A Novel Demonstration of the Dichroic Effect Exhibited by Gold Nanoparticles and their Incorporation into Polymer Materials

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ABSTRACT

When metal nanoparticles appear one colour in transmitted light, but a different colour in reflected light, it is known as the dichroic effect. This has been illustrated as early as the 4th century A.D. by the famous Lycurgus Cup, however the origin of the effect is still poorly understood. Here we present a synthesis of gold nanoparticles that display the dichroic effect in an aqueous system. A full characterisation of the colloids produced has enabled us to correlate the size and shape of the nanoparticles to the colours observed in transmitted and reflected light. We have further successfully transferred selected particles into a polymer system with complete conservation of their dichroic properties.

Keywords: dichroic, gold, nanoparticles, acrylic, nanocomposites

1 INTRODUCTION

Gold nanoparticles are well known and often utilised for the range of attractive colours they display. The observed colour arises from localised surface plasmon resonance (LSPR) effects; the oscillation of nanoparticle conduction electrons upon resonance interaction with incoming electromagnetic radiation. The size and shape of the nanoparticles determine the frequency at which the electron oscillation and incoming light are resonant, and hence the wavelength of the LSPR absorption. The typical red shade of nanogold made famous by its display in 17th century stained glass windows arises from spherical gold nanoparticles about 20 nm in diameter, which give a LSPR absorption at ~520 nm [1].

For certain nanoparticles scattering processes may need to be considered in addition to absorption, as the ratio of scattering to absorption increases with nanoparticle size. Calculations by El-Sayed and co-workers [2] have shown that for spherical 20 nm gold nanoparticles scattering is negligible and only absorption is relevant. Particles with 40 nm diameters are still dominated by absorption, but a small amount of scattering occurs, but for 80 nm gold particles both scattering and absorption contribute almost equally to the total extinction. The high scattering property of large gold nanoparticles is exploited in biomedical imaging and other applications [3].

The glass Lycurgus Cup, currently on display in the British Museum, is one of the oldest and most famous examples of the use of gold nanoparticles to provide colour. It is a particularly unique specimen in that the colour it displays depends on the direction of the light source; it appears red in transmitted light but green in reflected light. This has become known as the dichroic or Lycurgus effect. Some loose glass fragments were found when the base of the cup was removed in the 1950s, and these have enabled studies into the origin of this rare optical property. The most thorough of these studies, conducted in 1990 by Barber and Freestone [4], ran transmission electron microscopy (TEM) and energy dispersive X-ray spectrometry on a 2 mm^3 sample. They observed particles 50-100 nm in size, determining them to be alloy particles with a composition of 66.2 (± 2.5) at. wt% silver, 31.2 (± 1.5) at. wt% gold, and 2.6 (± 0.3) at. wt% copper. The colour in transmitted light has been attributed to the absorbance of light by these nanoparticles, and the colour in reflected light to the scattering of light. However the precious nature of the cup has meant that further analysis has not been completed, and the nature of the relationship between nanoparticle shape/size/metal composition and the observation of the dichroic effect is not well understood. Since the Lycurgus Cup studies, the dichroic effect has been observed and studied on several occasions with gold, silver and alloy nanoparticles, and has been attributed to nanoparticle size [5,6], shape [7], polarisation [8], etc. However there is no consensus on the determining factor that is necessary for this effect to be observed.

We present a demonstration of the dichroic effect displayed by gold nanoparticles in an aqueous system. The developed synthesis further allows us to control the extent of this effect. A thorough characterisation of these particles has shown a correlation between the size and shape of the particles and their observed dichroic properties, significantly contributing to understanding of the effect. Further, the nanoparticles have been transferred into an acrylic system with complete conservation of the dichroic effect.

2 EXPERIMENTAL

2.1 Materials and Reagents

A hydrogen tetrachloroaurate ($HAuCl_4$) solution was prepared by dissolving gold metal in aqua regia. The acrylic polymer utilised (NeoCryl XK-98) was provided by The Polymer Group Ltd, Auckland, and manufactured by DSM Coatings Resins. It is a water based, self-crossing acrylic emulsion but the exact chemical makeup is unknown. All other chemicals were sourced from Sigma Aldrich.

