

The Synthesis and Characterisation of Photocatalytic Silver/Silver Halide Nanocomposites of Kraft Paper Fibres and Calcium Silicate

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ABSTRACT

Novel silver/silver halide nanocomposite materials were produced by forming plasmonic photocatalyst silver/silver halide nanoparticles in the porous support materials of kraft paper fibres and nano-structured calcium silicate, via a simple aqueous synthesis method, followed by light induced chemical reduction. This method incorporated the silver/silver halide nanoparticles without modifying the structure of the support material. UV-visible spectroscopy, x-ray diffraction, and scanning electron microscopy were used to characterise the silver/silver halide nanoparticles and their distribution within the nanocomposites. The photocatalytic activity of the silver/silver halide nanocomposites was evaluated by the photodegradation of methylene blue dye. The nanocomposites were shown to retain the enhanced photocatalytic activity displayed by silver/silver halide plasmonic photocatalyst nanoparticles. The nanocomposite materials were also seen to display significant antimicrobial action against *Escherichia Coli*.

Keywords: silver halide, photocatalyst, kraft, calcium silicate

1 INTRODUCTION

In recent years it has been shown that silver halides have successfully been used to create silver/silver halide based photocatalysts [1-8]. These silver/silver halide (Ag/AgX, X= Cl,Br,I) nanoparticles are part of a family known as plasmonic photocatalysts [1]. Silver halides are also well known for their photoactivity with their traditional use in black and white photography. This photoactivity on the nanoscale allows for interesting photocatalytic properties to be developed. On the nanoscale AgX undergoes partial photoreduction on exposure to light, forming the Ag/AgX particles and imparting increased photocatalytic activity and increased stability [1-4]. This is due to the formation of Ag⁰ nanodomains on the surface of the AgX particles. These Ag⁰ nanodomains display surface plasmon resonance effects, making them plasmonic photocatalysts, creating a broad visible region absorption which is typical of Ag/AgX nanoparticles and provides increased spectral sensitivity [1, 8].

Increased stability and photocatalytic activity in these materials is facilitated through efficient charge separation from the metallic Ag⁰ nanodomains in contact with the semiconducting AgX [7, 9]. These nanoparticles show promise in the application of organic contaminant breakdown [1, 5]. The aim of this work was to form and incorporate these particles into the porous support materials described below. In particular, this paper will focus on the incorporation of Ag/AgCl nanoparticles, although similar results have been obtained through the incorporation of Ag/AgBr and Ag/AgI nanoparticles into the porous support materials [10].

Kraft fibres are cellulosic fibres produced from the chemical pulping of wood for use in paper and packaging products. These kraft fibres are porous in nature due to the areas of weak hydrogen bonding between the cellulose microfibrils. This porosity was exploited in the synthesis of these nanocomposites.

Nanostructured Calcium Silicate (NCS) is a proprietary material developed by Prof J. H. Johnston, Victoria University of Wellington [11]. It is a versatile material produced by the reaction of a silica-containing solution with calcium ions at an alkaline pH. The 3D open microstructure of NCS is similar to that of gypsum desert rose, formed through calcium silicate platelets, self-assembling into particles creating an open framework [12, 13]. This complex microstructure of the NCS gives it a high porosity, allowing synthesis of the silver/silver chloride nanocomposite material. The work herein describes the synthesis, characterisation and preliminary photocatalytic and antimicrobial evaluation of silver/silver chloride kraft fibre and nanostructured calcium silicate nanocomposites.

2 MATERIALS AND METHODS

All chemicals used in synthesis were used as received and are analytical grade unless otherwise stated. The silver nitrate (AgNO₃) was sourced from Scientific and Chemical Supplies and sodium chloride was provided by Unilab. Calcium hydroxide was from LobaChemie and sodium silicate from Orica Chemicals (N grade). Distilled water was used in all cases. Bleached kraft fibres used in this research project were of the New Zealand *Pinus radiata* genus, provided by Tasman Pulp and Paper Company Ltd, Kawerau, New Zealand.

2.1 Ag/AgX Kraft Fibre Synthesis

Kraft fibres were first doped with Cl^- ions. This was done by immersing 0.1 g of homogenised kraft fibres in 10 cm^3 of 0.1 M NaCl solution. After soaking, the kraft fibres were rinsed with distilled water and filtered for drying. To form the silver halide nanoparticles the doped fibres were then soaked in AgNO_3 solution. The concentrations of AgNO_3 solution were adjusted, to give final concentrations of 100 mg/kg Ag in the final composite. The formation of silver halides occurs when the fibres are immersed within the AgNO_3 . The fibres are then removed from solution after soaking and washed with distilled water, before being filtered and dried. AgCl bleached kraft nanocomposites are white in colour when first synthesised. The samples are then left in natural sunlight, behind window glass for a period three hours. During this period of time, the AgCl kraft nanocomposites develop a purple colour. This colour change is also seen to develop during the first hour at room temperature. This light exposure produces silver nanodomains, making silver/silver halide nanoparticles within the kraft fibre matrix.

