Silver Chloride – Wool Nanohybrid Materials: Synthesis and Properties

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ABSTRACT

New composite fibres comprising merino wool and silver chloride nanoparticles with a range of attractive and boutique colours from pink to purple have been produced. The merino wool – silver chloride wool composite is initially white but the colour develops upon exposure to light due to the photochemical reaction of silver chloride and surface plasmon resonance effects of Ag. It is also dependent on the concentration and size of the nanoparticles. The AgCl nanoparticles are chemically bound to the keratin protein in the wool and hence are chemically bound to them. As such, the composite fibres are stable to washing, rubbing and chlorinated pool water. The wool - silver chloride nanoparticle composite wool fibres also exhibit strong and effective antimicrobial properties typical of silver and silver compounds. These attributes provide a quality, valuable, multifunctional wool fibre for both fashion and interior furnishing applications.

Keywords: silver chloride nanoparticles, wool fibre, colourant, antimicrobial

1 INTRODUCTION

The preparation of nanoparticles is typically carried out in the liquid phase by bringing together solutions of the reactants in a controlled manner and using surfactants, capping agents or microemulsions to restrict particle growth within the nanosize range and to stabilize the resulting nanoparticles which are usually in the form of a colloidal suspension [1]. Silver halide nanoparticles have been most commonly synthesised using the reverse micelle and water-in-oil microemulsion approach [2-6]. Wool is a keratin based, natural porous fibre used in apparel, textiles and carpets. Merino wool has a fine fibre typically 12-20 microns in diameter and is used mainly in high quality fashion and knitwear apparel. Crossbred wool is a more coarse fibre typically 20-40 microns in diameter and is used for harder wearing textiles and carpets. Wool fibres are porous and can absorb water and aqueous solutions to a level of up to about 30% of its weight through a diffusion process. The nitrogen, sulfur and oxygen functional groups on the amino acids in the keratin proteins offer readily accessible sites that can chemically bind entities to the fibre that have a chemical affinity for these centres. We have recently developed proprietary new technology to form and bind gold and silver nanoparticles to wool fibres as novel colourants on the wool [7-9]. In addition the silver nanoparticles impart antimicrobial properties to the fibres. We have similarly captured the opportunity to synthesise and attach silver chloride nanoparticles onto the surface and within wool fires to provide colours through the photochemical properties of AgCl. The chemical affinity of Ag for S and N is utilised to bind the AgCl nanoparticles to the amino acids of the keratin protein. A major advantage of our approach is that the nanoparticles are chemically bound to the wool fibres and are not dislodged with normal wear and tear and washing. This is particularly important for silver nanoparticles which can destroy useful microbes used in waste water treatment plants, if they are unwantingly released to the environment.

2 MERINO WOOL - SILVER CHLORIDE NANOPARTICLE COMPOSITES

2.1 Colour

Merino wool - silver chloride nanoparticle composites have been prepared according to the proprietary method of Johnston et al. [9] . When first formed the composites are white, but upon exposure a photochemical reaction of the bound AgCl takes place and a range of colours from pink to dark purple (Figure 1) due to surface plasmon resonance effects of Ag can be achieved. The colour depends on the concentration and size of the nanoparticles [9]. SEM studies show the silver chloride nanoparticles are present across the cuticle plates of the wool fibres (Figure 2).

Figure 1: Merino wool coloured by silver chloride nanoparticles.

The nanoparticles on the pink wool are smaller in size and there are fewer aggregates than on the purple wool. As the colour darkens from pink to purple the surface density of the nanoparticles on the wool increase considerably and there is more aggregation. Also more nanoparticles are present along the cuticle edges (Figure 2).

