

Photocatalytic Silver/Silver Halide Polymer Nanocomposites

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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 the polymers nylon 6,6 and polyurethane. This was achieved 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 polymer support. UV-visible spectroscopy, X-ray diffraction, and scanning electron microscopy were used to characterise the silver/silver halide nanoparticles and their distribution within the composites. The photocatalytic activity of silver/silver halide polymer composites was evaluated by the photodegradation of methylene blue dye. The composite materials were shown to retain the enhanced photocatalytic activity displayed by silver/silver halide plasmonic photocatalyst nanoparticles. The silver/silver halide polymer composites were also seen to display significant antimicrobial action against *Escherichia Coli*.

Keywords: silver, silver halide, photocatalyst, nylon, polyurethane

1 INTRODUCTION

In recent years it has been shown that silver halides have been used successfully to create silver/silver halide based photocatalysts [1-9]. These silver/silver halide (Ag/AgX, X= Cl,Br,I) nanoparticles are part of a family known as plasmonic photocatalysts [1]. While silver halides are well known for their photoactivity with their traditional use in 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 Ag⁰ domains on the surface of the AgX particles. These Ag⁰ domains 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 to the photocatalyst [1, 8, 9].

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, 10]. These nanoparticles are promising materials in the application of organic contaminant breakdown [1, 5]. The aim of this work was to incorporate the nanoparticles into the polymer support materials of nylon 6,6 and polyurethane (PU). 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 polymer supports.

The two chosen polymer support materials were nylon 6,6 and polyurethane, which exhibit a degree of porosity. They are semicrystalline polymer materials which, along with their physical properties, is attributed to the hydrogen bonding that occurs between the of neighbouring macromolecules. Their porosity was exploited in order to synthesise these photocatalytic composites. The work herein describes the synthesis and characterisation of Ag/AgCl nylon and polyurethane composites and a preliminary evaluation of their photocatalytic and antimicrobial properties.

2 MATERIALS AND METHODS

All chemicals used in synthesis were used as received and are analytical grade unless otherwise stated. Silver nitrate (AgNO₃) was sourced from Scientific and Chemical Supplies and sodium chloride was provided by Unilab. Distilled water was used in all cases. Nylon 6,6 sheet precast and cut in 0.5 g squares was used for Ag/AgCl nylon composite synthesis. The commercially available aqueous polyurethane dispersion Kamthane K5000 PU was used to produce the Ag/AgCl polyurethane composites.

2.1 Ag/AgX Polymer Composite Synthesis

The polymer support materials nylon 6,6 sheet and K5000 PU, were first doped with Cl⁻ ions. This was done by immersing 0.5 g of nylon in 10 cm³ of 0.1 M NaCl solution. After soaking, the nylon was rinsed with distilled water and air dried. To form silver halide nanoparticles within the polymer matrix, the Cl⁻ doped nylon was then soaked in AgNO₃ solution, to give a final concentration of 0.1% Ag in the final composite. The Ag/AgCl nylon was removed from solution after soaking, and washed with distilled water before being dried.

K5000 PU composites were prepared similarly. The K5000 PU dispersion was doped with Cl⁻ by the addition of 1.0 cm³ of 0.5 M NaCl solution to 5 g of the suspension under stirring, followed by addition of AgNO₃ to give a final concentration of 0.1% Ag in the final composite.

AgCl nylon composites 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 composites develop a purple colour. This colour change is indicative of the partial photoreduction of AgCl to form Ag/AgCl by forming Ag⁰ nano regions on the AgCl nanoparticles, thereby producing Ag/AgCl nanoparticles within the polymer matrix.

2.2 Characterisation

UV-visible reflectance spectra (UV-vis) were recorded using a Varian Cary 100 scan spectrometer.

X-ray diffraction (XRD) was used to confirm the presence of silver and silver chloride in the silver/silver chloride nanocomposites. All measurements were carried out on an X'Pert Pro diffractometer, using a Cu X-ray tube, operating at 45 kV and 40 mA.

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

2.3 Photocatalytic Activity

Photocatalytic activity was determined through the breakdown of the organic dye methylene blue (MB). A 15 μM MB solution was used to determine the photocatalytic activity of the silver/silver chloride composites. 0.5 g of the composite was suspended in 10 cm³ of MB solution and stirred in dark conditions overnight to attain an adsorption equilibrium. The solution containing the composite was then irradiated by a 150 W Xe arc lamp, and the MB concentration monitored at time intervals via UV-visible spectroscopy to measure degradation over time. This was compared with the degradation rate of the MB with a blank nylon or K5000 PU matrix in solution, demonstrating the photocatalytic activity of the composites respectively.