2.2 Ag/AgX Nanostructured Calcium Silicate

Typical synthesis of silver halide NCS composites was as follows. A 0.1 g quantity of NCS was washed thoroughly with distilled water in order to remove residual Cl^- ions arising from the NCS synthesis method. After washing and filtration, the washed NCS was suspended in 10 cm^3 0.1 M NaCl, and agitated for a 1 hour period. This was followed by filtration, before immersing the halide doped NCS in AgNO_3 solution. The AgCl NCS nanocomposite formed a white nanocomposite after immersion in the AgNO_3 solution. With natural sunlight exposure behind window glass, the nanocomposite developed a purple colour, similar to the kraft nanocomposites.

2.3 Characterisation

UV-visible reflectance spectroscopy (UV/Vis) was carried out on a Varian Cary 100 scan spectrometer.

Scanning electron microscopy (SEM) imaging and Energy dispersive X-ray spectroscopy (EDS) was carried out on a JEOL 6500 F field emission gun scanning electron microscope.

X-ray diffraction (XRD) was used to characterise the composition of the silver halide nanocomposites. All measurements were carried out on an X'Pert Pro diffractometer, using a Cu source, operating at 45 kV and 40 mA.

2.4 Photocatalytic Activity

Photocatalytic activity of the silver/silver halide nanocomposites was determined through the breakdown of the organic dye methylene blue (MB). An amount of the

nanocomposite containing 0.4 mg of Ag was suspended in 10 cm^3 of 10 μM MB solution and stirred in dark conditions overnight to reach an adsorption equilibrium. The solution was then irradiated by a 75 W Xe arc lamp, and the MB concentration monitored at time intervals via UV/Vis spectroscopy to measure the extent of degradation. This was compared with the degradation rate of the MB with a blank matrix in solution. This gave a measure of the increased photocatalytic activity due to the nanocomposites, in comparison to unmodified kraft fibres and nanostructured calcium silicate.

3 RESULTS AND DISCUSSION

The UV/Vis reflectance spectra show a broad visible region absorption had developed with the formation of Ag/AgCl within the kraft and NCS matrix (Figure 1 & 2). This broad visible region absorption is typical of Ag/AgCl formation [1, 2]. The AgCl nanoparticles within the kraft fibre and NCS matrix upon light exposure absorb the light, and undergo light induced chemical reduction through photolysis. This forms the Ag^0 nanodomains of the Ag/AgCl nanoparticles in situ within the composite matrix by partially reducing the Ag^+ to Ag^0 . The increased visible absorption that is seen to develop upon light exposure is due to the surface plasmon resonance of these newly formed Ag^0 nanodomains on the surface of the silver halide nanoparticle.

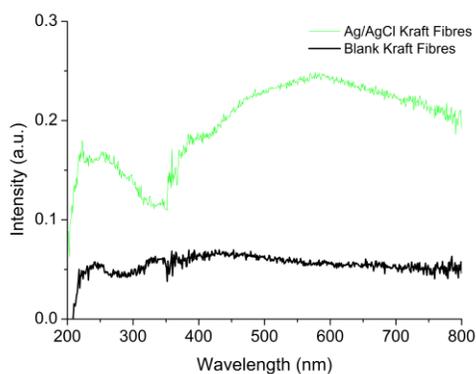


Figure 1: UV/Vis of Ag/AgCl kraft fibre composite.

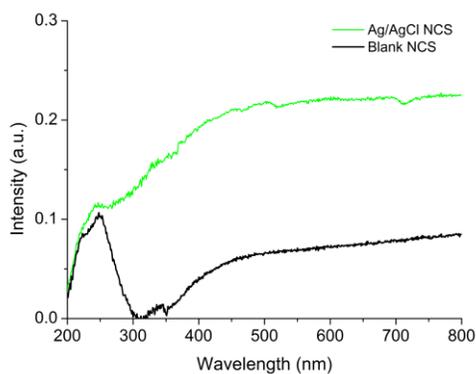


Figure 2: UV/Vis of Ag/AgCl NCS composite.