2.2 Electronmicroscopy

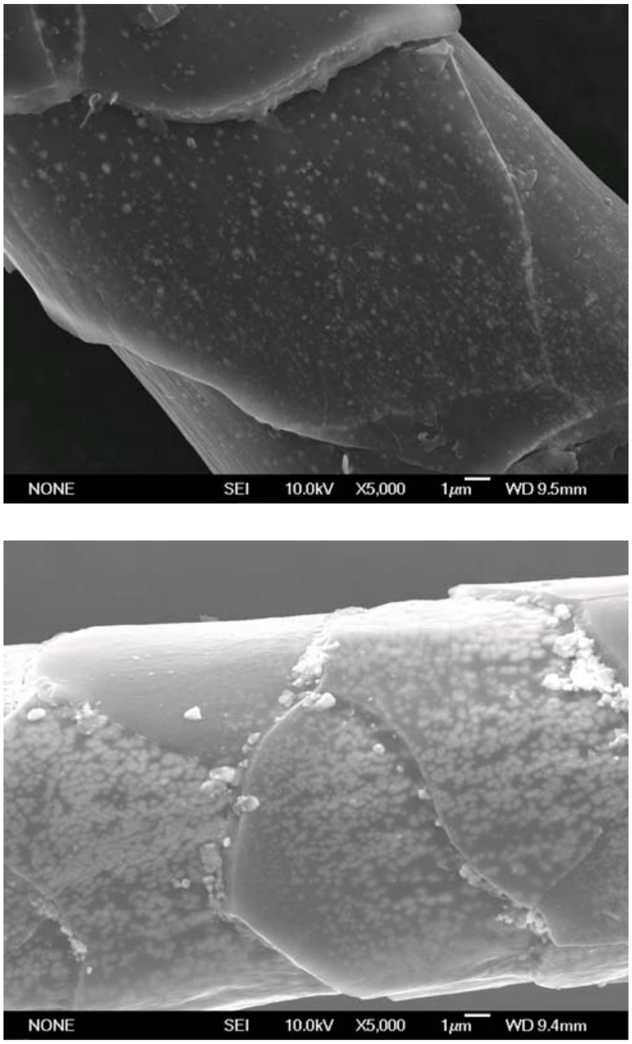

Figure 2: SEM micrographs of pink (top) and purple (bottom) coloured merino wool - silver chloride nanoparticle composites.

The Energy dispersive X-ray analysis (EDS) spectrum of the silver chloride nanoparticles on the wool fibre surface is shown in Figure 3. The X-ray peaks relating to the Ag Lα, present at 2.98 keV and Cl Kα at 2.62 keV are consistent with silver chloride. X-ray diffraction also confirmed the presence of silver chloride. A SEM image of a cross section of the merino wool – silver chloride nanoparticle composite together with the EDS elemental distributions for Ag and Cl are presented in Figure 4. These show that the Ag and Cl are located in a thin layer on and near surface of the wool fibre. There is a close overlap of the Ag and Cl distributions confirming the presence of AgCl as nanoparticles. The observation of Ag and Cl and hence AgCl below the wool fibre surface shows that the silver chloride nanoparticles have formed within the outer layers of the fibre and are likely to be chemically bound to it.

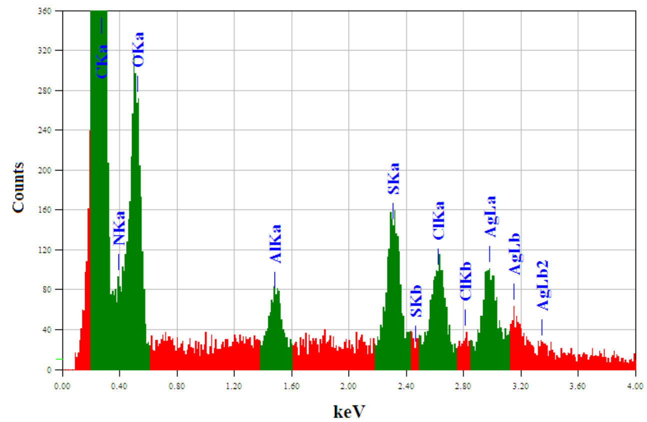

Figure 3: Energy Dispersive X-ray analysis (EDS) spectrum of a merino wool - silver chloride nanoparticle composite.