3 RESULTS AND DISCUSSION

The UV-vis reflectance spectra show a broad absorption in the visible region developed with the formation of Ag/AgCl within the nylon and K5000 PU matrix (Figures 1 & 2). This absorption is typical of Ag/AgCl formation [1, 2]. The Ag⁺ in the AgCl nanoparticles within the nylon and the K5000 PU matrix undergoes photoreduction upon light exposure. This forms the Ag/AgCl nanoparticles in situ within the composite matrix, by partially reducing the Ag⁺ to Ag⁰. The visible region absorption that develops is due to the surface plasmon resonance effect of these newly formed

Ag⁰ nano regions on the surface of the silver halide nanoparticles. This increased visible region absorption increases the photocatalytic efficiency of the plasmonic photocatalyst nanoparticles through visible region sensitisation.

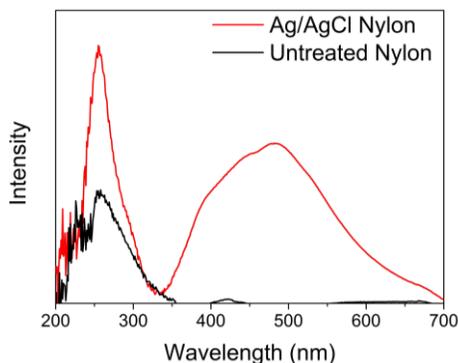


Figure 1: UV-Vis spectrum of the Ag/AgCl nylon composite.

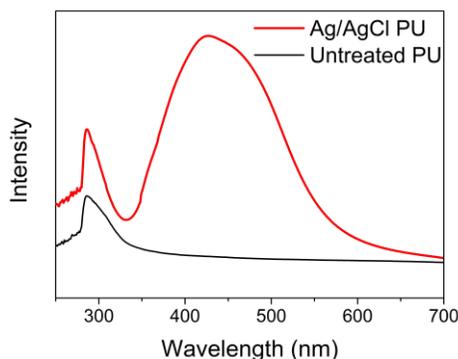


Figure 2: UV-vis spectrum of the Ag/AgCl K5000 PU composite.

XRD analysis was used as further confirmation that Ag/AgCl was incorporated into the polymers during synthesis. The diffraction patterns of the Ag/AgCl nylon (Figure 3) and the Ag/AgCl K5000 PU (Figure 4) composites after synthesis, show crystalline AgCl within each polymer matrix. Also, the diffraction pattern of both composites following exposure to light, and with the accompanying colour change, show that a silver 111 peak has developed. This confirms the presence of crystalline Ag⁰ within the Ag/AgCl nanoparticles contained in the composites.

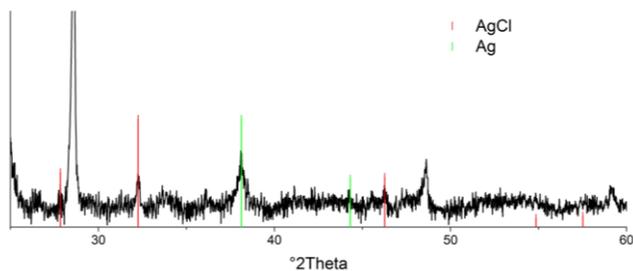


Figure 3: XRD pattern of the Ag/AgCl nylon composite.

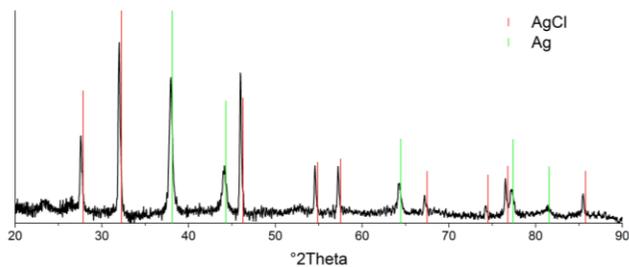


Figure 4: XRD pattern of the Ag/AgCl K5000 PU composite.

SEM was used to view the morphology of the Ag/AgCl polymer composites and the distribution of the Ag/AgCl nanoparticles within the matrix (Figures 5 & 6). As backscatter SEM images emphasise elements of high atomic number, this provided better contrast between the Ag/AgCl nanoparticles and the polymer matrix, for viewing the nanoparticle distribution.

