification shows that there are some particles visible that are almost 1µm in diameter. The majority of the particles are spherical in shape with diameters ranging from 50 to 100nm (see **Figure 3.96**-50,000 times magnification). As the samples (AW494P and AW495A) are visibly the same purple colour it is thought that large microparticles present on the fibre surface are responsible for this colour rather than the smaller nanoparticles.

Close-up images of the fibre under SEI and backscatter conditions and the corresponding EDS map can be seen in **Figure 3.97**. Like previous samples the gold nanoparticles appear as distinctive red areas. The nitrogen map shows some darker areas that are not caused by masking as seen in previous maps. It appears that the electron beam has distorted/melted the synthetic fibre in places causing pockets which limit the amount of reflected electrons that reach the detector. As usual chlorine is evenly mapped over the entire fibre surface.

AW495C (**Figure 3.97**) appears to have a moderate level of randomly sized spherical nanoparticles on the fibre surface. There are more nanoparticles visible than in AW495A but less than AW494P. Again some of these particles are bunched together giving a size distribution range of 80 to 500nm in diameter. Distribution of the particles over the fibre surface is more even than previous samples.

EDS map of AW495C (**Figure 3.99**) shows a large concentration of various sized gold nanoparticles along the right hand edge of the fibre. Again the electron beam has distorted/melted the synthetic fibre, this time on the right hand side of the fibre causing the reflected electrons to be shielded from the EDS detector (which is on the left hand side). Chlorine is evenly distributed over the entire fibre surface similar to previous samples.

XPS was performed on AW494P, AW495A and AW495C to confirm the gold binding site/s. The results can be seen in **Figures 3.100-3.108** below.

When the oxygen 1s spectra of the three samples are compared to the original Nylon spectrum (**Figure 3.13**) the main peak (C=O/C-O) has shifted from ~532.6 eV to ~532.1 eV, ~531.2 eV and ~531.4 eV (for AW494P, AW495A and AW495C respectively). Originally there is a tall fitted peak at ~532.6 eV and a much smaller one at ~531.2 eV. In the dyed samples these fitted peaks have shifted slightly downfield and their heights greatly vary. AW494P has the tall fitted peak at ~532.1 eV and the small peak at ~531.0 eV. AW495A has doesn't have as significant a difference in peak heights, the second fitted peak (~531.0 eV) is approximately two-thirds the height of the first fitted peak (~532.0 eV). In AW495C the peak heights are reversed with the tall peak at ~531.3 eV (instead of ~532.6) and the small peak at ~532.3 eV (compared to ~531.2 eV). These peak shifts and height changes suggests that there are strong interactions between the gold particles and the oxygens in the Nylon substrate.

Nitrogen 1s spectra of all three samples when compared to the nitrogen 1s spectrum of the original Nylon (**Figure 3.14**) show little (~0.1 eV) or no change in the main

peak (N-H peak) but AW495A and AW495C have a new small but broad peaks. AW495A has two new peaks, one at ~400.0 eV (N^0) and another at ~407.0 eV (oxidised nitrogen). AW495C has a new peak at ~400.8 eV. Again these results suggest that the amine groups are being oxidised to imine groups therefore causing the reduction of the Au^{3+} to gold nanoparticles on the surface of the fibre. Interactions are strong between the nitrogens in the Nylon substrate and the gold particles providing the fabric with a stable, colourfast colour.

The Gold 4f spectra of AW494P and AW495C show that two main peaks are observed at ~84.0 eV and ~87.8 eV. These correspond to the spin peaks of 7/2 and 5/2 respectively. AW495A has peaks slightly downfield at ~83.7 eV and ~87.4 eV. Gold nanoparticles prepared separately have these peaks even further downfield at ~82.3 eV and ~86 eV⁴. Just as in AW915D (gold) (**Figure 3.60**) there are a second set of fitted peaks for all samples corresponding to the Au-Cl interactions (pink and blue lines). These peaks are at ~84.7 eV, ~84.3 eV and ~85.0 eV (pink lines) and ~88.2 eV, ~88.0 eV and ~88.2 eV (blue lines) for AW494P, AW495A and AW495C respectively. AW495A has a third fitted peak at ~85.2 eV.

The combination of the oxygen 1s, nitrogen 1s and gold 4f spectra of these dyed fabrics show that gold nanoparticles present on the Nylon surface do interact with both nitrogen and oxygen present in the synthetic backbone providing a strong chemical bond which is not easily broken (ie gold does not rub off the surface).

Table 3.13c XPS-Oxygen 1s peak heights and positions

Sample ID	Fabric type	Peak 1		Peak 2	
		Binding energy (eV)	Height (counts)	Binding energy (eV)	Height (counts)
Undyed	Nylon	531.4	407	532.6	2556
AW494P	Nylon	531.2	593	532.2	1879
AW495A	Nylon	531.2	838	532.0	1233
AW495C	Nylon	531.4	1430	532.4	794

Figure 3.102 Oxygen 1s XPS spectrum of AW495C

Table 3.13d XPS-Nitrogen 1s peak heights and positions

Sample ID	Fabric type	Peak 1		Peak 2		Peak 3	
		Binding energy (eV)	Height (counts)	Binding energy (eV)	Height (counts)	Binding energy (eV)	Height (counts)
Undyed	Nylon	399.8	312				
AW494P	Nylon	399.8	902				
AW495A	Nylon	399.6	588	400.0	101	407.0	67
AW495C	Nylon	399.8	918	400.8	217

Figure 3.103 Nitrogen 1s XPS spectrum of AW494P

Figure 3.104 Nitrogen 1s XPS spectrum of AW495A

Figure 3.105 Nitrogen 1s XPS spectrum of AW495C

Table 3.13e XPS-Gold 4f peak heights and positions (all Nylon fabric)

Sample ID	Peak 1		Peak 2		Peak 3		Peak 4		Peak 5	
	Binding energy (eV)	Height (counts)	Binding energy (eV)	Height (counts)	Binding energy (eV)	Height (counts)	Binding energy (eV)	Height (counts)	Binding energy (eV)	Height (counts)
AW494P	84.0	418	84.6	200	87.6	293	88.2	149		
AW495A	83.6	715	84.4	338	85.2	125	87.4	501	88.0	254
AW495C	84.0	1381	85.0	643	87.6	844	88.2	608

Figure 3.106 Gold 4f XPS spectrum of AW494P

Figure 3.107 Gold 4f XPS spectrum of AW495A

Fluorescence spectroscopy was performed on samples AW494P, AW495A and AW495C (see **Figure 3.109**).

AW495A and AW495C show almost identical plots to that of untreated Nylon (see **Figure 3.15**), the only difference being a decrease in intensity of the main peak – 3.5-6 compared to ~7 in untreated Nylon.

AW494P has a peak shape similar to that of AW459D (**Figure 3.80**). Again a new plateau is observed between 550 and 700nm which may be caused by the gold nanoparticles fluorescing. Intensity of the main peak is approximately a tenth of the original fabric.

Figure 3.109 Fluorescence spectra of samples from Method 13

3.3.4 Effect of lowering gold concentration

Method 14: The amount of gold solution added to the fabric sample was lowered from 40 μ L to 10 μ L but visibly there is no change in the resulting fabric colour (untreated fabrics). Acid and base-treated Nylon samples show a small change in colour with the acid-treated samples being rose coloured instead of the normal purple colour and the base-treated fabric samples having little colour change from the undyed samples; only a faint pink/purple colour is observed. A more dramatic change was expected, i.e. a yellow or green as lowering the concentration of gold should have prevented the particles from aggregating to form larger particles which have been shown in previous methods to give the purple colour.

AA analysis shows that the untreated and acid-treated Nylon samples take up almost all (<1ppm remains) of the gold present but the base-treated Nylon only takes up 25-75% of the available gold. This may explain why the fabric has little or no colour visible.

Table 3.14a Results for Method 14 – overnight colour development.

Sample ID	Fabric	Colour after development
AW455B	Polyester	White with dark purple spots
AW455C	Nylon	Patchy white & pink/purple
AW455D	Polyester-Lycra	Faint purple/grey
AW455E	Nylon-Lycra	Patchy magenta, white & purple/grey

Table 3.14b Results for Method 14 – 3-14 day uptake and colour development (starting concentration 40ppm Au).

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA)	% Uptake
AW203D	Nylon	Red/purple with large grey patches in creases	0	100
AW203E	Nylon	Fairly even dark pinky grey	1	98
AW203F	Nylon	Cotton candy pink with white patches, one darker purple patch	10	75
AW205G	Nylon	Patchy blue/grey & purple	5	88
AW205H	Nylon	Very pale pink (almost white). Some odd spots	1	98
AW205I	Nylon	No colour change	29	28
AW205J	Nylon	Patchy red/purple & grey/purple	1	98
AW205K	Nylon	Very pale purple with a few white patches & one dark spot	0	100
AW205L	Nylon	White with a large faint pink patch	27	33
AW210B	Nylon	Patchy pink & purple	12	70

Method 15: The amount of gold solution added to the fabric sample was lowered further to the equivalent of 5 μ L (10 μ L gold solution in 20mL Millipore water). Again a dramatic change was expected but not observed, the fabrics are pink/rose coloured, pale purple or in the case of the base-treated fabric off white/grey is seen.

AA analysis shows a wide range of gold concentrations are up taken by the Nylon samples. Untreated and acid treated Nylon take up 85-100% of the available gold. Base-treated Nylon takes up 0% for two of the samples (3 and 7 days) but 95% for the 14 day sample. From these results it would be expected that the 14 day base-treated sample would have more colour than the off/white that is observed.

Table 3.15 Colour after development for Method 15 Nylon samples and Atomic Absorption results (starting concentration 20ppm Au).

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA)	% Uptake
AW205M	Nylon	Pastel red/purple with light grey patches near edges, darker on one side	0	100
AW205N	Nylon	Very light grey/off white with white patches	1	95
AW205O	Nylon	No colour change	20	0
AW206A	Nylon	Fairly even mid grey/purple, redder on edges with light patches	3	85
AW206B	Nylon	No colour change	0	100
AW206C	Nylon	No colour change	20	0
AW206D	Nylon	Fairly even red-purple with light grey spots near edges	3	85
AW206E	Nylon	Patchy pink-grey with white patches	2	90
AW206F	Nylon	Slightly off white/grey	1	95

Method 16: For this method the gold concentration was increased slightly from the previous two methods but is still only half the concentration of earlier methods at 20 μ L (instead of 40 μ L). Results are similar to all the previous methods with a range

of purples observed. Again the shade of purple seems to depend on the treatment of the fabric, with the acid and base-treated Nylon samples having more pink/red tints to them.

AA analysis shows that for all samples 85-100% of the gold present in solution is taken up by the fabric.

Table 3.16 Colour after development for Method 16 Nylon samples and Atomic Absorption results (starting concentration 80ppm Au).

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA)	% Uptake
AW203A	Nylon	Even dark purple-blue	1	99
AW203B	Nylon	Patchy light purple & grey	3	96
AW203C	Nylon	Fairly even red purple, lighter red & dark purple patches in creases	1	99
AW205A	Nylon	Pastel purple, lighter in creases	3	96
AW205B	Nylon	Off white with medium & dark pink patches	0	100
AW205C	Nylon	Dark red-purple with light purple in the creases	5	94
AW205D	Nylon	Fairly even pastel purple, odd lighter patch	2	98
AW205E	Nylon	Patchy grey/purple & pastel purple, a few dark purple spots	1	99
AW205F	Nylon	Even dark red/purple with one lighter stripe in crease	5	94
AW210A	Nylon	Patchy dark & light purple	12	85

Method 17: Previous methods maintained the samples at room temperature or heated in the water bath during uptake and development. Method 17 looks at the effect of lowering the temperature to $\sim 4^{\circ}\text{C}$, combined with lower gold concentrations ($10\mu\text{L}$) added to the Nylon samples.