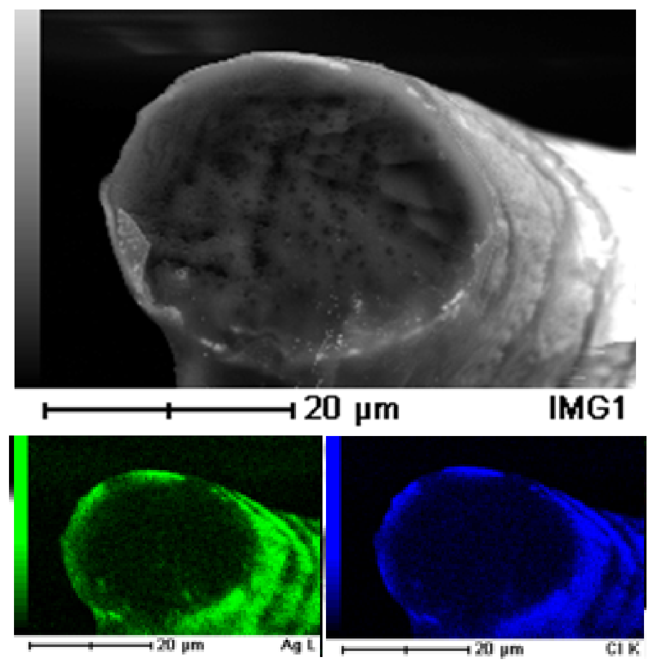

Figure 4: SEM image of a cross section of a merino wool - silver chloride nanoparticle composite fibre (top) and the corresponding Energy Dispersive X-ray analysis (EDS) elemental maps of Ag (bottom left) and Cl (bottom right). The brighness levels of the green and blue colours indicate the concentration of Ag and Cl respectively.

2.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was also used to characterise the nature of the silver in the merino wool - silver chloride nanoparticles. The XPS spectrum for silver (Figure 5) shows the typical Ag $3d_{5/2}$ and Ag $3d_{3/2}$ doublet peaks [10]. The experimental peak envelope has been fitted to two doublets. The more intense doublet has binding energies which are consistent with Ag^+ bonded to a Cl^- ion as in AgCl. The smaller doublet can possibly be assigned to Ag^+ bonded to oxygen which indicates some surface oxidation of the AgCl nanoparticles.

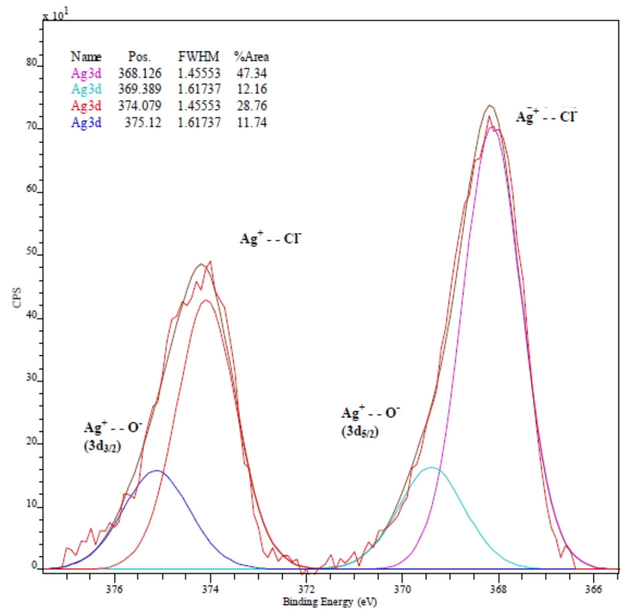

Figure 5: The X-ray Photoelectron Spectrum for Ag in the merino wool – silver chloride nanoparticle composite

2.4 Washfast and Rubfast Testing

In order to determine the robustness of the colour of the merino wool - silver chloride nanoparticle composites, colourfastness tests for washing (Australian/NZ Standard 2111.19.2 test), rubbing (Australian/NZ Standard 2111.19.1 test) and chlorinated swimming pool water (Australian Standard 2001.4.5 test) were carried out. For all tests the highest obtainable score is 5. The accepted pass level is 3 or 4 (Table 1). The testing was carried out on combed fibre (sliver or top form) and on carpet samples made from yarn spun from the sliver or top wool. The results in Table 1 show that the colour of merino wool - silver chloride nanoparticle composites is very stable, surpassing the pass level for each of the tests of colourfastness to washing, rubbing and to chlorinated swimming pool water. This confirms the presence of binding interactions between the AgCl nanoparticles and the wool fibres.