2.2 Methodology

Nanoparticles were synthesised from an aqueous $HAuCl_4$ solution at room temperature. Our choice of reducing agent and stabilising agent has enabled us to produce a range of colloids with different dichroic properties. The details of the synthesis are proprietary and are not presented here.

To produce a polymer sample, an aqueous colloid was washed to remove excess stabilising agent via centrifugation, and then redispersed in a volume of acrylic. The coloured polymer was dried on a glass slide overnight.

2.3 Analysis

Ultraviolet-visible (UV-vis) absorption spectroscopy was run for aqueous samples using a Shimadzu UV-2600 spectrophotometer. Reflection spectra were obtained for aqueous and acrylic samples, and transmission spectra for acrylic samples, using the ISR-2600PLUS integrating sphere attachment. TEM images were obtained of aqueous samples using a JEOL 2010 electron microscope. Samples were drop-cast onto copper grids, allowed to air dry, and then plasma treated using a JEOL EC-52000IC ion cleaner. In some cases the samples had to be centrifuged, washed and redispersed in water to remove excess stabilising agent prior to TEM analysis. Zeta size (ZS) measurements were run using a Zetasizer Nano ZS instrument.

3 RESULTS AND DISCUSSION

A range of aqueous gold nanoparticle colloids have been produced that display the dichroic effect to varying degrees (Figure 1). We are able to control the colour of the colloid in transmitted light from pink to purple to purple/grey (sample A→D). The observed colours are consistent with the UV-vis absorbance spectra, in which the LSPR peak has red-shifted from 530 nm for sample A to 544 nm for sample D, and has also become significantly broader (Figure 2). These changes are typically indicative of nanoparticle aggregation or agglomeration, or of increasing nanoparticle size.

Additionally, there is an intensification of the orange/brown shade observed in reflected light for samples A through B and C to D. (Figure 1). This increase in scattering processes is further demonstrated by a rise in the height of the reflectance peak (Figure 3). Greater scattering suggests larger particles, consistent with the absorption spectra results.

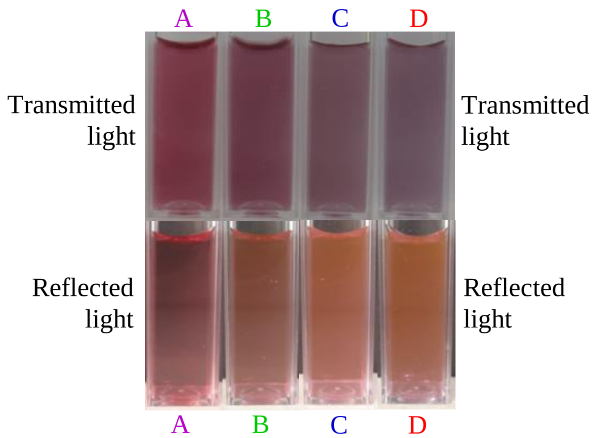

Figure 1: Sample A→D colloid colours in transmitted and reflected light.

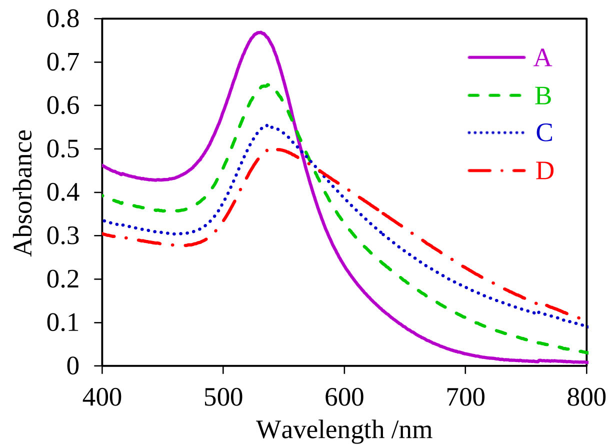

Figure 2: UV-vis absorption spectra of colloid samples A→D.

