

# Characterization of palladium nanoparticles embedded in a wool substrate

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## ABSTRACT

The synthesis of palladium nanoparticles on the surface and within wool fibres has been accomplished and characterized by synchrotron X-ray diffraction (XRD) and electron microscopy (SEM and TEM). The size and shape of the nanoparticles formed in the fibres can be chemically controlled, thus tuning the optical, antimicrobial and catalytic properties of the resulting wool composite.

As confirmed by synchrotron X-ray diffraction analysis the crystallite phase corresponds with fcc palladium metal. The average crystallite size of the nanoparticles was calculated from peak broadening of the XRD pattern. As confirmed by TEM and SEM, larger palladium nanoparticles are located on the surface of the fibre and smaller nanoparticles are located within the fibre. Nanoparticles range in size from 2 to 50 nm depending on the experimental conditions for the reduction of palladium and the type of wool used.

**Keywords:** palladium, nanoparticles, wool, crystallites, synchrotron.

## 1 INTRODUCTION

Over the past few decades, there has been an increasing development of nanostructured materials within scientific, industrial and biomedical sectors. In particular, metallic nanoparticles such as gold, silver, iron, and palladium have been widely used in a variety of applications such as biomedicine, labelling systems, catalysis, and in ultra filtration membranes for purification technologies among others [1-10].

Metallic nanoparticles due to their nanoscale size and large specific surface area exhibit remarkable physical, chemical, and biological properties. They can strongly bind to the electron-donating groups in the surface of the bacterial cells thereby exhibiting antibacterial action. In addition, metal nanoparticles display an optical phenomenon known as Localized Surface Plasmon Resonance (LSPR), where, because of their small size the nanoparticles reflect the incident light providing a range of colours that depend on the size and shape of the

nanoparticles [11]. Moreover, nanoparticles of precious metals such as gold and palladium not only combine their unique, optical, electronic and antimicrobial properties, but also present catalytic activity and are very stable once synthesized.

At Victoria University of Wellington [12-13] we have developed a new methodology to reduce metal salts of gold, silver and palladium into nanoparticles with simultaneous binding to wool fibres. Keratin, the main constituent of wool fibres, is a complex protein comprising amino acids containing amine, sulphur, carboxylate and hydroxy functional groups, all of them having the potential to bind to nanoparticles. Therefore metal nanoparticles can be synthesized and immobilized onto wool fibres by chemical reduction of the metal salt in the presence of the substrate. The formation of the metal nanoparticles can be chemically controlled, obtaining different nanoparticles sizes and shapes, thus finely tuning the properties of the resultant composite [13].

In the present paper we report the synthesis and characterization of palladium nanoparticles embedded in a wool substrate using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and synchrotron X-ray powder diffraction analysis (XRD).

## 2 EXPERIMENTAL

Merino (fine fibre) and crossbred (coarse fibre) wool were used for all the experiments as the natural substrate for the synthesis and attachment of nanoparticles. The wool was provided by AgResearch Limited, New Zealand and all chemicals were purchased from Sigma Aldrich.

Palladium nanoparticles were prepared by chemical reduction of a palladium chloride PdCl<sub>2</sub> solution, in the presence of the wool fibres, without the use of external reducing and stabilizing agents. Palladium nanoparticles reduced with simultaneous binding to wool fibres [13]. The reaction conditions comprise different pH values (pH=1.0 - 3.0), temperatures (50-100 °C), reaction times (2-24 hr), salt concentrations (6.5-260 mg L<sup>-1</sup>) and types of wool (merino and crossbred).

The palladium nanoparticles synthesized and embedded in the wool fibres were examined by a JEOL 6500F field-emission gun scanning electron microscope (SEM) operated at 15 kV and a JEOL 2010 transmission electron microscope (TEM) operated at an acceleration voltage of 200 kV. The presence of the palladium nanoparticles was confirmed by energy dispersive spectroscopy analysis (EDS) for SEM and scanning transmission electron microscopy (STEM) for TEM. All the samples were coated with carbon prior to analysis. In addition, the TEM samples were embedded in resin, cut into thin films and placed on a copper grid before coating.

The crystalline phases present in the composites were examined by synchrotron X-ray diffraction analysis, using the powder diffraction beam line (BM-10) at the Australian Synchrotron. The diffraction patterns were obtained by measuring samples of nanopalladium composites with different preparation treatments, along with their appropriate reference materials (untreated wool fibres). The samples were measured in a sample holder that consists of a bracket that attaches directly to the goniometer. The X-ray beam energy was 20 keV (wavelength = 0.6196 Å) and the patterns were obtained using the Mythen detector over an angular range of 80 °. For every sample, diffraction data were collected for five minutes for each of two positions of the detector or ten minutes for one position when required. The crystallite average diameter was calculated from the broadening patterns using TOPAS software [14].

