Gold Nanoparticles as Colourants in High Fashion Fabrics and Textiles

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ABSTRACT

This paper presents the novel use of gold nanoparticles with different particle sizes and hence colours, as stable colourfast colourants on wool and cotton fibres for use in high quality fabrics and textiles for high end fashions. The synthesis of gold nanoparticles using monomeric or polymeric amines that serve both as a reductant to facilitate the reduction of Au^{3+} to Au^0, and as a linker to attach the nanoparticles to the amino acids in wool keratin proteins is discussed. X-ray photoelectron spectroscopy supports the bonding of the gold nanoparticles to the wool through the amine linker molecules. Electronmicroscopy shows that the nanoparticles are present on the cuticles of the fibre surface and are concentrated at the edges of these cuticles. A range of coloured fibres and fabrics have been produced.

Keywords: gold, nanoparticles, wool, textile, fashion

1 INTRODUCTION

Wool fibres have been used since historical times in fabrics and textiles for garments, furnishings and floor coverings. The wool fibres are typically about 10-40 microns in diameter and several tens of centimeters in length. They are woven into yarn that is used to make a very wide range of fabrics and textiles. The yarn or the fabric and textiles can be dyed using conventional technology to produce many different colours. *Merino* wool with its smaller fibre diameter of about 10-20 microns is highly valued for fine fabrics and commands a price premium. Wool belongs to the group of fibrous proteins consisting of α-keratins and comprises long polyhedral inner cortical cells surrounded by flattened external cuticle cells and partially by an external fatty acid monolayer, mainly 18-methyleicosanic acid. The helix arrangement of the proteins gives wool its flexibility, elasticity and crimp properties. The fatty acid layer provides some hydrophobicity to the surface which can influence further processability such as dyeing, enhancing shrink resistance and anti-static properties.

Colouration of wool fibres is achieved by dyeing with either natural dyes such as *madder (red), indigo (blue)* or synthetic dyes which are typically anthraquinone-based (the first example *alizarin* was synthesised in 1869) or azo-based compounds, typically under mild acidic conditions of pH=3-5. Colour changes resulting from exposure to UV light, repeated washing and surface abrasion from wearing are issues that adversely affect colorfastness and hence the overall quality of the fabrics and textiles. Colourfastness is particularly important in high quality fabrics and textiles for the high fashion market.

Nobel metals such as gold and silver have long been known to form stable colloids of nanosize particles. Such nanoparticles exhibit different colours due to surface plasmon resonance effects which result from the interaction of incoming electromagnetic radiation in the visible region with the collective plasmon oscillations at the metal surface [1]. The colour is dependent on the particle size and shape. Gold colloids with spherical particles of about 7-20 nm particles appear as a deep red wine colour, which progressively changes through to a blue colour with increasing particle size up to about 80-100 nm. Such colours are stable towards UV light and do not change providing there is no change in particle size, through the growth or reduction of discrete nanoparticles or agglomeration. Interestingly, colloidal gold nanoparticles have been used to colour glass dating back to about the 17th century. Also, the Lycurgus Cup dating back to around 400AD used gold and silver nanoparticles as colourants. The science was not understood until 1869 when Michael Faraday recognized and explained the role of gold as a colourant in general terms. In 1908 Mie [2] provided a theoretical explanation by solving Maxwells equations for the absorption and scattering of electromagnetic radiation by very small metallic particles – nanoparticles.

In this paper we present the novel development and use of gold nanoparticles of different sizes and colours as stable colourfast colourants on *merino* wool and cotton for high value fashion fabrics and textiles. This utilizes proprietary science and technology developed by us [3,5,6] which relates to the controlled reduction of Au^{3+} to Au^0 and the incorporation of them into a variety of wool, cotton and synthetic fibres and their corresponding fabrics and textiles. Control of the nanosize of the Au^0 particles and their binding onto the fibres are critical and govern their use in this interesting application.

2 NANOGOLD – WOOL

Gold nanoparticles in the range of about 2 -100 nm can be readily synthesised by treatment of a Au^{3+} containing solution, usually as the complex $AuCl_4^-$ ion with a reducing agent such a tri-sodium citrate [4], or monomeric and polymeric amines which act as both a reductant and a

stabilizer [3]. The citrate can also act as a stabilizer. The colour of the resulting gold colloid depends on the size of the gold nanoparticles. Examples of these colours are shown in Fig. 1.

Figure 1: Colloids of gold nanoparticles of different particle size.