The XRD patterns showed the presence of crystalline AgCl and Ag and hence provided further confirmation that the Ag/AgCl was incorporated into both the kraft fibre and NCS matrix during synthesis. Diffraction patterns of the nanocomposites after synthesis show that a silver 111 peak has begun to develop, showing small amounts of crystalline silver present within the nanocomposite after the period of light exposure. This Ag 111 peak confirms that there is formation of silver/silver halide nanoparticles within the nanocomposite materials.

Present in the XRD pattern for Ag/AgCl kraft fibres (Figure 3) is titania, a common whitener and brightener additive to bleached kraft. Also of note is the large peak at $\sim 23^\circ 2\theta$, this is the characteristic crystalline cellulose peak. Similarly all unassigned peaks in the Ag/AgCl NCS pattern are characteristic of NCS (Figure 4).

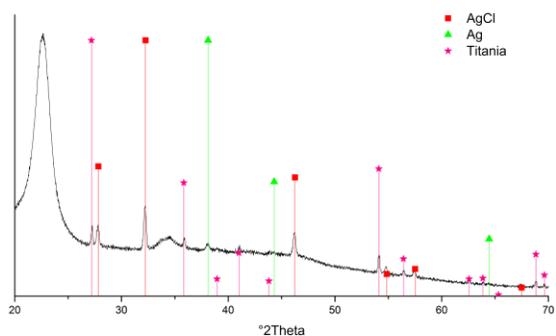


Figure 3: XRD pattern of Ag/AgCl kraft fibre composite.

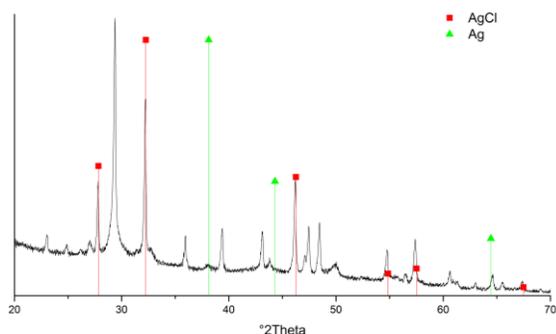


Figure 4: XRD pattern of Ag/AgCl NCS composite.

The morphology and nanoparticle distribution throughout the kraft fibre and NCS composites were observed via SEM. In the backscatter mode, the bright areas of high atomic mass are indicative of Ag/AgCl nanoparticles. The Ag/AgCl nanoparticles can be seen distributed through the kraft fibre as seen in cross-sectional SEM. It shows a variety of particle sizes and shapes, ranging from small discrete particles to large agglomerates. This was achieved through the precipitation of AgCl within the pores of the support materials, controlling the size and shape of the particles, which were then partially photoreduced to form the Ag/AgCl particles. The EDS

mapping further confirms the presence of the Ag/AgCl nanoparticles within the kraft fibre with a strong correlation between areas of high concentration of Ag and Cl.

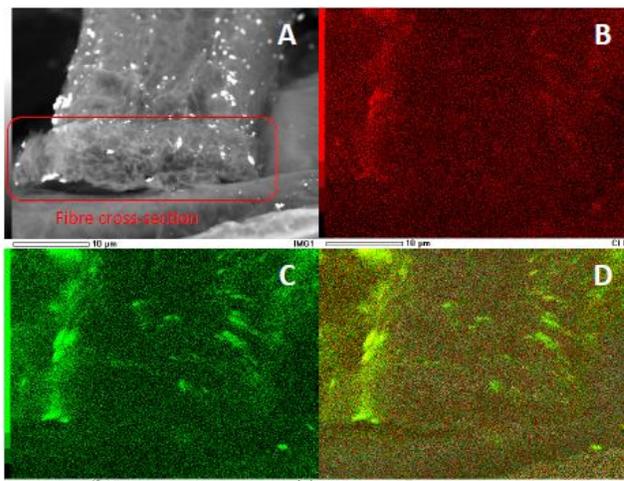


Figure 5: SEM/EDS of Ag/AgCl kraft fibre composite.

The SEM analysis of the Ag/AgCl NCS nanocomposite yields similar results as seen above with the kraft fibres. Here, the SEM analysis shows that large agglomerates have formed within the NCS matrix. This poor size control is presumably due to the large variations in pore size and shape from the highly open 3D structure of NCS. The EDS mapping is also confirms Ag/AgCl nanoparticle formation again, as seen with the kraft fibre composites.