After 7-21 days in the fridge the samples showed little or no colour development. However, once removed from solution and stored at room temperature some colour did eventually become visible. The untreated Nylon samples showed the most colour development with three shades of patchy purple the result. Acid and base-treated Nylon samples attained patchy off white, cream or pale pink colours. This suggests that in order to have colour development some heat is required (i.e. above room temperature) otherwise the gold sits on the surface of the fabric as Au^{3+} and does not reduce to form gold nanoparticles.

AA analysis shows that for all samples 68-100% of the available gold is taken up by the fabric samples.

Table 3.17 Colour after development and after storage for Method 17 Nylon samples and Atomic Absorption results (starting concentration 40ppm Au).

Sample ID	Fabric	Colour after development	Colour after storage	Au ppm left in solution (AA)	% Uptake
AW207A	Nylon	Patchy grey/yellow & white	Patchy purple-pink	3	93
AW207B	Nylon	Pale yellow	Pink patches in creases	0	100
AW207C	Nylon	No colour change	Patchy pale pink & orange	13	68
AW207D	Nylon	Pale yellow & white	Patchy light & medium purple-pink	13	68
AW207E	Nylon	No colour change	Patchy white & pale pink	2	95
AW207F	Nylon	No colour change	Slightly off white	11	73
AW207G	Nylon	Patchy light & medium purple, lighter in creases	Patchy light & medium purple, lighter in creases	4	90
AW207H	Nylon	Patchy cream & pink	Patchy cream & pink	2	95
AW207I	Nylon	Pale pink (accidently thrown out)

ColourQuest measurements were performed on all samples from Methods 14-17 and can be seen in **Figures 3.115-3.119** below.

As in previous methods, **Figure 3.115** shows that measurements can be arranged by fabric type. Polyester and Polyester-Lycra® with little or no visible colour have high L^* values and relatively neutral a^* and b^* values, indicating that there is only a small change from the original undyed fabrics (**Figure 3.2**). Nylon and Nylon-Lycra® have moderate L^* values, $+a^*$ (red) values and $-b^*$ (blue) values corresponding to the purple colour visible in the fabric samples.

The remaining ColourQuest graphs have the samples grouped by fabric treatment as they are all Nylon samples. Untreated Nylon for all methods (except AW207G from Method 17) have virtually identical $+a^*$ (red) and $-b^*$ (blue) values but differing L^* values indicating that they are just different shades of red-purple. AW207G from Method 17 has a much lower $+a^*$ value which can be seen visibly as the fabric is more blue-purple (rather than red-purple). The acid-treated samples from all methods are a mixed bunch – some show little variation from the original undyed Nylon (AW207B and AW207E), some have moderate to high (60-80) L^* values indicating that they are paler shades and the rest have similar or identical values to the purple untreated Nylon samples. Except for the samples from Method 16, all the base-treated Nylon samples show values similar to the undyed fabrics. The base-treated Nylon samples from Method 16 have similar values to the purple fabrics seen in other methods with moderate L^* (~50) values, $+a^*$ values and $-b^*$ values.

Further analysis was carried out on samples AW203E and AW203F from Method 14, AW206D and AW206E from Method 15 and AW203A and AW203C from Method 16.

UV/vis reflectance spectroscopy performed on samples AW203E, AW203F, AW206D, AW206E, AW203A and AW203C results in spectra (**Figure 3.120**) that are very similar to the other pink-purple samples from previous methods (e.g. AW909B from Method 4). Once again an absorption peak is observed at 525nm corresponding to the absorption of cyan/green light but the reflection percentages in the orange/red range (>600nm) vary greatly between the samples. The lighter samples have most of their reflection percentages greater than 50% with the darker samples having reflections below 50%. All samples also absorb around 60% of wavelengths in the ultraviolet region (<380nm).

SEM was performed under both SEI and backscatter conditions at varied magnifications on samples AW203E, AW203F, AW206E, AW203A and AW203C. Selected images and EDS maps can be seen below in Figures 3.121-3.129. Although the samples have similar visible colours, each sample shows different particle sizes and distributions.

SEM images of AW203E (**Figure 3.121**) show that gold nanoparticles have been formed on the fibre surface in various shapes and sizes. At magnifications over 20,000 times, it can be seen that the particles are mainly spherical in shape with a few trigonal and hexagonal plates visible. Distribution of the particles is reasonably even compared to previous samples. The spherical particles range in size from 50-80nm in diameter with the trigonal and hexagonal plates being slightly larger at around 50-100nm in diameter.

EDS mapping performed on AW203E (**Figure 3.122**) at 10,000 and 60,000 times magnification shows that the gold nanoparticles are again seen as bright red areas. There was some melting/distortion of the fibre by the electron beam (10,000 times magnification) which gives the nitrogen the appearance of an uneven distribution. Chlorine appears to have an even distribution over the whole fibre surface.

Cross sections obtained of AW203F (**Figure 3.123**) again show that the fibres are cylindrical in shape with the gold nanoparticles mainly observed on the uncut edges. A few gold nanoparticles are observed on the surface of the cross section but this is most likely from particles being dragged across the surface during the preparation process (cutting) rather than the particles being bonded to the surface. Upon magnifications up to 50,000 times it is observed for the most part the particles are uniform in size, shape and distribution across the fibre surface. The spherical particles are much smaller than in previous samples with most ranging between 20 and 40nm in diameter. A few larger nanoparticles and bunches are observed but the majority of particles are singular. This change in size however does not seem to have affected the colour of the Nylon much as it is still a pale purple.

Figure 3.123 SEM images of AW203F. (Clockwise from top) Under SEI conditions at 4,000 times magnification, corresponding image under backscatter conditions, under backscatter conditions at 50,000 times magnification, under backscatter conditions at 15,000 times magnification.

EDS mapping performed on AW203F at 4,000 times magnification under backscatter conditions produced an interesting result. The gold nanoparticles were too small to be clearly visible on the map but large concentrations of calcium, magnesium and silicon can be seen (**Figure 3.124**). As these elements were not present in the starting fabric or added to solution they must be contaminants from the lab, possibly obtained when the fabrics were dried or during the storage period. However, the colour of the sample does not appear to be affected by these contaminants.

AW206E has a fairly even distribution of gold nanoparticles across the fibre surface but it appears to be uneven as the particles are different shapes and sizes. Most particles are individual spheres with diameters ranging from 10 to 100nm but some are starting to fuse together along their edges. A few trigonal plates are observed with a wider range of sizes (20-300nm) and some nanorods (up to 100nm long) are starting to form.

Images at 10,000 times magnification under SEI and backscatter conditions and the corresponding EDS map (**Figure 3.126**) show that there is a large concentration of gold (red) along the right hand edge of the fibre. These particles are large with most being over 100nm in diameter. Nitrogen and chlorine are evenly distributed over the fibre surface.

The cross section of AW203A was not cut cleanly so the rough edges can be seen in **Figure 3.127** below. Like previous cross sections the majority of the gold can be seen on the side of the fibre and only a few are visible on the cut surface (due to transference from the cutting blade). The nanoparticles are exclusively spherical with diameters ranging from 20 to 130nm.

A close up of the ragged edge (18,000 times magnification) shows an interesting cluster of gold nanoparticles. On the one right hand edge there is a large concentration of particles even though virtually no others are present in the surrounding area. No scientific explanation can be given for this unusual cluster as it has the same elemental make up of the rest of the fibre.

Figure 3.127 SEM images of AW203A. (Left) Under SEI conditions at 3,000, 18,000 and 25,000 times magnification, (Right) Corresponding images under backscatter conditions.

EDS mapping performed on sample AW203A shows large concentrations of iron, sodium and silicon as well as the usual gold and chlorine (**Figure 3.128**). Again iron, sodium and silicon must be contaminants from the lab (sodium silicate is produced) as these elements were not present in the starting fabric or added to solution, but were possibly picked up when the fabrics were dried or during the storage period. The colour of the sample does not appear to have changed due to the presence of these contaminants. Under backscatter conditions at 15,000 times magnification the

gold nanoparticles appear as bright red spots with the chlorine having even distribution across the fibre surface.

SEI and backscatter performed on AW203C results in the images seen in Figure 3.129 below. The side-on image at 3,000 times magnification shows that the gold nanoparticles are fairly evenly distributed over the surface. On further magnification (15,000 times) it is seen that the particles are spherical with diameters of approximately 50nm. Some larger particles up to 500nm in diameter are also seen on the fibre surface.

Large black circles of various sizes can be seen in the SEI images and more clearly in the backscatter images. This appears to be a defect in the fibre itself, possibly from when the fibre was extruded. As the fibres have been coated in carbon it is hard to tell whether these are pores or not. Most likely these are pores caused by defects in the fibre which may not have been seen if the cross section wasn't performed.

Fluorescence spectroscopy was performed on samples AW203E, AW203F, AW206D, AW206E, AW203A and AW203C (see **Figure 3.130**).

All samples show almost identical plots to that of untreated Nylon (see **Figure 3.15**), the only difference being changes in intensity of the main peak.

AW203A (untreated) and AW203C (base-treated) have approximately the same peak intensity as the undyed Nylon – 6.5-8.2 compared to ~7. AW206D (untreated) shows

a decrease in intensity ~ 2 and the remaining three samples AW203E (acid-treated), AW203F (base-treated) and AW206E (acid-treated) all show approximately three times the intensity of the undyed fabric. From these results the intensity appears to be based on the amount of gold present in the sample rather than on the fabric treatment (pre dyeing).

Figure 3.130 Fluorescence spectra of samples from Methods 14-16

3.3.5 Effect of adjusting pH of solution before fabric is added

Method 18: The pH of the dilute gold solution was adjusted in 1 pH increments before the fabric samples were added to see if the colour produced by the gold nanoparticles can be tailored this way. Unfortunately this was not the case as the resulting fabrics are still red-purple in colour or off white/grey. What it did show is that there is a defined range of pH's (3-10) that the fabric has to be at in order for the gold nanoparticles to attach to the Nylon and Nylon-Lycra® fibres.

Table 3.18 Fabric type, colour after development and Atomic Absorption results for Method 18 (starting concentration 80ppm Au).

Sample ID	Fabric	pH	Colour after development	Au ppm left in solution (AA)	% Uptake
AW222A	Nylon	2	Pink-grey fabric, one large red/purple/blue spot on edge	0	100
AW222B	Nylon	3	Pink-purple fabric, light purple in creases	0	100
AW224A	Nylon-Lycra	2	Off white (pale grey-purple)	0	100
AW224B	Nylon-Lycra	3	Red-purple with pale purple patches in creases	0	100
AW224C	Nylon-Lycra	4	Fairly even red-purple with two pale purple patches	2	98
AW224D	Nylon	4	Red-purple with pale purple patches in creases (one large corner)	1	99
AW224E	Nylon-Lycra	5	Dark red-purple with lighter areas	1	99
AW224F	Nylon	5	Red-purple with lighter areas on two corners (opposite)	0	100
AW224G	Nylon-Lycra	6	Red-purple with pale purple patches in creases	0	100
AW224H	Nylon	6	Fairly even red-purple with a few slightly lighter areas	1	99
AW224I	Nylon-Lycra	7	Dark red-purple with light purple patches in creases	1	99
AW224J	Nylon	7	Relatively even red-purple	0	100
AW224K	Nylon-Lycra	8	Pastel purple with a few lighter patches	1	99
AW224L	Nylon	8	Purple-red with lighter areas in the creases	Water evaporated	-
AW224M	Nylon-Lycra	9	Purple with two blue spots & grey spots all over the fabric	Contaminated solution	-
AW224N	Nylon	9	Even purple-red with a few grey spots	13	84
AW224O	Nylon-Lycra	10	Fairly even purple with a few lighter patches	2	98
AW224P	Nylon	10	Even pastel purple-red with one grey corner	Contaminated solution	-
AW225A	Nylon-Lycra	11	Slightly off white	12	85

Table 3.18 cont Fabric type, colour after development and Atomic Absorption results for Method 18 (starting concentration 80ppm Au).