The UV-Visible spectra of the red and blue coloured colloids of gold nanoparticles prepared using amines are shown in Fig. 2. This shows that the absorbance due to the transverse plasmon band [1] shifts from about 510 nm (red colloid) to about 575 nm (blue colloid) with increasing particle size. The longitudinal plasmon band at about 750 nm is also shown (green colloid). A transmission electronmicroscope image of typical gold nanoparticles is shown in Fig. 3 [3].
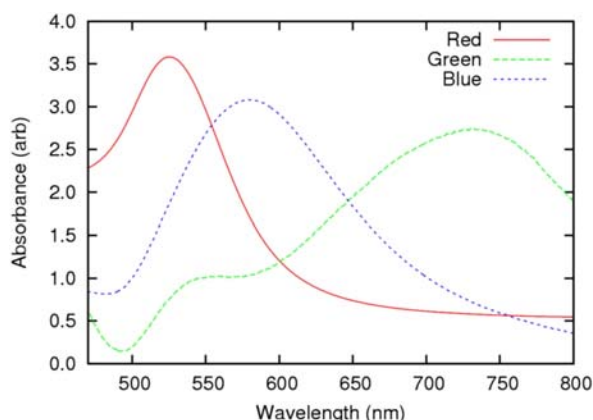

Figure 2: UV-Visible spectra of red and blue colloids of gold.
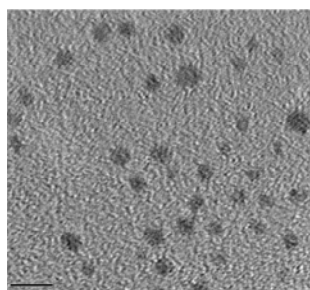

Figure 3: Transmission electronmicroscope image of gold nanoparticles. Marker bar = 5 nm.

The gold nanoparticles present in a colloid can be readily attached to wool, cotton or synthetic fibres using a linker, which can typically be an amine. When monomeric or polyamines are used as the reductant, they also conveniently function as linker molecules [3]. As gold has a strong affinity for S, it is likely that the gold nanoparticles would bind directly to the S of the cystine amino acids in the keratin proteins. However, when a stabilizer or linker is used, the gold nanoparticles are effectively isolated by the surrounding molecules and as such it is likely that the linker attaches to the N, S, O or OH groups of the amino acids in the protein chain through hydrogen bonding.

Photoelectron spectra for the Au 4f electrons of gold nanoparticles show the typical 5/2 and 7/2 peaks for gold metal. However these have been shifted to lower binding energies by about 0.6 eV, probably as a result of the amino groups bound to the gold increasing the negative charge at the gold surface (Fig. 4a) [5]. When the gold nanoparticles are bound onto *merino* wool these 5/2 and 7/2 peaks shift to higher binding energies indicating chemical bonding of the nanoparticles to the fibre through the amine (Fig. 4b) [5]. The peaks also broaden asymmetrically which probably reflect a range of possible binding sites with a slightly different chemical environment, or a component of partially reduced Au^+ [5]. The former is the preferred interpretation.
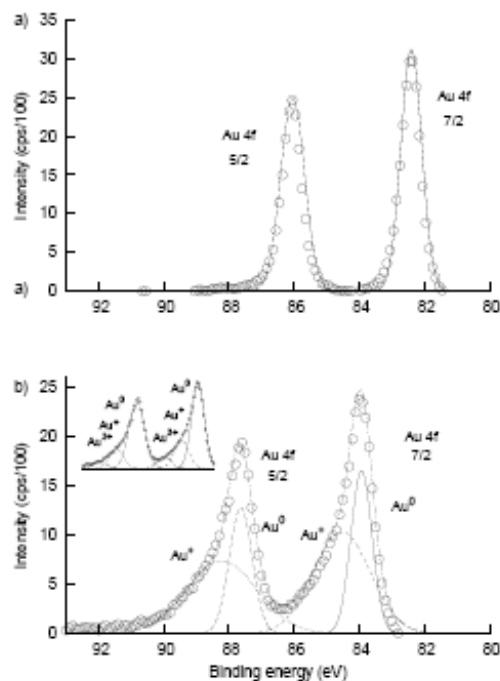

Figure 4: Au 4f X-ray photoelectron spectra for: (a) gold nanoparticles synthesised with polyamine; (b) gold nanoparticles synthesised with polyamine and bound to a *merino* wool fibre [5].