The SEM images show that in both cases there are nanoparticles present within both polymer substrate materials. The nanoparticles can be easily seen in the backscatter SEM images, where the Ag/AgCl nanoparticles are indicated as bright areas. The Ag/AgCl particles are distributed across the polymer substrates. However, there are a variety of sizes and shapes and they are not monodisperse.

The backscatter image of the Ag/AgCl nylon composite shows Ag/AgCl nanoparticles of about 100-200 nm in size (light grey) within the composite, as well as a few much larger particles of 1-2 μm (bright areas) on the surface with some agglomeration (Figure 5). The backscatter image of the Ag/AgCl K5000 PU composite shows the Ag/AgCl particles are smaller in size, about 50-100 nm, discrete and well dispersed. There is however, still a large distribution in sizes.

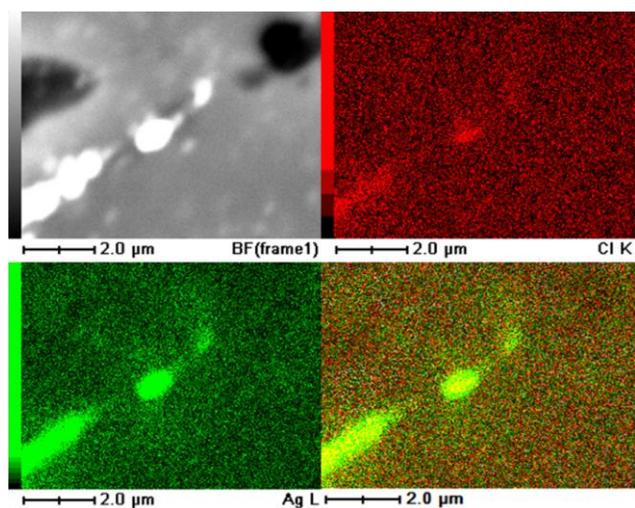


Figure 5: SEM/EDS of the Ag/AgCl nylon composite.

SEM EDS was used to provide additional confirmation of the composition of the nanoparticles within the polymer composites. The EDS mapping of both composites shows a good correlation between areas of high Cl concentration and areas of high Ag concentration. This is clearly shown in the EDS map overlay of Ag and Cl where areas coloured in yellow indicates both Ag and Cl in the same particle. The EDS mapping shows there are no particles which comprise only of Ag and therefore it is concluded that the Ag component identified in the XRD patterns must reside in the Ag/AgCl particles.

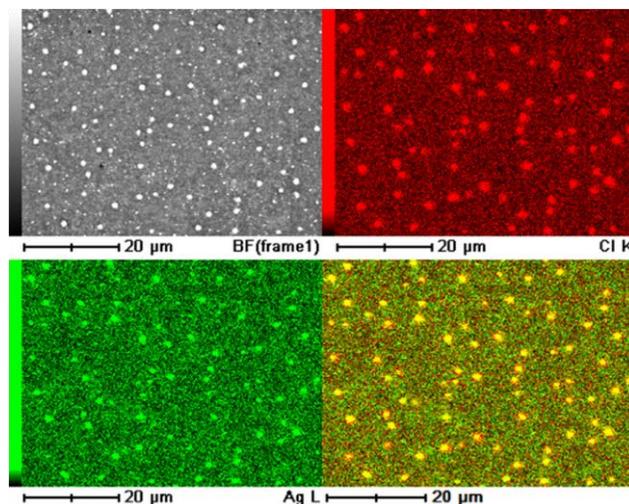


Figure 6: SEM/EDS of the Ag/AgCl K5000 PU composite.

The Ag/AgCl nanoparticles in the Ag/AgCl nylon and K5000 PU composites synthesised here show plasmonic photocatalytic properties. Photodegradation of organic dyes is a commonly used test for determining photoactivity of such nanoparticles. Having synthesised the Ag/AgCl composites it was important to establish if the Ag/AgCl nanoparticles maintained their photocatalytic activity when incorporated into the nylon and K5000 polyurethane matrix.