Sample ID	Fabric	pH	Colour after development	Au ppm left in solution (AA)	% Uptake
AW225B	Nylon	11	Faint grey	43	46
AW225C	Nylon-Lycra	12	No colour change	44	45
AW225D	Nylon	12	No colour change	29	64

ColourQuest measurements were performed on all samples from Method 18. The samples were grouped by fabric type and the results can be seen in **Figure 3.132** below. Each fabric type shows the same trend in ColourQuest values. The samples at either end (AW222A, AW225B, AW225D, AW224A, AW225A and AW225C) show little difference from the original undyed Nylon and Nylon-Lycra® samples. AW224N and AW224P have moderate L^* values (>50) and $+a^*$ (red) values backing up the visible pink colour of the samples. AW224K, AW224M and AW224O have lower a^* values (~ 10) leading to a blueing of the fabric (blue-purple compared to red-purple in

other samples). The remaining samples have slight variations in their L* values indicating that they are different shades of the same colour (red-purple). These results back up the visual observations made previously.

Figure 3.132 ColourQuest measurements of Method 18 fabric samples

Further analysis was carried out on samples AW222B, AW224B, AW224I, AW224J, AW224O and AW224P from Method 18.

UV/vis reflectance spectroscopy performed on samples AW222B, AW224B, AW224I, AW224J, AW224O and AW224P results in spectra (**Figure 3.133**) that are similar to the other red-purple samples from previous methods (e.g. AW206D from Method 15). The absorption peak at 525nm is observed corresponding to the absorption of cyan/green light but the reflection percentages in the orange/red range (>600nm) vary greatly between the samples. All samples show a gradual increase in reflection percentages between 525 and 900nm. Only AW224P shows peaks and absorption peaks in the ultraviolet region (<380nm), the remaining samples have almost a constant reflectance of 40% in this region.

Figure 3.133 UV/vis reflectance spectra of samples from Method 18

SEM was performed under both SEI and backscatter conditions at varied magnifications on samples AW222B, AW224B, AW224O and AW224P. Selected images and EDS maps can be seen below in **Figures 3.134-3.140**. Although the samples have similar visible colours, the particle sizes and distribution are different for each sample.

SEM images of AW222B (**Figure 3.134**) show an uneven distribution of various sized, spherical gold nanoparticles are present on the fibre surface. The particles

range in size from 40-100nm. Aggregates are not observed but there are quite a few particles that are close together on the fibre, mainly down the right hand side.

Like previous samples EDS mapping performed at 25,000 times magnification (**Figure 3.135**) confirms that the particles seen are gold. Nitrogen and chlorine are evenly distributed across the fibre surface.

SEM images of AW224B under SEI and backscatter conditions at various magnifications (**Figure 3.136**) show that spherical gold nanoparticles are present on the fibre surface although they have an uneven distribution. These particles appear to range in size from 20-80nm. A few particles appear to have aggregated and fused together at the edges to form larger bunches. Some large blocks of material appear to be sitting on the fibre surfaces but under backscatter conditions it is revealed that these are lighter elements than gold indicating that they are contaminants – the EDS maps below confirm this.

EDS mapping performed on sample AW224B shows a large concentrations of calcium and silicon along with the usual gold and chlorine (**Figure 3.137**). The majority of particles are bright red (gold) but there is one large calcium particle and one large silicon particle visible. As these elements were not added to solution or present in the original undyed fabric they are contaminants – possibly picked up from the lab environment. Again chlorine was also mapped and shows an even distribution across the image.

SEM images of AW224O (**Figure 3.138**) show that there are sparsely distributed, spherical gold nanoparticles on the fibre surfaces. A few particles are located close together but these have not fused together to form large clumps.

Under SEI conditions at 10,000 times magnification, large randomly shaped patches of material appear to be sitting on the fibre surface. Under backscatter conditions these areas appear dark with only a few bright white spots (gold) indicating that they are made up of lighter organic elements such as oxygen, nitrogen etc.

Unlike previous samples, SEM images of AW224P (**Figure 3.139**) show that hardly any gold nanoparticles are present on the fibre surface. There appears to be significantly more particles in the background than on the fibres themselves. The particles on the fibre surface are spherical with diameters ranging from 40 to 200nm.

Under SEI conditions at 10,000 times magnification large blocks of material appear to be sitting on the fibre surface. Under backscatter conditions these blocks do not appear as bright white spots (heavy elements such as gold) indicating that they are lighter organic elements such as carbon, chlorine etc.

EDS mapping performed on sample AW224P shows a large concentration of calcium (**Figure 3.140**). It appears as large blocks but as these blocks are in the background of the image and not on the fibre surface they most likely had no effect on the visible fabric colour. Gold and silicon were also mapped and show an even distribution across the image except for one large silicon block in the bottom right hand corner. This block also overlaps with one of the calcium blocks indicating that it may be calcium silicate present – another compound produced in the lab which may be causing the contamination of the samples.

Fluorescence spectroscopy was performed on samples AW222B, AW224B, AW224I, AW224J, AW224O and AW224P (see **Figure 3.141**).

All samples show similar plots to that of untreated Nylon and Nylon-Lycra® (see **Figure 3.15**), the main differences being changes in intensity of the main peak and a new plateau on the right hand side of the peak in some samples.

AW222B and AW224J show a decrease in peak intensity compared to the original undyed Nylon – 4 compared to ~7. AW224P is the only sample that shows an increase with a peak height close to 16. AW224B, AW224I and AW224O have approximately the same peak intensity as the undyed Nylon-Lycra® – 2.5-3.5 compared to ~3.

AW222B, AW224B and AW224J all show a small plateau between 550 and 650nm. Most likely this is caused by the gold nanoparticles fluorescing. As there is a small number of nanoparticles in comparison to the other functional group present in the fabric a larger peak is not seen.

Figure 3.141 Fluorescence spectra of samples from Method 18

3.3.6 Results of large scale uptake (Conical flasks and glass reactor tube)

Method 19: Larger samples of Nylon were cut and weighed so the same ratio of gold to fabric could be used to see if the colour obtained after uptake and development is the same. This was indeed successful as the two samples obtained (**Figure 3.142**) show an identical red-purple colour. Visibly there is no difference between the two samples and this is confirmed by the ColourQuest results below in **Figure 3.144**. As the samples were laid flat at the bottom of the conical flasks rather than being folded in to a small glass sample vial, none of the patchiness of the previous samples is observed. Instead an attractive even coloured fabric is produced.

Table 3.19 Colour after development for Method 19 Nylon samples and Atomic Absorption results (starting concentration 40ppm Au).

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA)	% Uptake
AW212A	Nylon	Even red-purple	2	95
AW212B	Nylon	Even red-purple	0	100

Method 20: As Method 19 was successful an even larger scale uptake and development was attempted. Large Nylon and Nylon-Lycra® samples were hung in a glass reactor tube in order to have flat surfaces like the previous method. Unfortunately the fabric was larger than the tube so some overlap of the fabric occurred at the edges. This affected the resulting colour as the gold solution could only effectively get to the fabric exposed directly to the solution. After uptake the fabrics were cut in half and developed under different conditions. The Nylon sample developed in the water bath shows the same colour result as the samples from Method 19 above where as the sample developed in the reactor tube is a darker purple. Both show a lighter gradient towards the edges where the fabric overlapped. These colour differences combined with the AA results suggest that there was some gold solution remaining when the samples were separated leading to further uptake and development of the reactor sample and therefore a darker colour due to particle growth or agglomeration.

Previous methods have showed that there is little colour difference between Nylon and Nylon-Lycra® samples when the same conditions are applied to both fabrics but

the result in this method is completely different. The sample developed in the water bath shows patchy red-purple fabric which is darker at one end and gradually gets lighter. This dark end was originally located at the bottom of the reactor tube (where the diluted gold solution comes in), which suggests that the fabric removed all the available gold from the solution before it reached further up the fabric i.e. top of the reactor tube. In future the gold solution would need to be circulated and evenly mixed to achieve an even uptake. The sample that was left in the reactor tube is only a faint purple indicating that little or no uptake was achieved by this half of the fabric (which was located at the top of the tube), backing up the original hypothesis above.

Table 3.20 Fabric type, reaction conditions, colour after development and Atomic Absorption results for Method 20 samples.

Sample ID	Fabric		Colour after development	Au ppm left in solution (AA)	% Uptake
AW213A	Nylon	Water bath	Red purple strip down the middle with lighter purple strips down edges	0	100
		Reactor	Dark purple/grey. Darker in the middle getting lighter towards the edges	0	100
AW218A	Nylon-Lycra	Water bath	Darker purple at one end (bottom of reactor)	0	100
		Reactor	Some patchy purple but mostly white	0	100

ColourQuest measurements were performed on all samples from Method 19 and Method 20. They can be seen in **Figure 3.144** and **Figure 3.145** below.

The Method 19 samples all have identical values, even after the colourfastness tests had been performed (see paragraph at end of section below), reaffirming the visual results. The $+a^*$ (red) and $-b^*$ (blue) values combined with the moderate (~ 50) L^* values gives rise to the red-purple colour seen in the fabric.

The Method 20 sample results have a bit more variety. AW213A (water bath) has identical values to the Method 19 samples. AW213A (reactor) is a darker blue-purple shown by a decrease in a^* and b^* values. AW218A (water bath) is similar to the Method 19 samples and AW213A (water bath) with the only difference being an increase in L^* value (lighter shade). AW218A (reactor) is close to the original undyed Nylon-Lycra® with neutral a^* and b^* values and an L^* value >80 .

Further analysis was carried out on all samples from Method 19 and Method 20.

UV/vis spectroscopy was performed on all samples from Method 19 and Method 20. The results can be seen in **Figure 3.146** below.

AW212A, AW212B, AW213A (water bath) and AW218A (water bath) all show similar spectra with the only difference being the amount of reflection in the 600-900nm range (orange to red). AW213A (reactor) has a similar spectrum to the dark purple samples from previous methods, for example AW901E from Method 1. Interestingly in the previous samples the reflectance was down at approximately 20% but in AW213A (reactor) the reflectance is up around 80% even though visibly the colour is identical. AW218A (reactor) shows a fairly constant reflection across the visible spectrum (380-740nm) with only a small absorption peak at ~525nm corresponding to the absorption of cyan/green. This gives rise to the faint purple colour observed in the fabric.

SEM was performed under both SEI and backscatter conditions at varied magnifications on samples AW213A (water bath) and AW213A (reactor). Selected images and EDS maps can be seen below in **Figures 3.147-3.150**.

In **Figure 3.147** (AW213A (water bath)) gold nanoparticles are observed to coat the entire fibre surface. This is the most even distribution of particles seen so far out compared to all the previous samples. The nanoparticles are spherical with most

having a diameter range of 20-80nm. A few larger particles are observed with diameters up to 250nm.

EDS mapping was performed on AW213A (water bath) at 50,000 times magnification (**Figure 3.148**). Although it is clear that the bright white particles in the backscatter image are gold the map was not run for long enough to show this as clearly as in previous maps. There is a high concentration of nitrogen present due to the fabric and chlorine from the starting gold solution ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) is also seen to be distributed across the sample surface.

SEI and backscatter imaging of AW213A (reactor) shows a relatively even distribution of gold nanoparticles over the fibre surface. The particles are mainly spherical in shape but some have fused together at the edges to form larger particles. Particle size is much larger than in previous samples with the smallest having diameters of 80nm and the largest bunch having a diameter up to 800nm. This large particle size may be the cause of the dark purple colour seen in the fabric.

This time the map was run for long enough for AW213A (reactor) showing the gold nanoparticles as bright red/pink circles (**Figure 3.150**). Again there are high concentrations of nitrogen and chlorine present due to the fabric and from the starting gold solution ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) which is evenly distributed across the surface of the fibre sample.

IR spectroscopy was performed on AW213A (water bath), AW213A (reactor), AW218A (water bath) and AW218A (reactor). The resulting spectra can be seen in **Figures 3.151-3.154**.

