

Nanogold and Nanosilver Wool: New Products for High Value Fashion Apparel and Functional Textiles

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ABSTRACT

We have developed a unique and exciting new proprietary nanotechnology and product suite of high value textiles involving the use of nanogold and nanosilver as colourants and functional components in wool. This innovatively links the high value and prestige of gold and silver with high value textiles and fashion apparel through nanoscience and technology. The products contain only pure wool and pure gold or silver respectively and are environmentally desirable. Gold and silver in bulk form exhibit their characteristic metallic colour. However, when their particle size is reduced to nano dimensions they exhibit different colours due surface plasmon resonance effects resulting from the collective oscillation of conduction band electrons. The colours depend on the size and shape of the nano entities and do not fade like traditional organic dyes. The nanogold and nanosilver entities are formed by the controlled reduction of Au^{3+} to Au^0 and of Ag^+ to Ag^0 respectively, on the surface and within the wool fibres. These entities are strongly chemically bound and do not leach out or rub off. By controlling the formation and particle size of the nanogold and nanosilver in the wool fibres, an attractive range of colours in shades of pink, purple, blue-grey, grey and yellow for nanogold wool and yellow, peach, purple and green for nanosilver wool are possible. The technology and product suite have been protected by New Zealand and PCT patent applications, and are being progressed to commercialization. Investment partners are being sought.

Keywords: gold, silver, nanoparticles, colourants, wool, textile, apparel, fashion.

1 INTRODUCTION

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 and the dielectric constant of the surrounding medium. Colloids of nanogold particles with spherical particles of about 10-20 nm in size are red. As the particle size

increases, the colour changes through darker shades of red to purple, then to blue-grey for particles up to about 80-100 nm. These colours relate to a shift and broadening of the transverse plasmon resonance absorption band at about 520 nm. Gold nanorods are typically green in colour as they show this transverse band as well as a longitudinal plasmon resonance band at about 720 nm [2, 3]. These colours are stable in sunlight and UV light and do not change providing there is no change in particle size, through the growth or reduction of discrete nanoparticles or agglomeration.

Colloids of nanosilver similarly exhibit a variety of colours. Spherical nanoparticles of silver of about 40 nm in size are yellow. Increasing the particle size progressively shifts the colour from yellow to red. By increasing the size of silver triangular prisms from about 60 nm to 100 nm to about 120 nm, the colour changes from purple to blue to green.

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 [4] provided a theoretical explanation by solving Maxwells equations for the absorption and scattering of electromagnetic radiation by very small metallic particles – nanoparticles.

Wool fibres have been used since historical times in fabrics and textiles for garments, furnishings and floor coverings. The wool fibres are typically about 12-40 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 10-25 microns is highly valued for fine fabrics and fashion apparel, and commands a price premium. *Strong* wool with a fibre diameter of about 25-40 microns is used in textiles for furnishing and carpet, where higher durability is required.

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 surface hydrophobicity which can influence further processability such as dyeing, enhancing shrink resistance and anti-static properties.

Wool garments are traditionally coloured by natural dyes such as *madder (red)*, *indigo (blue)* and synthetic dyes typically anthraquinone or azo-based compounds. Unfortunately, these dyes, particularly the natural ones are not colourfast. Hence colour changes resulting from exposure to sunlight and UV light, repeated washing and surface abrasion from wearing are issues that adversely affect the overall quality of the fabrics and textiles. Colourfastness is important in high quality fabrics and textiles for the high fashion market. This is becoming even more so due to the strong environmental awareness and move towards natural and sustainable dye formulations.

New Zealand is the world's second largest producer of *merino* wool which is renowned for its fine fibre and hence its use in very high quality knitwear and fashion apparel. Similarly, New Zealand is a large producer of *strong* wool which is used in the manufacture of high quality wool carpets and hard wearing textiles.

We have innovatively captured and developed a unique and exciting new proprietary nanotechnology and product suite of high value knitwear apparel and textiles involving the use of nanogold and nanosilver as colourants and functional components in wool and other substrates [5, 6]. This links the high value and prestige of gold and silver with high quality New Zealand *merino* and *strong* wool for high value fashion apparel and textiles through nanoscience and technology.