The photoelectron spectrum for the N 1s electrons for gold nanoparticles synthesised using polyamine [3] has been resolved into two peaks relating to N-Au bonds from the gold bonding to the amine linker and N-C bonds from the amine itself (Fig. 5a) [5].
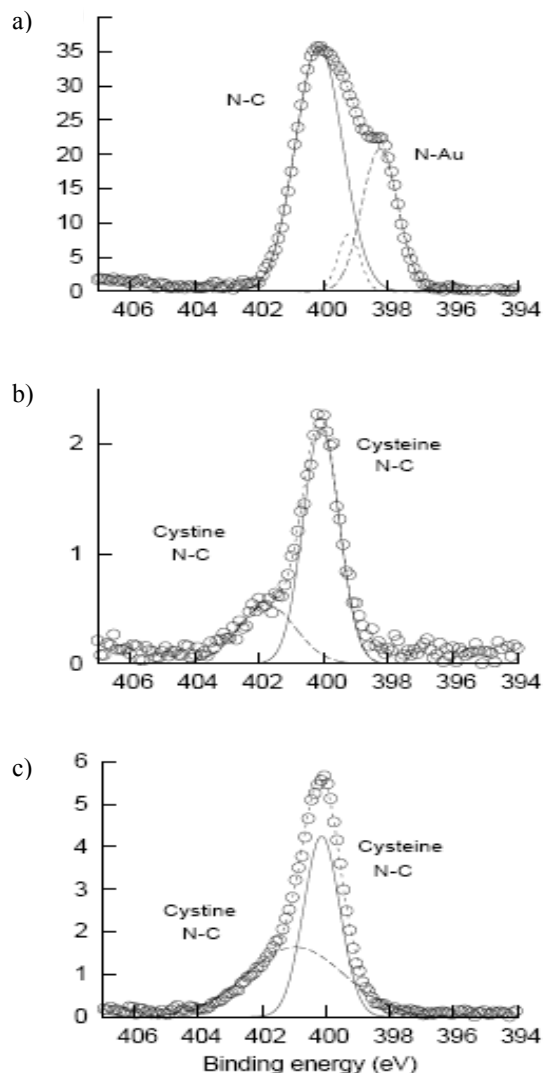
a)

b)

c)

Figure 5: N 1s X-ray photoelectron spectra for: (a) gold nanoparticles synthesised using a polyamine; (b) *merino* wool fibre; (c) gold nanoparticles bound to *merino* wool fibre [5].

The N 1s spectrum for *merino* wool fibre shows N-C bonds consistent with the cystine and cysteine amino acids in the keratin protein (Fig. 5b). For gold nanoparticles bound to the *merino* wool fibre, the N 1s spectra show the N-C cystine and N-C cysteine bonds. The N-C cystine peak is broadened and shifted to lower binding energies suggesting that the gold nanoparticles are predominately associated with the cystine amino acids (Fig. 5c). Also, the disappearance of the N-Au peak observed for gold nanoparticles when they are bound to the wool fibre, further suggests electron interaction between the gold and wool fibre through the amine nitrogen atoms [5].

Fig. 6a shows the scanning electronmicroscopy images of a *merino* wool fibre coated with gold nanoparticles where polyethyleneimmine was used as the reductant and linker. The characteristic morphology and surface cuticles of a wool fibre are shown in Fig. 6a. At higher magnification it can be seen that the cuticles are covered with an essentially uniform layer of gold nanoparticles of about 10 nm in size (Fig. 6b). Some agglomeration is present as shown by the larger particles of about 50 nm in size. The overall fibre is a pink-red colour.
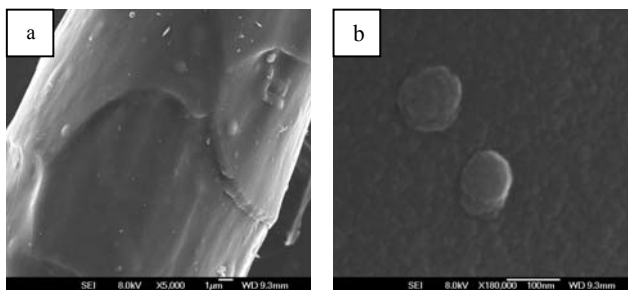

Figure 6: SEM images at different magnifications of a *merino* wool fibre coated with gold nanoparticles.

When a proprietary new methodology developed by us [6] is used to produce nanogold wool fibres at lower gold concentrations, it can be seen from backscattered electronmicroscope images that the gold nanoparticles adhere mainly to the edges of the cuticles (Fig. 7). This is due to the higher surface free energy associated with an edge rather than a planar surface. As the density of surface nanoparticles increases, there is a corresponding increase in surface coverage, although the edge coverage still dominates (Fig. 7). This is further illustrated by energy dispersive X-ray analysis for Au, which shows the highest concentration of gold at the cuticle edges (Fig. 8).
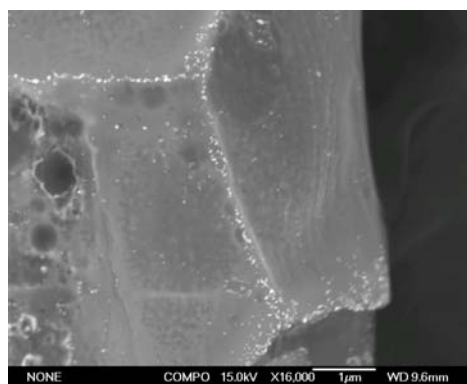