When the IR spectra of AW213A (water bath) and AW213A (reactor) are compared to original undyed Nylon (**Figure 3.7**) the same general spectrum is seen (same peaks present but different baselines). Like the undyed Nylon the expected IR peaks are visible in the spectra – N-H stretch $\sim 3300\text{ cm}^{-1}$, C-H stretch $3000\text{--}2900\text{ cm}^{-1}$, C=O (visible as a shoulder) $\sim 1700\text{ cm}^{-1}$, N-H bend $\sim 1630\text{ cm}^{-1}$, C-H bend $\sim 600\text{ cm}^{-1}$ and C-O $\sim 1250\text{ cm}^{-1}$.

The IR spectra of AW218A (water bath) and AW218A (reactor) were also compared to original undyed Nylon-Lycra® (**Figure 3.9**). Again the spectra have roughly the same shape as the undyed with the only differences occurring in the peak intensities and the overall baseline.

The spectra are virtually the same probably due to the fact that the amount of gold nanoparticles present (bonded) on the fibre surface is minute compared to the quantity of structural groups in the fibre itself. Any interactions with the gold would be masked by the overall fabric interactions. A decrease in all peaks compared to the main N-H peak is observed. As the N-H bend peak is merged with the C=O peak it is

hard to decisively determine from these spectra whether the gold nanoparticles are binding through the nitrogen, oxygen or both. The XPS results do determine that they bond through the nitrogen as it is a surface analysis method so small variations in the fibre surface are detected.

Figure 3.151 IR spectrum of AW213A Water bath

Figure 3.152 IR spectrum of AW213A Reactor

Figure 3.153 IR spectrum of AW218A Water bath

Figure 3.154 IR spectrum of AW218A Reactor

Fluorescence spectroscopy was performed on samples AW212A, AW212B, AW213A (water bath), AW213A (reactor), AW218A (water bath) and AW218A (reactor) (see **Figure 3.155**).

Most of the samples show similar plots to that of untreated Nylon and Nylon-Lycra® (see **Figure 3.15**). All samples show a decrease in the intensity of the main peak and a new plateau on the right hand side of the peak.

AW212A has the closest plot to that of the original undyed Nylon with only a decrease in the peak height observed – ~3.4 compared to ~7 in the undyed fabric. It also has a small plateau between 550 and 650nm, with an intensity of approximately 0.4. The remaining samples appear jagged as the intensity of the main peak is greatly decreased, therefore magnifying the peak. The main peak height ranges from ~0.1-1.3.

AW218A (water bath) has a very rough and broad spectrum due to the fact that the intensity is so low (<0.15). This shows that the sample is producing hardly any fluorescence at all, either from the gold nanoparticles or the fabric itself. The gold nanoparticles present may be masking the fluorescence from the fabric or the bonding of the particles has disrupted the fibre backbone causing the fabric to lose its fluorescence.

Figure 3.155 Fluorescence spectra of samples from Method 19 and Method 20

3.3.7 Results of gold nanoparticles prepared using a reductant after gold uptake

Method 21: The fabric samples were soaked in the diluted gold solution for 30-120 minutes before being removed and added to glass sample vials containing trisodium citrate for development to see if the colour of the fabric can be adjusted by an external reductant after the initial uptake. Unfortunately this method did not really work and the fabric colours obtained show little difference to those seen in previous methods (**Figure 3.156** and **Figure 3.157**). The Polyester and Polyester-Lycra® samples showed little or no colour change and the Nylon and Nylon-Lycra® samples gained the same red-purple or blue-purple shades as previous samples.

AA analysis confirms this as for the Polyester and Polyester-Lycra® samples only 23-51% of the gold solution was taken up by the fabric. Nylon and Nylon-Lycra® have better results with 96-99% of the gold solution up taken by the samples.

Table 3.21a Results for Method 21 – Acid-treated fabric (starting concentration 160ppm Au).

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA)	% Uptake
AW481A	Polyester	No colour change	84	48
AW482A	Nylon	Dark patchy grey-purple	2	99
AW482B	Polyester-Lycra	Fairly even purple-grey (very light)	80	50
AW482C	Nylon-Lycra	Patchy dark grey & red-purple	6	96
AW484B	Polyester	No colour change	123	23
AW484C	Polyester-Lycra	Very faint light purple/grey	109	32
AW484D	Nylon-Lycra	Patchy red-purple & grey-purple	2	99
AW484E	Polyester	No colour change	119	26
AW484F	Nylon-Lycra	Patchy red-purple, grey-purple & light pink	2	99

Table 3.21b Results for Method 21 – Base-treated fabric (starting concentration 160ppm Au).

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA)	% Uptake
AW483A	Polyester	No colour change except small purple stripe	124	23
AW483B	Nylon	Patchy dark purple/red with light areas	2	99
AW483C	Polyester-Lycra	Fairly even light grey/purple	100	38
AW483D	Nylon-Lycra	Patchy dark purple/red with light areas	1	99
AW483E	Polyester	No colour change	78	51
AW483F	Nylon	Patchy dark & light purple with some white spots	1	99
AW484A	Nylon-Lycra	Patchy purple & red-purple with a few white patches	1	99

ColourQuest measurements were performed on all samples from Method 21 and can be seen in **Figure 3.158** and **Figure 3.159** below. The samples have been grouped by fabric type to show obvious trends.

Polyester samples, both acid and base-treated, show little change in ColourQuest values from the original undyed fabric with L* values over 80, and virtually neutral a* and b* values. The Polyester-Lycra® samples show the same trend but with slightly lower L* values which gives the fabric its off-white colour.

The base-treated Nylon and Nylon-Lycra® samples as well as AW484F and AW484D (acid-treated Nylon-Lycra®) all have roughly the same $+a^*$ (15-20) and b^* values (close to neutral) but slightly different L^* values indicating that they are all shades of the same red-purple colour. AW482A (Nylon) and AW482C (Nylon-Lycra®) have slightly lower $+a^*$ values (<10) which gives the fabric a bluer colour.

Further analysis was carried out on samples AW483A, AW483B, AW483C, AW483D, AW484C and AW484D.

UV/vis spectroscopy was performed on samples AW483A, AW483B, AW483C, AW483D, AW484C and AW484D from Method 21. The results can be seen in **Figure 3.160** below.

The Polyester (AW483A) and Polyester-Lycra® (AW483C and AW484C) samples absorb strongly in the UV region (<380nm) and reflect strongly in the visible region (380-740nm). A small absorption peak is visible at ~525nm corresponding to the absorption of cyan/green light. This absorption combined with the high reflectance at other wavelengths gives the fabric its off-white appearance.

The Nylon (AW483B) and Nylon-Lycra® (AW483D and AW484D) samples absorb strongly in the 190-520nm region and gradually increase in reflection percentages up to 70% from 520-900nm. This strong reflection in the orange and red region of the spectrum gives the fabric its red-purple colour.

Figure 3.160 UV/vis reflectance spectra of samples from Method 21

Fluorescence spectroscopy was performed on samples AW483A, AW483B, AW483C, AW483D, AW484C and AW484D (see **Figure 3.161**).

All samples except AW484D show similar plots to the original undyed fabrics (see Figure 3.15), the main differences being changes in intensity of the main peak and a new plateau on the right hand side of the peak in some samples.

AW483A has the same peak shape as the original undyed Polyester but with almost twice the intensity (~20 compared to 11 in the original Polyester). AW483B shows a decrease in peak intensity compared to the original undyed Nylon – 1.8 compared to ~7 and a new small plateau is observed between 550 and 700nm. Most likely this is caused by the gold nanoparticles present in the sample fluorescing.

AW483C, AW484C show the same peak shape as the original undyed Polyester-Lycra® but both show an increase in peak intensity - 18-25 compared to ~ 5.5 in the original fabric. The fabric is faintly coloured suggesting that it is the gold nanoparticles present that are enhancing the fluorescence.

AW483D shows little difference from the original undyed Nylon-Lycra® with only a slight increase (~0.5) in peak height observed. AW484D however has a similar spectrum to AW218A (water bath) from Method 20. The spectrum is very rough and broad due to the fact that the intensity is very low (<0.2). This shows that the sample is producing hardly any fluorescence at all, either from the gold nanoparticles or the fabric itself. The gold nanoparticles present may be masking the fluorescence from the fabric or the bonding of the particles has disrupted the fibre backbone causing the fabric to lose its fluorescence.

Figure 3.161 Fluorescence spectra of samples from Method 21

3.4 Results of gold nanoparticles prepared by growth of seed particles.

Method 22: Small additions of gold were added over time to try and grow particles with uniform size and hopefully new colours. This was marginally successful as the colours produced in this method are different from all the previous methods. The fabrics are still patchy due to the way they were folded in the glass sample vials and have colours ranging from dark purple to brown/grey. Small volumes of gold solution were added in different orders yet the colours are still similar to each other indicating that it is the total amount of gold available in the sample that influences the colour.

AA analysis shows that the Nylon samples have taken up 99-100% of the available gold.

Table 3.22 Colour after development for Method 22 Nylon samples and Atomic Absorption results.

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA)	% Uptake
AW215A	Nylon	Patchy dark purple/brown with black spots	0	100
AW215B	Nylon	Slightly patchy lighter tan/purple with a few black spots	0	100
AW215C	Nylon	Dark pink/brown, darker in creases	1	100
AW215D	Nylon	Purple/grey with a light purple patch in the centre	0	100
AW215E	Nylon	Patchy light & dark brown/grey (pink)	1	99
AW216A	Nylon	Patchy pink/purple & grey/pink	1	100
AW216B	Nylon	Grey/purple/pink, purple in creases	0	100
AW216C	Nylon	Slightly lighter grey/purple/pink, purple in creases	0	100

Method 23: Gold concentrations were varied and the results show that the colour changes towards brown as the amount of gold available to the fabric increases. AW219A and AW219B had similar volumes of gold solution added to them as previous samples and unsurprisingly the colours are red-purple and blue-purple. AW220A has almost twice the gold concentration (280ppm compared to 160ppm in AW219A) and the colour is a darker red-brown. As the concentration increases further (up to 560ppm) the Nylon takes on a light brown colour similar to AW924E from Method 8. AW924E developed over time in a dark drawer but the samples in

this method developed the desired colour during the development process so the colours are stable.

Table 3.23 Colour after development for Method 23 Nylon samples and Atomic Absorption results.

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA)	% Uptake
AW219A	Nylon	Nice deep purple	0	100
AW219B	Nylon	Attractive red purple	6	93
AW219C	Nylon	Pastel red-brown with darker red patches in creases	0	100
AW220A	Nylon	Fairly even red-purple, dark purple in creases	0	100
AW220B	Nylon	Pinky brown	0	100

Figure 3.163 Photographs of samples dyed with gold nanoparticles formed by growing seed particles (Method 23)

Method 24: Following the success of Method 23 it was attempted to develop the brown colour further on Nylon and Nylon-Lycra® samples measuring the quantity of gold up taken after each addition. As the samples were removed from solution and placed in a new glass sample vial with each addition of gold solution the total amount of gold on the fibre surface could be calculated (see paragraph on cost calculation further below). Colours produced are red to tan browns indicating that there are either more gold particles on the fibre surfaces or that the particles have grown in size. AA results show that 99.4-100% of the gold from the starting solution is taken up by the fabric.

Table 3.24a Colour after development of Method 24 samples and Atomic Absorption results.

Sample ID	Fabric	Colour after development	Au ppm left in solution (AA) (separate sample vials)								
			1	2	3	4	5	6	7	8	9
AW227A	Nylon	Red-purple-brown	1	1	1	0	1	0	0	0	0
AW227B	Nylon-Lycra	Red-purple-brown	1	0	0	0	0	0	0	0	0
AW227C	Nylon	Orange-tan brown	0	0	0	4	0				
AW227D	Nylon-Lycra	Orange-tan brown with purple spots	0	0	0	1	0				

Table 3.24b Percentage uptake from each sample vial (starting concentration 80ppm (AW227A-B) or 160ppm (AW227C-D) Au in each separate vial) .