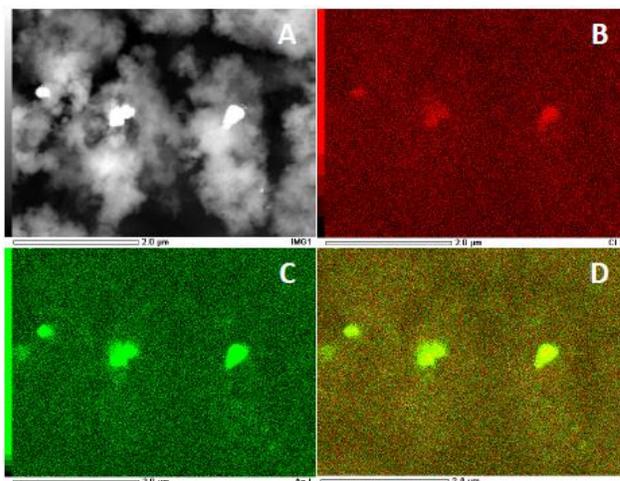


Figure 6: SEM/EDS of Ag/AgCl NCS composite.

Characterisation of the kraft fibre and NCS nanocomposite materials confirms that the simple aqueous precipitation method followed by light induced reduction has formed Ag/AgCl nanoparticles in situ within the porous support materials. The next step was to evaluate the photocatalytic activity of the composite materials to ascertain if the photocatalytic activity of the Ag/AgCl nanoparticles was exhibited. This was monitored by MB dye degradation as described previously. The rates of dye

degradation for both nanocomposite materials show substantial increases when compared to matrix blank samples (Figure 7 & 8). The rate of degradation for Ag/AgCl NCS nanocomposite samples is increased further still due to the inherent base photocatalytic activity of the NCS support materials itself.

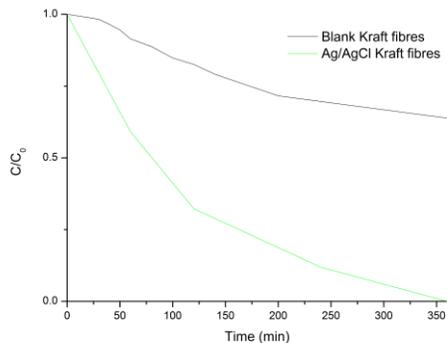


Figure 7: Rate of MB degradation of Ag/AgCl kraft.

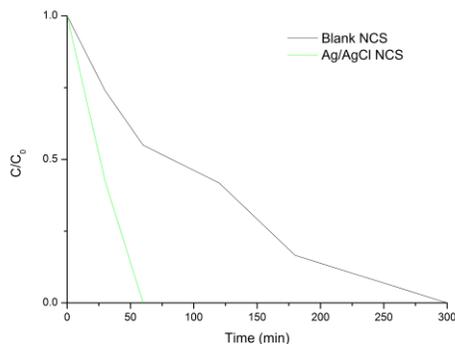


Figure 8: Rate of MB degradation of Ag/AgCl NCS.

Finally the antimicrobial activity of the Ag/AgCl kraft fibre and NCS nanocomposite materials was evaluated. This was done through zone of inhibition testing against the gram negative bacteria *Escherichia Coli* (*E. Coli*). It can be seen that both the Ag/AgCl kraft fibre and NCS nanocomposite materials display a substantial zone of inhibition against the *E. Coli* (Figure 9).

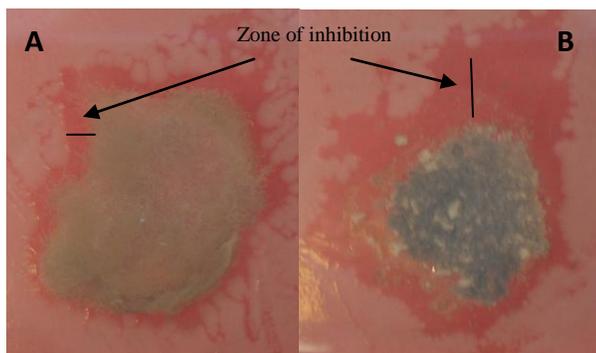


Figure 9: Zone of inhibition of (A) Ag/AgCl kraft fibres (B) Ag/AgCl NCS against *E. Coli*.

4 CONCLUSIONS

Simple aqueous synthesis methods were used to synthesise silver/silver chloride kraft fibre and nanostructured calcium silicate nanocomposite materials. UV/Vis and XRD confirmed the silver/silver chloride nanoparticle formation within the composites, and the distribution throughout the kraft fibres and nanostructured calcium silicate were observed through SEM and EDS.

Through methylene blue dye degradation, silver/silver chloride kraft fibre and nanostructured calcium silicate nanocomposites were shown to exhibit the photocatalytic properties observed in silver/silver chloride nanoparticles themselves.

Antimicrobial testing showed both silver/silver chloride kraft fibre and NCS nanocomposite materials display significant antimicrobial effectiveness. These are promising results for potential applications in air filtration and waste water purification, where both antimicrobial and photocatalytic activity are beneficial.

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