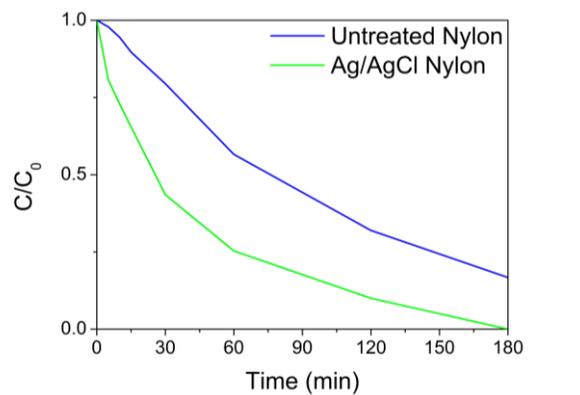


Figure 7: Rate of MB degradation by the Ag/AgCl nylon.

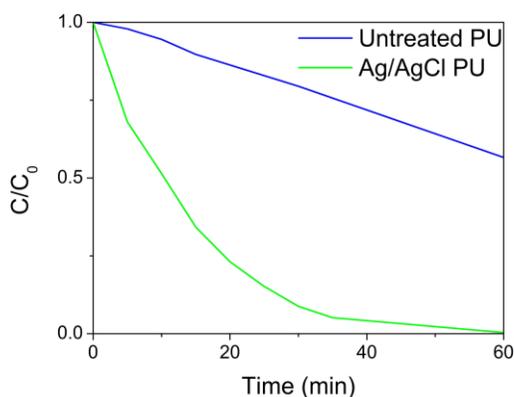


Figure 8: Rate of MB degradation by the K5000 Ag/AgCl PU.

An evaluation of the photocatalytic activity of the Ag/AgCl composites was carried out by this dye degradation method, using methylene blue as the dye. The rate of methylene blue degradation was monitored by the reduction in colour of the dye solution containing the Ag/AgCl polymer composites, compared to blank polymer samples. This showed an increase in the rate of degradation for both the Ag/AgCl nylon and Ag/AgCl K5000 PU composites (Figures 7 & 8). There was a significantly greater increase in the rate of degradation for the Ag/AgCl K5000 PU composite than the Ag/AgCl nylon composite.

This is likely due to the porosity of the polymer matrix with the Ag/AgCl K5000 PU being much more porous than the nylon sheet. This provides for increased accessibility, allowing dye molecules to come into direct contact with Ag/AgCl nanoparticles within the composite matrix. It also facilitates an increase in the diffusivity of radicals, generated during irradiation of the plasmonic photocatalysts. Both of these effects will increase the degradation of the MB dye.

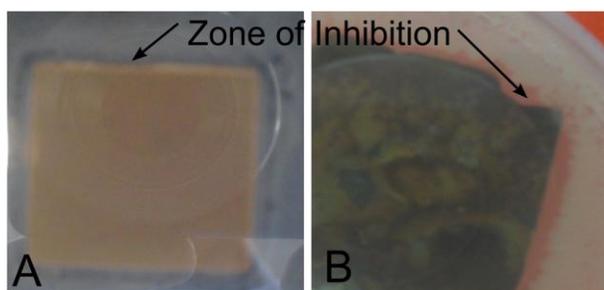


Figure 9: Zone of inhibition of (A) The Ag/AgCl nylon (B) The K5000 Ag/AgCl PU composites against *E. Coli*.

The antimicrobial activity of the Ag/AgCl composites was also evaluated. This was carried out using the zone of inhibition method against the gram negative bacteria *Escherichia Coli* (*E. Coli*). It can be seen that both the Ag/AgCl nylon and Ag/AgCl K5000 PU composite materials exhibit a significant zone of inhibition against the *E. Coli* (Figure 9), which is due to both the antimicrobial

effect of silver and silver compounds, along with plasmonic photocatalyst effects such as free radical generation.

4 CONCLUSIONS

Simple aqueous synthesis methods were used to synthesise Ag/AgCl polymer composite materials in nylon and K5000 PU substrates. UV-vis spectroscopy and X-ray diffraction confirmed the formation of Ag/AgCl nanoparticles within the composites. The distribution of nanoparticles in the nylon and K5000 PU polymer matrix was characterised by through SEM and EDS.

The photocatalytic properties of the Ag/AgCl nanoparticles in the composites were measured by their ability to degrade methylene blue dye.

Antimicrobial testing showed both the Ag/AgCl nylon and K5000 PU polymer composites displayed significant antimicrobial action. These nanocomposite polymer materials are therefore potentially useful in providing self cleaning and antimicrobial surfaces, where both photocatalytic and antimicrobial activity are desirable properties.

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