Sample ID	Fabric	% Uptake (separate sample vials)								
		1	2	3	4	5	6	7	8	9
AW227 A	Nylon	99	99	99	100	99	100	100	100	100
AW227 B	Nylon-Lycra	99	100	100	100	100	100	100	100	100
AW227 C	Nylon	100	100	100	98	100				
AW227 D	Nylon-Lycra	100	100	100	99	100

Figure 3.164 Photographs of samples dyed with gold nanoparticles formed by growing seed particles (Method 24)

Method 25: An attempt to grow particles on a larger Nylon fabric sample resulted in patchy dark red-purple fabric with a visible metallic gold strip. This metallic gold strip indicates that the gold has agglomerated to form particles that are no longer nanometres in diameter therefore not exhibiting Surface Plasmon Resonance. The colour of the rest of the fabric is darker than the samples from the previous upscale

(Method 19 and Method 20) suggesting that the growth of seed particles was successful.

Table 3.25 Colour after development of AW227E from Method 25.

Sample ID	Fabric	Colour after development
AW227E	Nylon	Patchy dark red/purple, one metallic gold strip in middle

ColourQuest measurements were performed on all samples from Methods 22-25 and can be seen in **Figures 3.166-3.169** below.

Samples from Method 22 all show slight variations in all their values with L^* values of 57-65, $+a^*$ values of 9-11 and $+b^*$ values of 1-7 which give the faint changes in the visual colour of the Nylon samples.

Method 23 samples have ColourQuest values that reinforce the visual differences in colour. AW219A, AW219B and AW220A have similar L^* (<40) and $-b^*$ (2-6) values but differ in visual colour due to their range of $+a^*$ values (8-18) with the redder samples having the higher values. AW227E from Method 25 also has similar values to these three samples with only the b^* value changing (positive instead of negative).

The brown/tan coloured fabrics (AW219C and AW220B from Method 23 and AW227A-D from Method 24) have positive values for all their ColourQuest measurement. Increasing the b^* value gives the change from blue to yellow seen in the fabric i.e. tan colour seen instead of purple. If these values were increased further (possibly by further additions of gold solution over time) it is expected that a gold colour would be observed.

Further analysis was carried out on samples AW215B and AW215E from Method 22, AW219A-C from Method 23, AW227A-D from Method 24 and AW227E from Method 25.

UV/vis reflectance spectroscopy performed on the various samples results in the spectra seen in **Figure 3.170**.

Samples AW215B, AW219A-C, AW227A, AW227C, AW227D and AW227E have spectra with a fairly constant reflectance line with only a slight concave curve (absorption) between 400 and 600nm. In these samples the reflectance percentage stays between 70-85% which is much higher than previously coloured samples and the ColourQuest measurements for these samples. Normally the samples with reflectance percentages in this range are off-white in colour. These results are unusual as the samples exhibit a range of colours (red-purple, blue-purple and tan) so therefore the spectra should be noticeably different but only slight changes in the green range (~600nm) are observed.

AW215E and AW227B show similar results to the red-purple coloured fabrics seen in previous samples even though visually they are not different from the other samples. This may be caused by the patchiness in the sample i.e. the detector is picking up a range of results from the various colours present so an overall spectrum is produced.

Figure 3.170 UV/vis reflectance spectra of samples from Methods 22-25

SEM was performed under both SEI and backscatter conditions at varied magnifications on samples AW215B, AW215E, AW227A, AW227D and AW227E. Selected images and EDS maps can be seen below in **Figures 3.171-3.182**. Compared to previous samples there are a wide range of particle sizes and distributions seen.

AW215B (**Figure 3.171**) has a large number of triangular and hexagonal plates visible on the fibre surface. Compared to previous samples these particles are enormous with diameters of up to 1 μm . One triangular plate was able to be observed side on and has a thickness of 80nm. At its widest point this plate is almost 1.4 μm , proving that gold nanoparticles have been successfully grown from smaller seed particles. Nestled amongst the plates some spherical particles are visible but these are much smaller with diameters of 50-100nm.

Like previous samples EDS mapping performed at 2,500 times magnification (Figure 3.172) confirms that the particles seen are gold. Nitrogen from the fibre and chlorine from the starting HAuCl_4 solution are evenly distributed across the fibre surface.

SEM images of AW215E (**Figure 3.173**) again show a variety of particle sizes and shapes. There are very few particles visible on the surface and the ones that are visible have diameters of 100nm-1µm. Spherical particles appear as bunches with the edges starting to fuse together in some places. Some nanorods, triangular and hexagon plates can be seen with one large odd shaped particle as well. Under backscatter conditions these particles appear as bright white so can be assumed to be gold.

Figure 3.173 SEM images of AW215E. (Clockwise from top) Under SEI conditions at 5,000 times magnification, corresponding image under backscatter conditions, under SEI conditions at 50,000 times magnification, under backscatter conditions at 25,000 times magnification.

EDS mapping confirms the particles are gold with higher concentrations at the edges of the plates and in the spherical particles suggesting that this is where the gold is the thickest. Nitrogen and chlorine once again show even concentrations across the whole of the map.

SEM images of AW227A (**Figure 3.175**) show that the sample has a fairly even distribution of gold nanoparticles across the fibre surface. Spherical particles with diameters ranging from 20 to 220nm are visible along with some long nanorods (some >1µm) and a few triangular plates. This combination of particle shapes may be what causes the pink/tan colour of the fabric as the visible colour is similar to that of AW215A and AW215E.

Figure 3.175 SEM images of AW227A. (Clockwise from top) Under backscatter conditions at 2,500 times magnification, under backscatter conditions at 10,000 times magnification, under backscatter conditions at 50,000 times magnification, corresponding image under SEI conditions.

EDS mapping (AW227A – **Figure 3.176**) shows the large gold nanoparticles as bright pink areas. The smaller nanoparticles can be seen in the gold map but once nitrogen and chlorine are overlaid they are harder to spot.

During the preparation process of AW227D dark purple fibres were observed in the fabric. When one of these fibres was pulled out individually it was unusually stretchy indicating that it was a Lycra® fibre. Under the microscope the fibre appeared to be very different from the usual Nylon fibres – the gold nanoparticles completely coat the surface of the fibre and some layers are also observed (**Figure 3.177**). As can be seen in the image below Nylon fibres were laid over top to give a comparison. Under backscatter conditions it can be seen that the gold nanoparticles have preferentially attached to the Lycra® fibre. This is an extremely interesting result but unfortunately was discovered at the end of the study therefore no further investigation was performed.

AW227D (Nylon) has a few spherical particles scattered over the fibre surface. These particles have diameters of 100-500nm with the larger particles caused by the edges of smaller particles fusing together.

In comparison AW227D (Lycra®) has layers of spherical nanoparticles visible along with triangular plates, nanorods and even some rectangular prisms. This preferential deposition of gold nanoparticles on the Lycra® surface is probably due to the increased nitrogen component in the backbone of the fibre (see **Figure 1.12**) i.e. more functional groups to attach to. It is also likely that the shape and quantity of gold nanoparticles present on the fibre surface gives the colour of the fabric in this sample, rather than from the Nylon as in previous samples.

EDS mapping shows the high concentration of gold present as bright red/pink areas. These particles block out the signals from the nitrogen and chlorine leading to black areas in their individual maps (**Figure 3.180**).

AW227E had a visible metallic gold strip on the fabric surface so a sample of this fabric was taken to compare it to the images from the remaining purple fabric (see **Figure 3.182** below). The gold coloured fabric (**Figure 3.181**) has large clumps of gold particles with each particle in the clump having a diameter over 500nm. Some smaller spherical gold nanoparticles cover the rest of the fibre surface with diameters of approximately 50-100nm. The large clumps are no longer small enough to display Surface Plasmon Resonance so the fabric gains the metallic colour of gold.

Figure 3.181 SEM images of AW227E (gold coloured fabric). (Clockwise from top) Under backscatter conditions at 2,500 times magnification, under backscatter conditions at 25,000 times magnification, under backscatter conditions at 40,000 times magnification, corresponding image under SEI conditions.

In comparison these large clumps are not visible in the SEM images of the purple coloured fabric (**Figure 3.182**). Instead spherical particles ranging from 20 to 100nm in diameter cover the fibre surface. A few of these particles have fused together at the edges but the majority are seen as individual, randomly dispersed nanoparticles. The particles observed in this sample are the most evenly dispersed and most uniform size out of all the samples observed in this research.

Florescence spectroscopy performed on selected samples from Methods 22-25 (**Figure 3.183**) showed that all dyed Nylon samples show similar peak shapes to that of the undyed fabric. AW215B, AW215E, AW219A and AW227E show a decrease in peak intensity (1.2-5.5 compared to ~7 in the original fabric) as well as a new small plateau between 550 and 700nm, most likely due to fluorescence from the gold nanoparticles in the samples. AW219B also shows this plateau but has the same intensity as the original fabric. AW227A has the same intensity and instead of a plateau the peak intensity drops off slower leading to a gradual decline of the tail end of the peak. AW219C and AW227C also show this gradual decline as well as an increase in peak intensity (12-16) suggesting that this peak shape is also due to gold nanoparticles producing fluorescence of their own.

The two Nylon-Lycra® samples AW227B and AW227D show slightly smoother peak shapes to the original undyed fabric. An increase in intensity is seen in AW227B but it is a small change - ~5 compared to 3 in the undyed Nylon-Lycra®, AW227D has an identical intensity of the main peak.

Figure 3.183 Fluorescence spectra of samples from Methods 22-25

3.5 Results summary, colourfastness tests and cost calculations

3.5.1 Results Summary

A wide range of methods were attempted on samples of Polyester, Nylon, Polyester-Lycra® and Nylon-Lycra®. Some of the fabric samples were acid or base-treated before the addition of gold solution but the resulting colours were not remarkably different when compared to the untreated fabric samples. Colours of the fabrics were mainly various shades of red-purple but there were some pink, blue-purple and tan coloured fabrics produced.

AA analysis proved that for Polyester samples some gold is taken up by the fabric but most leaches back out over time and is not reduced. Polyester-Lycra® retains more of the gold solution and this is shown by the decrease in ppm (part per million) gold left in solution after uptake as well as a visual colouring in the fabric. Nylon and Nylon-Lycra® show excellent uptake results with 90-99% of the available gold taken up by the fabric in most cases.

ColourQuest measurements performed on all samples showed that the L^* , a^* and b^* values usually confirmed the visual results, the only problems came when samples were patchy in colour so the results became average readings of the sample. Small differences in colour shade were detected and could be seen easily on the graphs. Results showed general trends based on fabric type with Polyester and Polyester-Lycra having ColourQuest measurements closest to the original undyed fabrics. Darker fabrics tended to have L^* values under 50 and the red-purple coloured fabrics were shown on the graphs by positive a^* and b^* values.

UV/vis reflectance spectroscopy showed similar results between samples of the same colour. Dark purple fabrics had virtually a straight line of reflectance under 50%. The remaining samples were mostly red-purple and had spectra with a small absorption peak ~525nm corresponding to the absorption of green/cyan wavelengths. From ~525nm to 900nm a gradual increase in reflectance was seen giving the fabrics their redder appearance. Most samples showed a series of absorption and reflection peaks in the UV region of the spectrum so further research may need to be done into the stability of the fabric over time (absorption of UV light may degrade the fabric eventually).

SEM and EDS analysis showed that a variety of particle shapes and sizes were formed. Gold nanoparticles formed were mainly spherical in size with diameters of 20-100nm, some did fuse together at the edges to form larger aggregates though. In the tan and gold coloured fabrics, triangular and hexagonal plates were formed with diameters as large as 1µm.

As seen in Table 3.26 below the particle size, shape and amount of coverage on the fibre surface influences the visually observed colour of the fabric. Samples that appear tan or gold in colour have mainly large particles (>500nm) that are either made up of small spheres fused together or are large plates (trigonal, hexagonal); therefore, Mie's laws do not appear to apply. Light coloured samples generally have a few small particles (<100nm) that are spaced out over the fibre surface. Most of the samples produced are shades of purple. There seem to be two scenarios to explain this:

1. Small particles (<100nm) that have aggregated together or have a higher percentage of coverage on the fibre surface.
2. Large particles (agglomerates mainly, 100>500nm) that are sparsely distributed across the fibre surface.