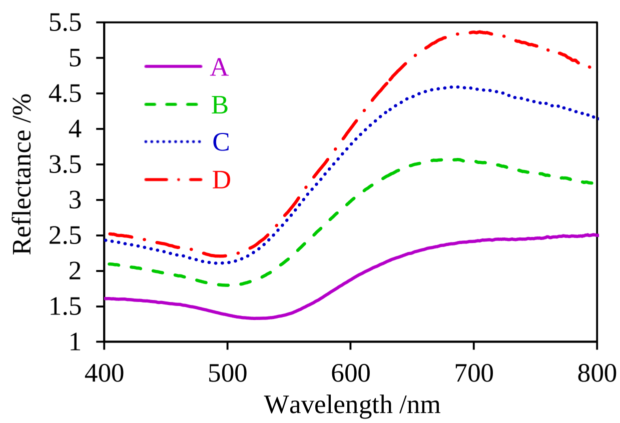

Figure 3: UV-vis reflectance spectra of colloid samples A→D.

Zeta size measurements have likewise suggested an increase in nanoparticle sizes for samples A→D (Table 1). It has given ZS diameters that are significantly larger than what is theoretically required for scattering to occur. However zeta size analysis measures the hydrodynamic radius of the particles and therefore the zeta size value includes the stabilising agents and any nanoparticles that are associated together.

	A	**B**	**C**	**D**
ZS /nm	89.6 ± 1.9	103 ± 1	116 ± 3	122 ± 6

Table 1: ZS measurements for aqueous samples A→D.

The data obtained suggest that a large nanoparticle size has produced high levels of light scattering and the resulting observation of the dichroic effect. However large nanoparticles and aggregation/agglomeration are often observed in gold nanoparticle chemistry but are not always accompanied by the dichroic effect. Therefore TEM analysis has been utilised to obtain more accurate information on the size and shape of the particles present, to determine how they are uniquely able to scatter and absorb light in this way.

Samples B and D were chosen to be examined, and both were found to possess a combination of smaller particles based on a spherical shape, and larger 'flat' or planar nanoparticles (Figures 4 and 5). The ratio of small quasi-spherical particles to large planar particles was calculated to be 30:1 for sample B and 10:1 for sample D, with care being taken to ensure representation of the entire sample was achieved. Because of the understanding that the magnitude of scattering increases with increasing particle size, and that the reflection of light off the colloids has increased with an increased proportion of the large planar particles (sample B→D), the colour of the colloids in reflected light has been attributed to the large planar particles.

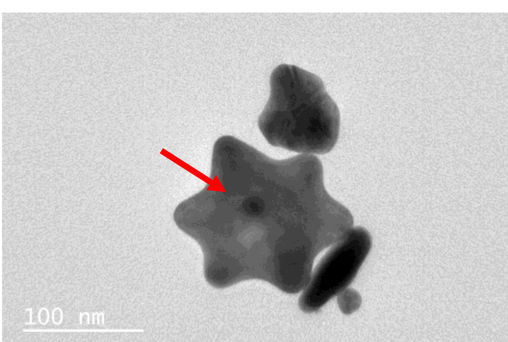

Figure 4: TEM image of sample D showing a large planar particle (red arrow) amongst smaller particles of various shapes.

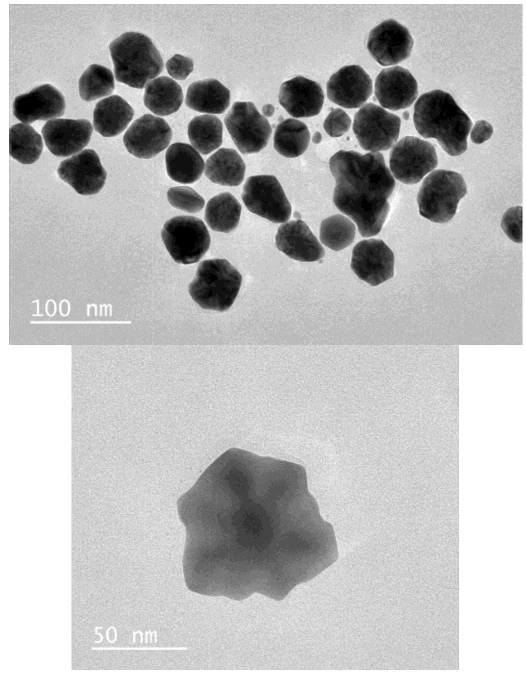

Figure 5: TEM images of sample B showing small quasi-spherical particles (top) and large planar particles (bottom).