### 3 RESULTS AND DISCUSSION

Nanoparticles of palladium were synthesized and immobilized on and within the wool fibres by the controlled reduction of Pd<sup>2+</sup> to Pd<sup>0</sup>. The natural support acts as the reducing agent as well as the stabilizer for the nanoparticle formation and immobilization [13].

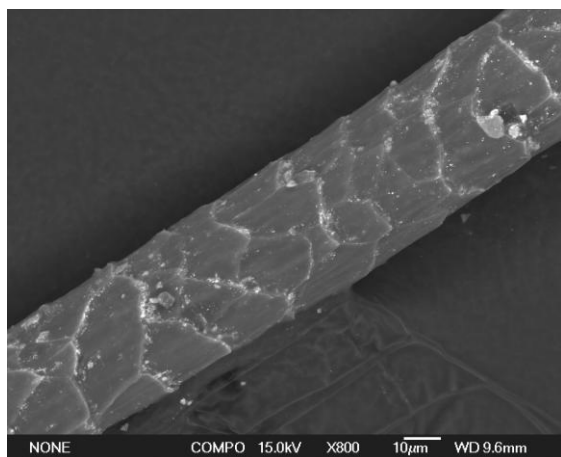


Figure 1: SEM image of a crossbred wool fibre with palladium nanoparticles attached (PdCl<sub>2</sub> solution of 260 mg L<sup>-1</sup>, pH 3.0 and 100 °C)

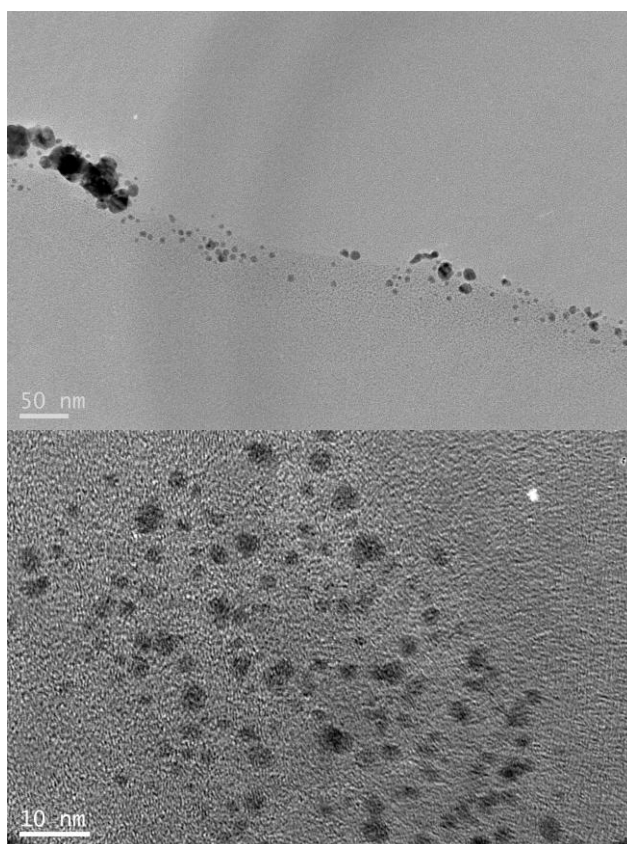


Figure 2: TEM image of a crossbred wool fibre – palladium nanoparticle composite synthesized at high concentration of PdCl<sub>2</sub> (top), and of a merino wool fibre – palladium nanoparticle composite at low concentration of PdCl<sub>2</sub> (bottom).

Scanning and transmission electron microscope images show the distribution of the nanoparticles on and within the wool fibres. SEM backscatter images show that palladium nanoparticles are located mainly on the cuticle edges of the wool fibres (white particles) as shown on Figure 1. TEM images show that the nanoparticles of palladium are localized both on the surface and within the fibres. For both types of wool it was observed that larger nanoparticles are located on the surface of the fibres as shown in Figure 2 (top image). When 260 mg L<sup>-1</sup> of palladium salt was used, the nanoparticles presented a polydisperse particle distribution, varying in size from 2-50 nm in diameter for merino wool fibres and from 2-20 nm for crossbred wool fibres. When 6.5 mg L<sup>-1</sup> of palladium salt is employed a narrow particle distribution was observed and the nanoparticles ranged in size from 2-5 nm in diameter for merino wool fibres and 2-3 nm for crossbred fibres as shown on Figure 2.

Synchrotron X-ray diffraction (XRD) was used to determine the crystal phases present in the composite materials and to calculate the average crystallite size. The primary phase formed for both substrates (crossbred and

merino wool) corresponds with fcc palladium (00-005-0681), with unit cell dimension  $a = 3.890 \text{ \AA}$ . The intense peaks of the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) Bragg reflections at  $2\theta = 15.7^\circ$ ,  $18.2^\circ$ ,  $25.8^\circ$  and  $30.2^\circ$ , respectively, confirmed the presence of palladium nanoparticles for both types of fibres (Figure 3). At low pH ( $\text{pH} < 2.0$ ) there was no presence of crystalline phases of palladium. At higher pH values ( $\text{pH}=2.0-3.0$ ), the presence of fcc palladium lattice planes confirms the formation of nanoparticles (Figure 3). The temperature is also important in determining the formation of the palladium crystallites. When the temperature is  $50^\circ\text{C}$ , small Pd Bragg reflection peaks are observed. When the temperature is  $80^\circ\text{C}$ , intense Bragg (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflections for Pd are observed (image not shown).