Sample Form	Test			Score	Pass Level
Top	Washing	AS/NZS 2111.19.2	Change of shade	4-5	4
Top	Washing	AS/NZS 2111.19.2	Staining on wool	5	3
Top	Washing	AS/NZS 2111.19.2	Staining on cotton	4-5	3
Carpet	Washing	AS/NZS 2111.19.2	Change of shade	4-5	4
Carpet	Washing	AS/NZS 2111.19.2	Staining on wool	5	3
Carpet	Washing	AS/NZS 2111.19.2	Staining on cotton	4-5	3
Top	Rubbing	AS/NZS 2111.19.1	Wet	3-4	3
Top	Rubbing	AS/NZS 2111.19.1	Dry	3-4	3-4
Carpet	Rubbing	AS/NZS 2111.19.1	Wet	3-4	3
Carpet	Rubbing	AS/NZS 2111.19.1	Dry	3-4	3-4
Top	Chlorinated water	AS 2001.4.5	Change of shade	4	3
Top	Chlorinated water	AS 2001.4.5	Staining on wool	4-5	3
Top	Chlorinated water	AS 2001.4.5	Staining on cotton	5	3
Carpet	Chlorinated water	AS 2001.4.5	Change of shade	4	3
Carpet	Chlorinated water	AS 2001.4.5	Staining on wool	4-5	3
Carpet	Chlorinated water	AS 2001.4.5	Staining on cotton	5	3

Table 1: Results from colourfastness testing on wool - silver chloride nanoparticle composites to washing, rubbing and chlorinated swimming pool water.

2.5 Antimicrobial Testing

Silver is well known for its antimicrobial properties have been widely used in synthetic textile fibres in recent years to impart antimicrobial properties to the product [11,12]. Antimicrobial testing for merino wool - silver chloride nanoparticle composites, with varying loadings of silver chloride, was carried out against the bacteria *Staphylococcus aureus*. The bacteria appear as cloudy areas on the agar plates in Figure 6. The clear areas surrounding the fibres are zones of inhibition where bacterial growth has been actively inhibited, which confirm that the merino wool - silver chloride nanoparticle composites show positive antimicrobial properties.

The extent of the clear areas or zones of inhibition surrounding the merino wool - silver chloride nanoparticle composites containing different amounts of silver, are directly proportional to the silver loading in the composite fibre. The inhibition mechanism requires dissolution of the AgCl to provide Ag^+ ions that can migrate away from the composite fibre surface to enter the cell wall of the bacteria thereby destroying them. The nanoparticulate nature of the AgCl provides a large specific surface area for this dissolution to take place and hence imparts excellent antimicrobial effectiveness to the merino wool - silver chloride nanoparticle composites. As the solubility of silver chloride is greater than silver, the silver chloride nanoparticles have a greater antimicrobial effectiveness than silver nanoparticles of the same size.

Figure 6: Inhibition zones of *Staphlococcus aureus* microbial growth by merino wool - silver chloride nanoparticle composites loaded with (7) 4.9 wt % Ag; (8) 3.8 wt % Ag; (9) 2.2 wt % Ag; (10) 1.3 wt % Ag.

2.6 Conclusion

New merino wool - silver chloride nanoparticle composites of different colours have been successfully prepared and characterised. The silver chloride nanoparticles are formed and bind to the surface and near surface of the wool fibres. The colour develops on exposure to light due the the photochemical properties of silver chloride and the surface plasmon resonance effects of Ag. Electronmicroscopy shows the silver chloride nanoparticles spread across the cutical surfaces with a concentration at the cuticle edges. The lighter pink coloured wool has a lower density of nanoparticles than the darker purple wool. The silver chloride nanoparticles are chemically bound to the fibre giving the merino wool – silver chloride nanoparticle composites excellent wash fast and rub fast properties. The composites also exhibit very effective antimicrobial activity against *Staphlococcus aureus* bacteria. Collectively these attributes provide a new multifunctional wool product for both fashion and interior furnishing applications, including carpets.

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