Table 3.26 Results summary of particle size given by SEM, overall coverage percentage of fibre surface and fabric colour observed visually

Method	Sample ID	Fabric	Particle size	Coverage	Visual colour
1	AW901E	Nylon	~30nm, aggregates <200nm	~50%	Dark purple
2	AW916A	Nylon	30-100nm	<20%	Pale pink/peach
4	AW909C	Nylon	20-50nm, aggregates <100nm	~40%	Dark pink/rose
4	AW910E	Nylon	20-60nm	<20%	Light purple
7	AW915B	Nylon	>1µm	<10% +contaminants	Gold middle, peach edges
7	AW915D	Nylon	<100nm (peach), >500nm (gold)	10-30% +contaminants	Gold middle, peach edges
8	AW924A	Nylon	~100nm	<20%	Dark purple
8	AW924E	Nylon	100nm (spheres), >2µm (plates)	~30%	Tan brown

Table 3.26 cont Results summary of particle size given by SEM, overall coverage percentage of fibre surface and fabric colour observed visually

Method	Sample ID	Fabric	Particle size	Coverage	Visual colour
9	AW459D	Nylon	10-80nm	~40%	Light, medium & dark purple
13	AW494P	Nylon	20-100nm, aggregates <500nm	~50%	Dark purple/red
13	AW495A	Acid-treated Nylon	50-100nm, aggregates <1µm	<20%	Red & purple
13	AW495C	Base-treated Nylon	Aggregates 80-500nm	~30%	Dark purple
14	AW203E	Acid-treated Nylon	50-100nm	~40%	Dark pinky grey
14	AW203F	Base-treated Nylon	20-40nm	<20%	Cotton candy pink
15	AW206E	Acid-treated Nylon	10-100nm (spheres), 20-300nm (plates)	~40%	Pink-grey
16	AW203A	Nylon	20-130nm	~30%	Dark purple-blue
16	AW203C	Base-treated Nylon	~50nm, aggregates <500nm	~40%	Red purple
18	AW222B	Nylon	40-100nm	<20%	Pink-purple
18	AW224B	Nylon-Lycra®	20-80nm	<20%	Red-purple
18	AW224O	Nylon-Lycra®	Aggregates <500nm	<20%	Purple
18	AW224P	Nylon	40-200nm	<20%	Pastel purple-red
20	AW213A (water bath)	Nylon	20-80nm, aggregates <250nm	~60%	Red purple
20	AW213A (reactor)	Nylon	Aggregates 80-800nm	<20nm	Dark purple/grey
22	AW215B	Nylon	50-100nm (spheres), <2µm (plates)	~30%	Light tan/purple
22	AW215E	Nylon	100nm-1µm	<20%	Light & dark brown/grey
24	AW227A	Nylon	20-220nm, >1µm (nanorods)	~50%	Red-purple-brown
24	AW227D (Nylon)	Nylon-Lycra®	100-500nm	~20%	Orange-tan brown

Table 3.26 cont Results summary of particle size given by SEM, overall coverage percentage of fibre surface and fabric colour observed visually

Method	Sample ID	Fabric	Particle size	Coverage	Visual colour
24	AW227D (Lycra®)	Nylon-Lycra®	200nm-2µm	~90%	Dark purple fibre
25	AW227E (gold)	Nylon	50-100nm, aggregates >500nm	~60%	Gold strip
25	AW227E (purple)	Nylon	20-100nm	~50%	Dark red/purple

XPS spectra obtained show changes in both nitrogen and oxygen suggesting that both are needed for the reduction of Au^{3+} to gold nanoparticles. Similar work within the group suggests that for wool the gold nanoparticles bind primarily through sulfur with nitrogen as a secondary binding site ³. As there are no sulfur groups in any of the synthetic fabrics used in this project it would make sense that nitrogen and another atom, in this case oxygen, are needed for the reduction to take place on the fibre surfaces. This may also explain why little success has been achieved with Polyester as only one functional group ($\text{C}=\text{O}$) is available to reduce the gold.

The amine groups appear to be oxidising to imine groups allowing this reduction to occur. Shifts in the main peaks and formation of new peaks in some spectra show that the gold nanoparticles are binding to the fabric directly and are not just sitting on the surface. This provides the fabric with the desired colourfastness property.

IR spectroscopy run on selected samples showed little change from the original undyed fabrics, most likely due to the fact that the amount of gold on the surface compared to the quantity of functional groups on the fabric surface is very small. The signals from the fabric probably masks any structural changes caused by the gold nanoparticles.

Fluorescence spectroscopy run on selected samples also showed little change from the original undyed fabrics. Most samples had the same peak shapes as the original samples but peak intensity either increased due to fluorescence from the gold nanoparticles or decreased due to masking.

3.5.2 Colourfastness Tests

AW212B was sent away to Ag Research in Christchurch for industry standard rubbing tests. The sample was subjected to The Woolmark Company™ 165 August 2002 colourfastness to rubbing (textile materials and dyed sheepskins) tests. The test assessed staining onto a white cloth when the fabric is rubbed, wet and dry under standard conditions. The stained cloths are then assessed both wet and dry and graded against a set of Standard Grey Scales. Grading is on a scale of 1 to 5 with 1 being excessive staining and 5 being no staining at all.

AW212B achieved a grade of 4 for wet fabric against the Grey Scales and 5 for dry fabric against the same scales. The instrumental assessment gave a grade of 3-4 for wet fabric.

These are excellent results as it shows that the fabrics are colourfast and stable so would be a viable alternative to current organic dyes which wash out of your clothes and fade over time.

3.5.3 Cost calculations

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution costs ~NZ\$40 per 10mL of solution (4% w/w Au). Samples AW227A-D use 180-200 μL of this gold solution therefore 0.007-0.008g Au is present in the sample (0.014-0.016g $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) totalling a cost of \$0.70-0.80/0.4g fabric or \$1.75-2.00/g fabric. AW227E costs slightly less as a larger fabric sample was used. 0.014g of gold is present on the Nylon fabric costing \$1.44/1.7g fabric or \$0.85/g fabric.

The majority of samples however only use 20-40 μL of gold solution, reducing the cost to ~NZ\$0.40/g fabric.

From these costs it can be seen that currently this process is expensive but as the fabric size increases the cost of the gold used to dye the sample decreases. Before this process is viable for industry the sample colours would need to be consistent and the amount of gold used minimal as to keep the cost at a reasonable level.

3.5.4 Future Work

The main focus of future work could be expanding the colour range of the Nylon and Lycra® fabrics by extending the range of metals used. Silver, Palladium and Platinum nanoparticles could be either produced on their own or as bimetallic colloids e.g. AuAg^{53, 54} so as to retain the stability properties of the gold and add antimicrobial properties from the silver.

Other work could include further research into Lycra® fibres on their own or combined with other fibres, including a more in depth characterisation of the fibres to determine binding sites. If this is successful then other fabrics containing the functional groups needed for the reduction process of gold nanoparticles could be explored.

4 Conclusions

Colloidal gold nanoparticles of various sizes and hence colours were successfully prepared and transferred to samples of Polyester, Nylon, Polyester-Lycra® and Nylon-Lycra® fabrics. However, the resulting fabric colours were mainly red and purple. Some tan coloured fabrics were produced in the later methods suggesting that growing particle size from seed nanoparticles is the most successful way to tune colours produced and provide even colour distribution. The patchiness of the samples appears to be caused by the way the fabric was folded in the glass sample vials but it may also be due to processing lubricants added during the fibre and fabric formation.

Uptake of the gold solution and development of the resulting colours had the best results at 50°C. Above this temperature the particles tended to aggregate slightly forming darker, dirtier colours. At and below room temperature the reduction process occurred very slowly so would not be suitable for industrial processes but some of the colours produced were very attractive. In order to get attractive colours at a reasonable development time future work could look into the effect of using temperatures between 25 and 50°C combined with longer development times (e.g. 7 days instead of overnight or 2 days).

Nylon and Nylon-Lycra® samples had the most even and vibrant colours indicating that the presence of nitrogen (amine) is needed for the reduction of Au^{3+} in AuCl_4^- to form gold nanoparticles. Polyester samples were the most unsuccessful and this is due to the fact that there is no nitrogen present, only oxygen functional groups, but surprisingly some uptake and development is still observed. Polyester-Lycra® samples were marginally successful as the Lycra® contains some amine groups allowing some gold nanoparticles to attach and impart a faint colouring on the fabric. The comparison of the different synthetic fibre types allows the conclusion that the functional groups need to be picked carefully in order to produce the best possible colours. Further research may be needed that looks into a wider variety of synthetic fabrics that contain amine groups as part of the chemical backbone.

Analysis by XPS shows that the gold nanoparticles appear to be chemically bound to the surface of the fibres through the N-amide bonds present in the fabric. Spectra from both the pre-prepared colloids and the in-situ method show little difference,

indicating that in both cases the amine groups in the fabric are the main influence on gold nanoparticle formation (via reduction) and, in the case of the pre-prepared colloids, the external reductant plays a supporting role. This strong bonding provides the fabric with excellent wash and rub fastness properties, allowing the consumer to have a product where the colour will outlast the life of the garment. Fabric tested by Ag Research Ltd, Textiles Division, Lincoln Research Centre, Christchurch showed excellent results – 4 for wet rubbing and 5 for dry rubbing against grey scales (scale 1 = excessive staining, 5 = no staining).

SEM images show that the gold is present on the surface of the fabric and does not penetrate into the fibres due to lack of porosity allowing smaller amounts of gold to be used during synthesis. Particle size and shape is varied so further methods will need to be devised to produce uniform nanoparticles. Distribution of these particles also appears to be random suggesting that particles are binding across more than one site – possibly a fabric with more nitrogen present is needed to ensure even distribution.

Cost calculations show that for the fabric samples with colours produced by growth of seed particles (180-200 μ L gold solution added) the cost of dyeing the fabric is very expensive (NZ\$1-2/g) so only suitable for high end markets but the other samples that used only 20-40 μ L of gold solution are more attractive economically to the discerning consumer who wants an alternative to the current dyes that rely on crude oil and cause heavy pollution of rivers by the dyeing factories IF the colour is attractive and reproducible.

If the colour range can be extended and the results reproducible at larger scales, then this research provides industry with an environmentally friendly alternative to current organic dyes.

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6 Appendix A

6.1 XPS reference spectra

6.1.1 Polyester⁵¹

6.1.2 Nylon 6-6⁵¹

6.1.3 Gold⁴

Fig. 5. Deconvoluted high resolution Au 4f peaks for (a) polyamine-synthesised nanocrystalline gold, (b) the same particles adsorbed onto Merino wool fibres. Inset: Au³⁺ peaks fitted to the deconvoluted data in (b), in addition to Au⁰ and Au⁺.

6.1.4 XPS spectra of original, undyed fabrics

Major differences can be seen in some of the spectra below.

- Base treated Polyester-Lycra® carbon 1s and oxygen 1s spectra show shift towards lower binding energies and broadening.
- The acid treated Nylon carbon 1s spectrum shows a large broadening in the main peak which hides the smaller secondary peak. When peaks are fitted only three peaks are observed compared to four in the untreated fabric. In the acid treated Nylon oxygen 1s spectrum there is a large broad hump and two smaller humps observed compared to the single asymmetric peak in the untreated fabric. A new shoulder peak has appeared in the acid treated Nylon nitrogen 1s spectra broadening the peak (untreated nylon has one sharp symmetric peak).
- In the base treated Nylon spectra only the nitrogen 1s spectrum is the same as the untreated fabric. Only three peaks can be fitted to the carbon 1s spectrum instead of the four in the untreated fabric spectrum. The oxygen 1s peak has split with the larger peak now being 2eV lower in binding energy. This broadens and distorts the asymmetry of the peak.