The products contain only pure wool and pure gold or silver, making them environmentally attractive compared with current environmentally problematic dyes. Nanosilver wool and nanogold wool exhibit effective anti-microbial properties even at very low levels due to the natural anti-microbial properties of silver and gold. A key competitive advantage is that these nano entities are chemically bound to the fibres and do not wash or rub off, obviating any consumer concerns.

The technology and product suite have been protected by New Zealand and International patents (pending) [5]. *This exciting new technology and product suite is a world leading innovation and a world first. It offers attractive new investment and business opportunities for the high value fashion apparel, carpets and functional textiles markets where high quality, uniqueness, functionality and environmental attractiveness, rather than price, are the key drivers and product hallmarks.*

2 NANOGOLD - WOOL

Nanogold entities have been attached to *merino* and *strong* wool fibres using our proprietary methodology [5]. In this, we control the reduction of Au^{3+} in the AuCl_4^- ion to Au^0 to produce nanogold entities of the required particle size and shape to yield the desired colour and chemically bind them to the keratin in the wool fibres, to provide stable colourfast nanogold-wool products in an attractive range of colours. An electronmicroscope image (Fig. 1) shows the nanogold particles (white dots) binding primarily to the cuticle edges of the wool fibre with a lesser distribution over the cuticle surface. The very strong extinction coefficient of nanogold due to surface plasmon resonance effects, means that very little nanogold is required to provide a strong colour. This is shown by the very small amount of nanogold on the surface of the fibre (Fig. 1).

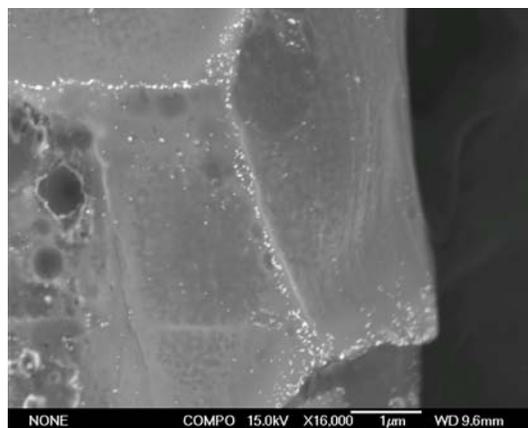


Figure 1: Backscattered electronmicroscope image of a *merino* wool fibre with nano gold on the surface and mainly at the cuticle edges.

The technology was initially developed on the laboratory scale using small quantities of *merino* and *strong* wool fibres in top or sliver form. Samples of spun yarn and woven fabric were also used but difficulties were encountered here due to the processing lubricants that were used during yarn and fabric production absorbing into the wool and interfering with the process chemistry. Further work is being carried out here. A selection *merino* wool fibres coloured with nanogold are shown in Fig. 2

The technology has been successfully scaled up to colour larger quantities of wool, preferably in the sliver or top form which have then been spun into yarn and fashioned into textiles, scarves and carpet (Figs 3, 4). No difficulties were encountered in the spinning or fabrication processes. Interestingly however, the presence of nanogold reduced the static electricity build-up which often arises during spinning in conventionally dyed wools. From this it appears that the electrical conductivity of the wool is

enhanced by the nanogold which desirably dissipates the build up of static electricity.



Figure 2: A selection of nanogold coloured *merino* wools



Figure 3: Purple nanogold-*strong* wool in coloured top form and spun into yarn.

X-ray photoelectron spectroscopy (XPS) measurements show that the nanogold is chemically bound to the sulfur in the cystine amino acids of the keratin protein. This is shown by the appearance of peaks in the XPS spectrum (Fig. 5) of the Au 4f electrons of gold in the nanogold-wool which can be assigned to Au-S bonds. Peaks from Au⁰ and Au³⁺ are also present. The sulfur 2p XPS spectrum of the nanogold wool shows a complementary reduction in the -S-S- peak compared with the -S-H peak due to the -S-S- bonds being broken and Au-S bonds being formed (Fig. 5). In the

merino wool itself, the sulfur 2p peaks for the -S-S- of cystine and the -S-H of cysteine are similar in size [6].



Figure 4: Mauve nanogold-*merino* wool as a ball of yarn and woven into a scarf.