The colour of the colloids in transmitted light has been attributed to the LSPR absorption of the observed small quasi-spherical particles. Calculated in ImageJ, sample B and D spherical particles have an average diameter of 35.3 ± 1.4 nm and 42.0 ± 3.3 nm respectively, explaining the red-shift in the LSPR peak in the absorbance spectra. Additionally, sample D nanoparticles were significantly more anisotropic (Figure 6) and hence the LSPR band was broader. Therefore, in the case of these colloids, the dichroic effect can be attributed to the presence of two types of nanoparticles; one that effectively scatters light and gives the colour in reflected light, and another that undergoes absorbance and results in the colour in transmitted light.

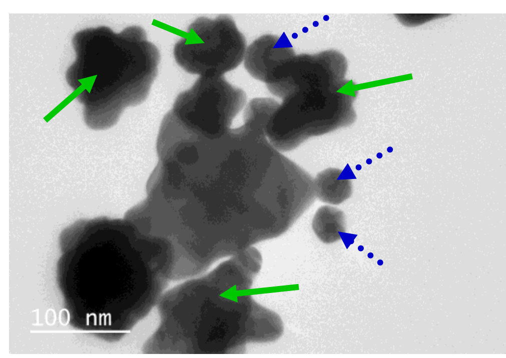

Figure 6: TEM image of sample D showing a large planar particle (centre) with smaller particles, both spherical (blue dotted arrows) and anisotropic (green arrows).

Sample B was chosen for incorporation into an acrylic material. The inclusion of these nanoparticles has resulted in solid, dried samples that appear purple in transmitted light and orange/brown in reflected light (Figure 7). These samples have been analysed via UV-vis absorption and reflection spectroscopy (Figure 8). The LSPR absorption band has red-shifted slightly from when the nanoparticles were in an aqueous solution, suggesting some aggregation may have occurred upon interaction with the acrylic. However the reflection bands are very similar in shape and position. Therefore we have shown that it is possible to transfer nanoparticles from a liquid aqueous system to a solid acrylic with retention of the dichroic effect. The production of such materials has significant and novel potential applications in fields such as security and design.

Transmitted light | Reflected light

Figure 7: Sample B nanoparticles in acrylic, dried on a glass slide, in transmitted and reflected light.

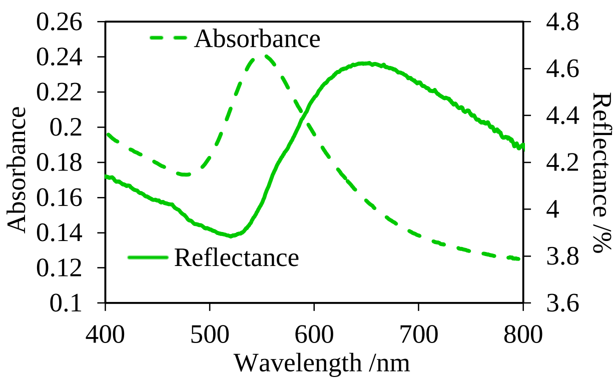

Figure 8: UV-vis absorption and reflectance spectra of sample B nanoparticles in an acrylic system.

4 CONCLUSIONS

We have given a novel demonstration of the Lycurgus effect in an aqueous system. The synthesised gold nanoparticles appear purple or grey in transmitted light and orange/brown in reflected light, and we are able to control the colour and the extent of scattering. A thorough characterisation has enabled us to attribute the colour in reflected light to the presence of large planar nanoparticles, and the colour in transmitted light to the smaller three-dimensional nanoparticles present. We have further incorporated these nanoparticles into an acrylic system with complete retention of the dichroic effect.

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