7 Appendix B

7.1 ColourQuest raw data

7.1.1 Original fabrics

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
Polyester	95.00	-1.18	2.60	87.84	84.61
Nylon	95.72	-0.99	2.94	89.75	85.77
Polyester-Lycra	94.93	-1.10	2.50	87.66	84.56
Nylon-Lycra	95.90	-1.09	2.21	89.88	87.16

7.1.2 Pre made colloids

Method 1

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW901A	57.13	6.72	-2.91	25.87	26.79
AW901B	90.64	2.85	0.86	79.03	76.90
AW901C	75.16	8.48	-2.92	49.17	51.49
AW901D	86.90	4.19	0.34	70.95	69.74
AW901E	49.20	0.12	-3.54	17.47	19.55
AW901F	38.15	1.12	-2.30	10.20	10.93
AW901G	45.37	0.60	-3.59	14.64	16.34
AW901H	37.83	4.35	-4.85	10.02	11.63
AW904A	57.25	7.60	-3.80	25.78	27.48
AW904B	79.06	7.75	-2.37	56.49	57.49
AW904C	63.21	5.79	-6.55	31.07	36.73
AW904D	65.27	10.48	-3.36	35.64	36.94

Method 2

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW916A	75.44	10.34	6.70	53.24	42.99
AW916B	75.07	9.98	-1.59	50.60	49.93
AW916C	78.02	8.34	-1.09	55.05	54.48
AW916D	79.83	6.91	-0.09	57.65	56.81

Method 3

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW903A	81.53	3.28	3.22	60.45	56.46
AW903B	73.13	4.58	3.97	46.67	42.04
AW903C	92.30	-0.21	2.10	81.77	79.03
AW903D	85.94	2.12	4.05	68.93	63.39
AW904E	71.77	6.18	2.56	44.41	41.24
AW904F	65.82	4.61	-0.27	35.34	35.24
AW904G	92.06	0.04	1.98	81.23	78.67
AW904H	80.52	4.23	3.66	59.27	53.84

Method 4

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW909A	57.95	10.67	-4.15	25.90	28.52
AW909B	81.61	7.49	0.13	61.32	59.62
AW909C	67.42	9.16	-0.04	39.75	37.29
AW909D	57.76	3.07	-2.23	26.53	27.09
AW909E	53.03	1.85	-4.50	21.07	23.53
AW909F	53.12	1.58	-4.51	21.02	22.92
AW910A	80.76	2.95	-1.19	58.97	59.48
AW910B	91.42	0.26	0.83	79.65	78.64

AW910C	89.92	1.08	0.46	76.59	75.80
AW910D	79.83	4.70	-1.79	57.32	58.36
AW910E	76.53	3.43	-2.01	51.10	52.88
AW910F	70.40	4.19	-3.74	41.45	44.58

Method 5

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW911A	56.43	3.55	-2.79	24.64	26.05
AW911B	49.84	2.27	-4.41	18.24	20.53
AW922C	83.80	3.90	7.68	66.22	56.03
AW922D	86.57	2.57	5.59	70.77	63.24
AW922E	80.59	4.61	8.84	60.84	49.30
AW922F	82.59	4.37	7.18	63.80	54.38
AW922G	76.01	4.83	4.36	51.59	45.91
AW923A	43.67	1.82	-4.07	13.60	15.29

Method 6

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW919A	91.26	-1.25	9.35	80.91	68.92
AW919B	90.30	-0.99	9.70	79.33	67.03
AW919C	91.07	-1.15	9.50	80.48	68.41
AW919D	90.20	-0.54	8.86	78.57	67.32
AW919E	89.49	-0.27	10.10	77.46	64.58
AW919F	90.02	-0.77	9.12	78.22	66.64
AW919G	80.52	5.84	4.54	60.51	53.51
AW919H	71.63	3.44	2.39	43.86	41.71
AW920A	66.54	2.56	0.88	36.06	35.90
AW920B	59.88	3.72	-0.18	27.95	28.51
AW920C	61.21	2.63	0.81	29.49	29.35

AW920D	56.30	1.55	1.23	24.15	23.81
AW921D	66.30	9.86	1.62	38.27	34.62
AW921E	50.17	7.51	-1.25	19.52	19.24
AW921F	52.74	5.77	-2.26	21.04	22.15
AW921G	48.90	4.55	-1.81	17.46	18.59
AW922A	40.55	5.05	-2.19	11.52	12.47
AW922B	51.48	1.51	0.91	19.69	19.41

7.1.3 Gold nanoparticles prepared In-Situ on fibre surface

Method 7

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW915A	68.21	5.09	0.68	38.67	37.82
AW915B	58.85	8.36	11.70	29.63	20.29
AW915C	52.95	8.20	12.40	23.42	15.10
AW915D	60.07	8.44	12.27	31.07	21.10

Method 8

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW924A	50.57	11.90	0.13	19.91	18.83
AW924B	79.96	7.15	11.88	61.30	45.49
AW924C	73.86	4.21	11.27	49.48	37.41
AW924D	62.27	6.78	14.67	33.96	21.95
AW924E	50.14	8.45	12.48	20.55	13.15
AW924F	67.71	4.83	-0.78	37.57	38.18
AW925A	79.04	4.16	10.26	57.99	45.75
AW925B	63.02	4.78	7.58	33.31	26.72
AW925C	60.39	4.69	7.84	30.26	23.82
AW925D	59.71	6.65	11.72	30.35	21.04

AW925E	72.74	4.63	0.93	45.12	44.10
AW925F	78.43	1.69	7.36	55.58	47.47
AW925G	72.79	2.59	7.77	46.58	38.69
AW925H	58.08	5.51	9.22	27.91	20.87
AW925I	55.37	6.61	11.00	25.24	17.64
AW926A	67.92	6.57	2.51	39.16	35.91
AW926B	68.48	4.75	9.42	40.78	31.81
AW926C	65.86	3.98	8.03	36.75	29.70
AW926D	61.36	5.40	9.82	31.67	23.73
AW926E	52.30	8.83	12.81	22.79	14.45

Method 9 - Untreated fabric uptake.

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW933A	87.56	0.30	-0.64	69.71	72.34
AW933B	46.33	10.49	-0.99	16.41	15.96
AW933C	78.04	-0.62	-2.95	51.44	56.39
AW933D	48.47	9.81	-1.64	18.01	17.93
AW933E	87.59	-0.12	-2.52	68.62	74.67
AW933F	50.34	9.72	0.11	19.73	18.65
AW933G	78.03	-0.41	-2.08	51.71	55.42
AW933H	48.69	10.23	-0.54	18.37	17.59
AW934A	87.22	-0.47	-3.12	67.24	74.61
AW934B	49.02	9.58	-0.83	18.37	17.98
AW934C	77.43	0.07	-2.86	50.47	55.15
AW934D	48.37	11.28	-0.18	18.22	17.17
AW934E	87.64	0.14	-0.86	69.57	72.78
AW934F	48.07	10.87	-0.42	17.81	17.01
AW934G	78.66	0.62	-1.01	53.61	55.38
AW935A	48.05	11.36	-0.62	17.84	17.12
AW935B	87.32	0.87	1.16	70.53	69.61

AW935C	48.85	14.34	1.38	19.22	16.79
AW935D	78.06	0.88	-1.14	52.63	54.41
AW935E	47.82	12.55	-0.34	17.97	16.78
AW937A	88.28	0.31	1.22	72.43	71.56
AW937B	48.24	12.34	0.82	18.27	16.58
AW937C	78.00	0.96	-0.85	52.66	54.01
AW937D	49.15	10.62	-0.25	18.75	17.83

Method 9 – Second untreated fabric uptake.

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW455F	91.08	0.61	1.74	79.19	76.85
AW456A	45.74	11.73	-0.32	16.11	15.24
AW456B	78.87	1.97	0.73	55.15	54.00
AW456C	46.64	13.63	1.88	17.33	14.92
AW457A	90.32	0.95	1.68	77.59	75.31
AW457B	42.77	12.92	-1.44	13.85	13.53
AW458A	80.50	0.54	-0.59	57.25	58.26
AW458B	42.95	14.38	-1.52	14.12	13.67
AW458C	87.87	2.17	1.20	72.56	70.69
AW458D	42.47	13.99	-1.17	13.81	13.20
AW458E	78.32	1.26	-0.61	53.60	54.44
AW458F	47.05	13.01	-1.34	17.16	16.60
AW458G	88.46	2.08	0.48	73.54	72.67
AW458H	43.39	12.91	-1.78	14.31	14.10
AW459A	75.73	1.50	-1.28	49.22	50.69
AW459B	42.56	13.43	-2.23	13.65	13.68
AW459C	90.13	0.51	1.74	77.00	74.77
AW459D	45.28	13.25	-1.90	15.56	15.54
AW459E	76.38	1.33	-0.97	50.40	51.46
AW459F	42.28	13.41	-2.18	13.56	13.47

Method 9 – Acid treated fabric uptake.

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW462B (AW468E)	90.60	0.75	2.18	78.24	75.30
AW462C (AW468F)	40.83	15.29	-0.69	13.02	11.97
AW462D (AW468G)	78.59	1.88	0.33	54.67	53.90
AW462E (AW468H)	44.37	12.66	-2.26	15.00	14.97
AW469A (AW473E)	90.79	0.47	1.70	78.38	76.30
AW469B (AW473F)	37.73	19.11	-0.47	11.01	10.05
AW469C (AW473G)	78.84	2.11	-0.06	54.83	54.83
AW469D (AW473H)	42.05	17.75	-0.78	13.84	12.75
AW469E (AW473A)	91.78	-0.22	2.26	80.48	77.75
AW469F (AW473B)	40.45	16.22	-1.80	12.38	12.13
AW470A (AW473C)	78.61	1.29	-1.36	53.85	55.62
AW470B (AW473D)	44.43	14.90	-1.53	15.34	14.73
AW470C (AW472I)	90.48	0.68	1.84	77.83	75.48
AW470D (AW472J)	42.78	15.66	-1.70	14.10	13.63
AW470E (AW472K)	77.82	2.82	-0.83	52.94	53.83
AW470F (AW472L)	44.10	15.80	-1.67	15.04	14.54
AW470G (AW472E)	90.74	0.71	1.57	78.31	76.31
AW471A (AW472F)	47.29	12.75	-1.84	17.19	17.05
AW471B (AW472G)	77.46	3.16	-0.93	52.42	53.29
AW471C (AW472H)	48.49	13.80	-1.95	18.18	18.06
AW471D (AW472A)	92.13	-0.42	2.90	81.51	77.72
AW471E (AW472B)	40.28	14.93	-0.22	12.46	11.46
AW471F (AW472C)	78.32	1.16	-0.15	53.68	54.06
AW471G (AW472D)	45.06	14.27	-2.03	15.71	15.37

Method 9 – Base treated fabric uptake

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW461A (AW468A)	88.96	0.91	1.77	74.52	72.31
AW461B (AW468B)	38.60	14.00	-1.74	11.15	10.98
AW461C (AW468C)	74.53	2.43	-1.88	47.22	49.32
AW462A (AW468D)	43.58	12.62	-2.33	14.28	14.47
AW462F (AW467K)	89.53	0.81	0.75	75.24	74.68
AW462G (AW467L)	42.30	13.27	-2.15	13.44	13.47
AW463A (AW467M)	76.74	2.74	-2.24	50.97	53.28
AW463B (AW467N)	38.72	13.88	-2.40	11.20	11.28
AW463C (AW467G)	92.33	-0.02	1.76	81.75	79.65
AW463D (AW467H)	40.62	14.46	-2.31	12.40	12.42
AW463E (AW467I)	75.16	2.19	-2.20	48.19	50.64
AW463F (AW467J)	38.90	14.50	-2.13	11.32	11.30
AW463G (AW467C)	91.73	0.42	1.69	80.51	78.38
AW463H (AW467D)	40.30	14.84	-1.68	12.25	11.99
AW464A (AW467E)	76.21	3.07	-2.29	50.06	52.48
AW464B (AW467F)	37.92	14.03	-2.68	10.72	10.90
AW464C (AW466E)	91.53	0.41	1.54	79.98	78.11
AW464D (AW466F)	40.17	12.74	-2.02	11.98	12.04
AW464E (AW467A)	78.69	1.75	-1.58	53.95	56.14
AW464F (AW467B)	39.41	11.21	-2.95	11.52	11.91
AW464G (AW466A)	90.63	0.85	1.75	78.30	75.90
AW464H (AW466B)	44.25	14.03	-1.36	14.99	14.52
AW465A (AW466C)	80.43	1.50	-1.98	56.98	59.70
AW465B (AW466D)	44.94	13.20	-2.06	15.36	15.30