Figure 7: Backscattered electronmicroscope image of a *merino* wool fibre with gold nanoparticles on the surface and mainly at the cuticle edges.
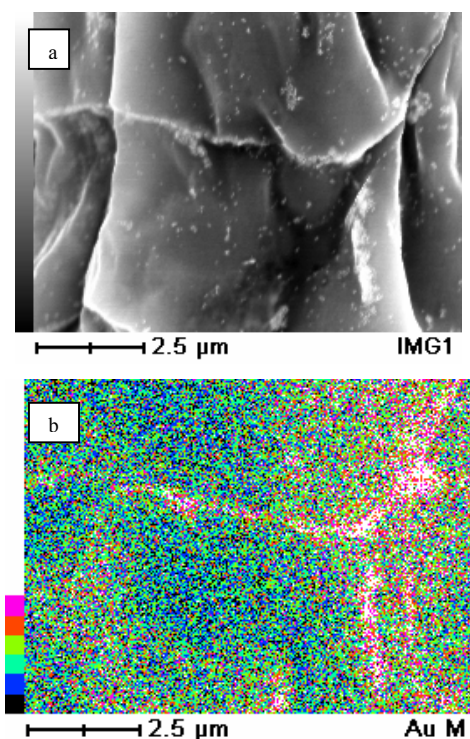
Figure 8: (a) backscattered electronmicroscope image of image of a *merino* wool fibre with gold nanoparticles on the surface; (b) energy dispersive X-ray analysis pattern for Au showing a concentration at the cuticle edges

3 NANOGOLD – WOOL AND COTTON FABRIC

Using the methodology discussed here [3,5] and more particularly new proprietary science and technology developed recently by us [6], we have coated raw top *merino* wool, *merino* wool yarn, *merino* wool fabric and cotton thread and fabric with gold nanoparticles of different sizes and hence colours, to provide new and potentially high value fabrics and textiles for the high end fashion markets. These products are colourfast since the gold nanoparticles are not degraded by UV light as many traditional dyes are. However with the current high cost of gold, the resulting nanogold products are expensive and is therefore suited to the high end market sector. In particular, our new proprietary technology enables a range of "softer" and more desirable colours to be produced. Hence we have used fine *merino* wool and added further value by the novel use of gold nanoparticles as colourants. In addition, as gold exhibits mild antimicrobial properties, these fabrics and textiles have some inherent anti-microbial resistance. Examples of wool and cotton coated with gold nanoparticles are shown in Fig. 9.
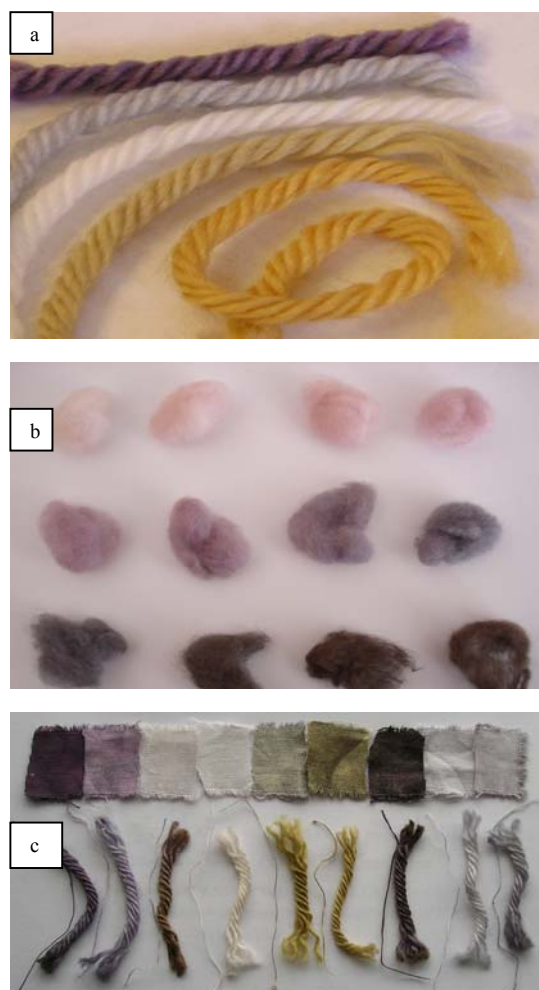

Figure 9: gold nanoparticle coloured samples of (a) wool yarn; (b) top (loose) wool; (c) cotton fabric (top) and wool yarn (bottom).

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