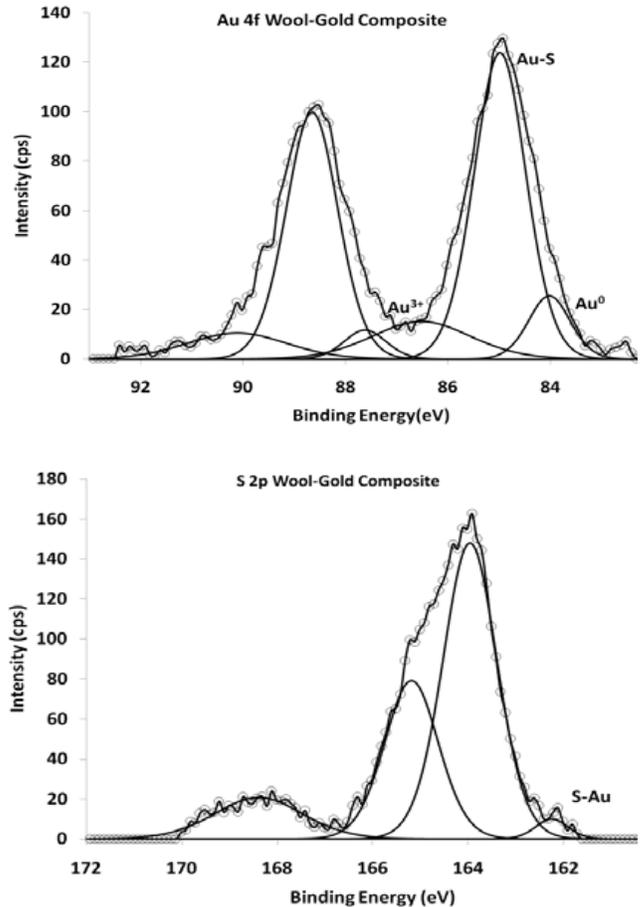


Figure 5: Top – Au 4f XPS spectrum of nanogold-wool; Au-S peaks at 84.2, 87.8 eV; Au⁰ at 82.8, 86.4 eV; Au³⁺ at 85.8, 89.4 eV. Bottom – S 2p XPS spectrum of nanogold-wool; S-S at 165.2 eV, S-H at 163.8 eV, S-Au at 162.2 eV, SO₃⁻ at 168.6 eV.

3 NANOSILVER - WOOL

Nanosilver entities have been similarly attached to *merino* and *strong* wool fibres using our proprietary methodology [5]. For this, we control the reduction of Ag^+ to Ag^0 to produce nanosilver entities of the required particle size and shape to produce the desired colour and again chemically bind them to the keratin in the wool fibres to provide nanosilver-wool products in an attractive range of colours (Fig. 6).



Figure 6: A selection of nanosilver coloured *merino* wools

These wool fibres have also been spun into yarn. As an example of an apparel garment, the nanosilver-*merino* wool has been woven into a scarf and the nanosilver-*strong* wool has been made into carpet (Fig. 7).



Figure 7: Nanosilver-*merino* wool woven into a scarf and nanosilver-*strong* wool made into carpet.

The anti-microbial activity of silver has been known for a long time. It has been shown to be effective against *Escherichia coli*, *Staphylococcus Aureus*, and *HIV-I*. [7] Due to their large relative surface area and crystallographic surface structure, silver nanoparticles exhibit increased chemical and microbial activity [7]. Anti-microbial testing of nanosilver-*merino* wool was carried out against *Staphylococcus aureus* (ATCC 25923) with an incubation time of 24 hrs. The anti-microbial activity was compared to that for untreated *merino* wool and silver wire. Fibres coloured with nanosilver significantly inhibited the growth of *Staphylococcus aureus* microbes, as shown by the zone of inhibition (clear area) in Fig. 8. For individual nanosilver-*merino* wool fibres, the zone of inhibition was up to 100 times the fibre diameter, whereas for silver wire it

was only 3 times the diameter. Untreated *merino* wool showed no anti-microbial activity. Nanosilver wool therefore exhibits excellent anti-microbial activity which is considerably enhanced over other forms of silver.



Figure 8: The anti-microbial activity of nanosilver-*merino* wool against *Staphylococcus aureus* (ATCC 25923) shown by the clear area around clumps of nanosilver-*merino* wool (bottom) and loose fibres (top).

4 CONCLUSION

High quality *merino* and *strong* wool have been successfully coloured with nanogold and nanosilver to provide a new suite of novel wool fibres for high value fabrics and textiles. A range of attractive colours have been produced and the wool made into examples of high fashion apparel and carpet. *The technology and products are being commercialised. Investment partners are being sought*

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