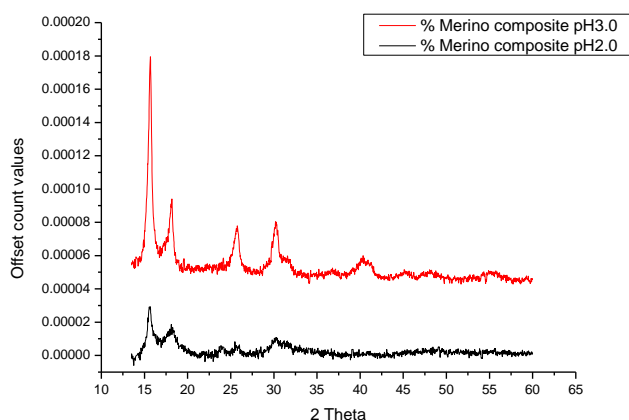


Figure 3: Synchrotron X-ray diffraction (XRD) pattern of palladium nanoparticles embedded in merino wool fibres synthesized at  $80^\circ\text{C}$  with a palladium salt concentration of  $260 \text{ mg L}^{-1}$ .

The average crystallite sizes of the nanoparticles from XRD peak broadening for composites synthesized with a palladium salt concentration of  $260 \text{ mg L}^{-1}$  have also been determined using TOPAS software. The crystallite size varied from 4.5 to 8.8 nm for the different composites as shown on Table 1. This results correlate with the observation from TEM images.

Sample	pH	Size (nm)
Merino $80^\circ\text{C}$	3.0	$4.9 \pm 0.1$
Merino $80^\circ\text{C}$	2.0	$4.6 \pm 0.2$
Merino $50^\circ\text{C}$	3.0	$5.3 \pm 0.5$
Crossbred $80^\circ\text{C}$	3.0	$4.5 \pm 0.2$
Crossbred $80^\circ\text{C}$	2.0	$8.8 \pm 0.5$
Crossbred $50^\circ\text{C}$	3.0	$8.7 \pm 0.9$

Table 1: Average crystallite size for palladium nanoparticles embedded in wool substrates.

From SEM, TEM and synchrotron X-ray diffraction analysis it is clear that the experimental conditions are favourable for the formation of the nanoparticles. The

amount and size of the palladium nanoparticles varied and depended on the experimental conditions employed for the reduction of  $\text{Pd}^{+2}$  to  $\text{Pd}^0$ , the concentration of the palladium solution and the type of wool used.

As presented in our earlier work [13] the wool fibre - palladium nanoparticle composites tested positive against the gram positive bacteria *Staphylococcus aureus*. It was observed that the palladium nanoparticles in the composites inhibit the growth of the bacteria on, underneath and around the vicinity of the fibres. Wool fibre - palladium nanoparticle composites therefore provide the opportunity to develop new materials for applications where the antibacterial properties are desired to prevent the proliferation and growth of bacteria that can cause bacterial infections and diseases. Due to the nanoscale dimensions of the palladium, these composite fibres were tested on their catalytic properties showing promising initial results. Catalysis tests based on hydrogenation of cyclohexene were carried out at low temperature. Furthermore, the resulting crossbred and merino composites vary in color ranging from light brown to dark green due to the different Localized Surface Plasmon Resonance bands (LSPR). This unique optical property can be used to colour textiles.

## 4 CONCLUSION

Composite materials of wool fibre and palladium nanoparticles have been successfully synthesized and characterized. By varying the reaction conditions the size and amount of the palladium nanoparticles can be controlled. SEM, TEM and synchrotron X-ray diffraction analysis showed that the nanoparticles are present on surface and within the fibres. They range in size from 2-50 nm, with the larger nanoparticles located mainly at the cuticle edges of the fibres.

Synchrotron XRD patterns showed that primary crystalline phase formed for both substrates (crossbred and merino wool) is cubic palladium (00-005-0681). Temperature and pH are controlling parameters in the synthesis of the nanocomposites. The temperature is also important in the formation of the crystalline palladium nanoparticles. This was confirmed with synchrotron X-ray diffraction experiments. The average crystallite sizes of the nanoparticles determined from XRD peak broadening are consistent with those observed by TEM.

SEM, TEM and synchrotron X-ray diffraction analysis therefore confirm the formation of palladium nanoparticles on and in the wool fibres. The size and shape of the nanoparticles formed in the fibres can be chemically controlled, thus tuning the optical, antimicrobial and catalytic properties of the resulting wool fibre - palladium nanoparticle composites.

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