Method 10 – Development overnight

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW946D	42.94	9.55	-2.23	13.85	13.98
AW946E	45.06	11.87	-2.81	15.34	15.78
AW946F	41.50	8.41	-1.78	12.78	12.83
AW946G	44.43	9.66	-1.43	14.96	14.74
AW947A	41.07	9.36	-2.12	12.43	12.66
AW947B	43.36	10.86	-2.14	14.12	14.24
AW947C	41.62	7.48	-3.52	12.54	13.55
AW947D	42.74	9.99	-3.59	13.49	14.41
AW451B	89.10	1.61	2.30	75.34	71.91
AW451C	77.84	3.18	1.32	53.81	51.39

Method 10 – 1 hour development

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW950C	83.76	2.06	-1.04	58.99	65.05
AW950D	45.25	12.99	-2.32	15.46	15.71
AW950E	78.00	2.66	-0.25	53.26	53.53
AW950F	49.08	12.38	-2.16	18.59	18.73

Method 11

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW486A	50.90	10.47	-1.21	20.18	19.78
AW486B	51.80	9.67	-1.80	20.92	20.88
AW486C	59.15	8.58	-0.52	28.64	27.51
AW486D	51.82	10.91	-1.04	21.28	20.49
AW486E	48.87	8.91	-2.60	18.26	18.71
AW486F	44.35	9.20	-1.72	14.92	14.76

AW487A	55.37	9.73	-1.00	24.19	23.83
AW487B	55.24	8.43	-1.21	24.25	23.81
AW487C	55.22	8.10	-0.59	24.21	23.45
AW487D	61.44	7.81	-0.29	31.04	29.96
AW487E	57.81	9.07	-0.21	27.03	25.87
AW487F	58.89	9.30	-0.71	28.39	27.34
AW487G	52.84	9.81	-1.72	21.82	21.76
AW488A	52.15	9.37	-1.87	21.28	21.22
AW488B	43.67	9.74	-1.46	14.44	14.17

Method 12 – Room temperature

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW493A	72.12	10.86	2.82	46.82	41.50
AW493B	61.48	7.84	-2.63	30.37	31.59
AW493C	79.09	5.48	1.24	56.55	53.90
AW493D	90.95	0.83	1.50	78.85	76.85
AW493E	92.01	0.66	1.69	81.33	78.92
AW493F	92.39	0.41	2.07	82.22	79.27
AW493G	48.51	11.57	-3.23	17.63	18.73
AW493H	43.16	11.69	-3.63	13.41	14.70
AW493I	43.80	10.30	-4.91	13.50	15.75

Method 12 – 50°C

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW494A	48.53	10.38	-1.41	17.88	17.84
AW494B	57.49	5.98	-0.62	25.57	25.78
AW494C	54.58	4.66	-1.32	22.46	23.24
AW494D	66.97	10.05	1.22	38.66	35.68
AW494E	62.80	9.27	0.06	32.52	31.32

AW494F	60.25	8.99	2.31	29.68	26.87
AW494G	49.38	10.22	-1.90	18.64	18.80
AW494H	49.96	9.82	-1.87	19.08	19.30
AW494I	46.71	9.80	-1.60	16.52	16.46

Method 13 – Room temperature

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW494J	53.77	11.07	-1.23	23.16	22.41
AW494K	58.81	10.73	-0.65	28.31	27.22
AW494L	70.61	9.97	0.41	43.97	41.42
AW494M	74.55	8.03	0.70	49.53	46.96
AW494N	42.94	13.14	-3.55	13.45	14.48
AW494O	44.52	10.11	-2.19	14.88	15.08
AW496A	60.68	11.00	0.05	30.47	28.88
AW496B	88.35	2.90	4.09	74.82	68.42
AW496C	55.55	9.48	-0.72	24.68	23.83

Method 13 – 50°C

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW494P	45.07	7.27	-3.90	14.43	16.27
AW494Q	43.82	7.39	-2.57	14.01	14.74
AW495A	50.87	10.07	-2.85	19.60	20.58
AW495B	43.65	11.75	-2.91	13.72	14.76
AW495C	44.15	8.89	-2.67	14.45	15.05
AW495D	47.74	9.11	-2.93	17.20	17.88
AW496D	78.74	10.49	-2.23	17.87	18.38
AW496E	53.06	13.84	-1.92	22.24	22.12
AW496F	44.48	10.41	-2.10	14.85	15.02

Method 14 – Development overnight

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW455B	89.99	0.82	1.11	76.56	75.26
AW455C	56.54	9.99	-0.96	25.34	25.05
AW455D	78.27	2.24	0.38	53.87	53.43
AW455E	52.54	10.48	-2.77	21.26	22.10

Method 14 – 3-14 days uptake and development

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW203D	51.40	10.92	-4.62	19.59	22.04
AW203E	65.12	9.08	-0.52	35.47	34.68
AW203F	77.67	7.58	-0.97	54.15	53.76
AW205G	58.16	9.07	-2.72	26.58	27.77
AW205H	69.83	11.47	-0.19	43.09	40.72
AW205I	88.45	2.99	3.89	75.36	68.68
AW205J	55.41	9.86	-3.61	23.55	25.43
AW205K	67.40	12.74	-0.92	39.10	37.89
AW205L	86.25	4.30	2.51	70.85	65.86
AW210B	78.93	5.45	-1.29	56.02	56.24

Method 15

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW205M	52.82	12.23	-5.53	20.51	23.92
AW205N	59.87	15.17	-3.17	28.82	30.08
AW205O	92.16	0.00	1.79	81.68	79.09
AW206A	49.71	13.93	-3.91	18.70	20.10
AW206B	56.67	18.10	-3.01	26.04	26.40
AW206C	92.54	0.42	2.62	82.87	78.88

AW206D	51.27	10.70	-5.85	18.84	22.63
AW206E	70.29	8.28	0.49	42.68	40.84
AW206F	88.97	1.83	0.96	75.18	73.19

Method 16

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW203A	55.67	5.75	-3.62	23.25	25.75
AW203B	63.58	8.45	1.27	33.58	31.40
AW203C	50.28	11.01	-2.95	19.02	20.10
AW205A	53.70	11.22	-1.82	22.52	22.66
AW205B	61.22	13.35	-1.75	31.09	30.62
AW205C	50.52	11.83	-1.73	19.70	19.68
AW205D	57.46	7.23	-1.62	25.91	26.35
AW205E	64.12	12.16	-2.07	34.33	34.51
AW205F	51.27	11.54	-2.50	20.10	20.74
AW210A	52.86	5.83	-5.17	20.04	23.75

Method 17

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW207A	52.50	11.17	-3.62	20.92	22.54
AW207B	85.32	4.34	0.56	67.44	66.32
AW207C	87.12	4.27	4.56	72.92	65.17
AW207D	54.70	10.92	-4.24	22.84	25.10
AW207E	84.43	2.36	-0.09	64.65	65.24
AW207F	90.97	1.78	3.70	80.21	74.10
AW207G	61.78	6.01	-3.59	30.11	32.63
AW207H	70.73	10.09	3.01	44.14	39.35

Method 18

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW222A	70.27	6.89	4.72	43.26	37.41
AW222B	42.11	13.88	-4.30	12.55	14.23
AW224A	75.79	2.37	1.24	50.08	48.48
AW224B	45.12	17.78	-1.00	15.62	15.01
AW224C	45.07	16.61	-0.85	15.64	14.89
AW224D	50.65	16.88	0.44	20.47	18.69
AW224E	48.61	16.40	-0.28	18.56	17.32
AW224F	46.88	18.80	-1.03	17.14	16.30
AW224G	44.33	18.05	-1.29	15.06	14.53
AW224H	47.13	19.15	0.89	17.55	15.66
AW224I	46.45	16.21	-2.02	16.50	16.42
AW224J	45.03	18.11	-1.68	15.37	15.22
AW224K	53.77	12.50	-1.95	22.43	22.74
AW224L	42.19	18.91	-2.24	13.25	13.41
AW224M	48.53	9.53	-3.31	17.43	18.76
AW224N	57.53	13.94	0.29	26.66	25.21
AW224O	48.63	11.65	-2.66	17.63	18.49
AW224P	65.31	11.80	-0.16	35.73	34.54
AW225A	90.24	0.64	2.15	77.38	74.58
AW225B	87.35	1.96	-0.22	70.46	71.39
AW225C	92.65	-0.07	1.62	82.32	80.44
AW225D	94.18	-0.52	2.03	86.04	83.34

Method 19

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW212A	51.92	9.55	-0.89	20.90	20.54
AW212B before scrub test	52.68	9.48	-1.42	21.16	21.49
AW212B (1) after scrub test	53.51	9.35	-2.21	21.81	22.72
AW212B (2) after scrub test	54.22	8.99	-2.12	22.53	23.33

Method 20

Sample ID		L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW213A	Water bath	54.78	11.62	-2.10	23.47	23.92
	Reactor	56.01	1.14	-3.68	23.26	26.20
AW218A	Water bath	61.71	9.04	-2.34	30.36	31.68
	Reactor	82.84	2.05	-0.40	61.86	62.40

7.1.4 Preparation of gold nanoparticles using a reductant after gold uptake

Method 21 – Acid treated fabric.

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW481A	90.11	0.97	1.34	76.95	75.24
AW482A	45.97	7.75	-2.92	15.57	16.50
AW482B	75.48	2.04	-1.82	48.98	50.78
AW482C	40.88	6.70	-2.73	12.03	12.77
AW484B	88.13	2.32	0.10	72.87	72.54
AW484C	76.53	3.42	-1.65	50.94	52.39
AW484D	45.99	16.83	0.42	16.63	15.07
AW484E	87.76	3.54	0.42	72.66	71.33
AW484F	45.26	17.44	0.53	16.23	14.45

Method 21 – Base treated fabric.

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW483A	89.12	1.33	1.60	75.07	72.86
AW483B	45.55	16.90	2.04	16.77	14.01
AW483C	77.54	3.07	0.27	53.02	52.22
AW483D	44.78	17.54	-0.54	15.82	14.56
AW483E	89.64	1.39	1.04	76.10	74.64
AW483F	48.49	18.26	2.36	19.56	16.03
AW484A	43.99	15.33	-2.06	14.89	14.62

7.1.5 Gold nanoparticles prepared by growth of seed particles.

Method 22

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW215A	59.05	10.63	5.85	29.52	23.43
AW215B	58.72	10.83	3.10	28.40	24.77
AW215C	64.97	10.91	7.44	37.19	28.73
AW215D	58.90	9.37	2.08	28.54	25.59
AW215E	59.56	11.12	6.60	30.14	23.53
AW216A	57.79	9.07	0.89	26.75	25.16
AW216B	59.39	10.17	4.95	29.44	24.33
AW216C	62.73	10.12	6.11	33.83	27.11

Method 23

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW219A	36.90	7.75	-6.61	8.81	11.71
AW219B	38.18	18.19	-3.93	10.46	11.50

AW219C	56.65	8.11	3.69	26.07	22.35
AW220A	35.35	10.23	-1.85	8.75	9.23
AW220B	53.32	11.35	7.31	23.58	17.55

Method 24

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW227A	50.55	11.68	7.66	21.27	15.22
AW227B	47.31	12.31	7.58	18.36	12.99
AW227C	59.46	13.36	13.18	31.68	19.82
AW227D	60.61	10.88	10.90	32.35	22.12

Method 25

Sample ID	L*	a*	b*	Iso Brightness 577 nm	Tappi Brightness 457nm
AW227E	29.31	16.20	2.12	6.73	5.46