Discovery of the dichroic effect in cuprous oxide particles for the development of novel composite materials that change colour with direction of light source

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ABSTRACT

When a material appears 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 by the famous Lycurgus cup, however the effect is still poorly understood. We present cuprous oxide (Cu_2O) particles that display the dichroic effect in solution. To the best of our knowledge this is the first time dichroic Cu_2O materials have been reported.

Keywords: dichroic, colour change, cuprous oxide, novel

1 INTRODUCTION

The Lycurgus cup, dated to the 4th century and currently on display in the British Museum, is the oldest and most famous example of the dichroic effect. When the cup is lit from within and the glass viewed in transmitted light it appears red, but when the direction of the light source is changed to outside of the cup, i.e. it is viewed in reflected light, it appears green. In the case of the Lycurgus cup, and in other published dichroic examples, the observed dichroism has resulted from the presence of metallic nanoparticles.

Metallic nanoparticles undergo localised surface plasmon resonance (LSPR); 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 the incoming light are resonant, and hence the wavelength at which absorption and scattering are greatly enhanced. This gives the displayed colour. The typical red shade of nanogold made famous by its inclusion in 17th century stained glass windows arises from spherical gold nanoparticles about 20 nm in diameter, which give a strong LSPR absorption at ~520 nm [1].

The ratio of LSPR absorption to scattering has been found to be strongly dependent on nanoparticle size. Calculations by El-Sayed and co-workers have shown that for spherical 20 nm gold nanoparticles scattering is negligible and only absorption is relevant [2]. Particles with 40 nm diameters are still dominated by absorption, but a small amount of scattering occurs, but for 80 nm gold particles both absorption and scattering contribute almost equally to total extinction. It was concluded that the ratio of scattering to absorption increases with increasing nanoparticle size.

In order to better understand the origin of the dichroic effect in the Lycurgus cup, studies have been done on small glass fragments found when the base of the cup was removed in the 1950s. The most thorough of these studies, conducted in 1990 by Barber and Freestone, ran transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy on a 2 mm^3 glass sample [3]. They observed metallic nanoparticles embedded within the glass. These particles were 50-100 nm in size, and were determined to be alloys 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. However the precious nature of the cup has precluded further analysis, and the nature of the relationship between the colours displayed by the Lycurgus cup and the nanoparticle shape, size and composition is still poorly understood.

Since analysis of the Lycurgus cup, a small number of studies have examined the dichroic effect for gold and silver nanoparticles, and have attributed the effect to nanoparticle size [4,5], shape [6], polarisation [7], etc. In previous work we have presented gold nanoparticles that display dichroism [8]. A thorough characterisation determined that the dichroic effect resulted from a mixture of nanoparticle types; smaller particles that effectively absorb light and give the colour in transmitted light, and larger particles that undergo scattering and result in the colour in reflected light. However further work is still necessary to determine what factors dichroism can be exclusively assigned to. It is therefore desirable to find alternative materials that display the effect to further understand it, whilst also increasing the available colour range.

Cuprous oxide has attracted attention for many applications from optoelectronic devices to sensors, and the synthesis of Cu_2O particles has been well studied [9-11]. However to the best of our knowledge the dichroic effect has not been reported in the literature for Cu_2O. We present cuprous oxide particles that display one colour in reflected light but a different colour in transmitted light. The formation of Cu_2O has been confirmed and the size and shape of the particles characterised.

2 EXPERIMENTAL

2.1 Methodology

Cuprous oxide particles were synthesised with careful control over reaction conditions and choice of materials, allowing the formation of a dichroic solution. The details of the synthesis are proprietary and are not presented here.

2.2 Analysis

Fourier-transform infrared (FTIR) spectra were aquired with a PerkinElmer Spectrum One spectrometer and X-ray diffraction (XRD) patterns with a PANalytical XPert Pro diffractometer.

Ultraviolet-visible (UV-vis) absorption spectra were obtained using a Shimadzu UV-2600 spectrophotometer. Use of a ISR-2600PLUS integrating sphere attachment allowed reflection spectra to be collected.

TEM images were obtained using a JEOL 2100 electron microscope. Samples were drop-cast onto copper grids, allowed to air dry, and plasma treated using a JEOL EC-52000IC ion cleaner before analysis.

3 RESULTS AND DISCUSSION

A cuprous oxide solution has been produced that displays the dichroic effect. The optimised methodology allows control of the colours presented; the sample appears bright yellow in reflected light and pale blue in transmitted light (Figure 1).

Figure 1: Dichroic Cu_2O solution appears bright yellow in reflected light (left) and pale blue in transmitted light (right). See online version for colours.

The formation of Cu_2O particles was confirmed using various techniques. The FTIR spectrum has shown a strong peak at 626 cm^{-1} which was assigned to the Cu(I)-O vibrational frequency (Figure 2). This is consistent with reported values for this stretching band [12,13]. The powder XRD pattern showed peaks corresponding to cubic cuprous oxide (JCPDS 04-007-9767) (Figure 3). Peaks with 2θ values of 29.4°, 36.2°, 42.1°, 61.2°, 73.4° and 77.2°, correspond to 110, 111, 200, 220, 311 and 222 phases of cuprous oxide respectively. No major impurities were observed.

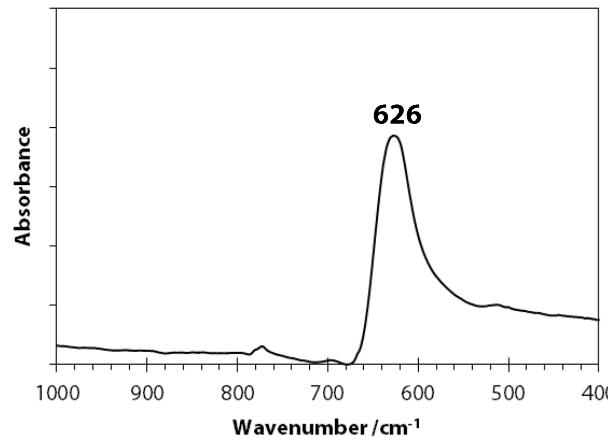

Figure 2: FTIR spectrum showing the characteristic Cu(I)-O stretch at 626 cm^{-1}.

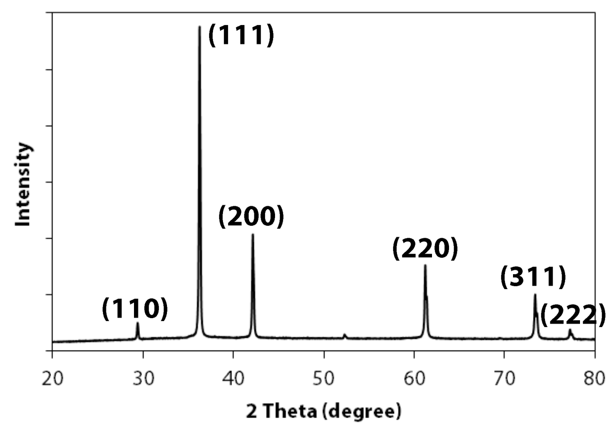

Figure 3: Powder XRD pattern showing the characteristic pattern for cuprous oxide.

UV-vis absorption and reflectance spectra were obtained in the wavelength range of 400 nm to 800 nm (Figure 4). The reflectance spectrum for this sample shows a strong peak at 602 nm which is consistent with the bright yellow colour observed in reflected light. The absorption peak lies at 482 nm. The light reflected off these particles is intense and the colour in transmitted light is very pale, and therefore the pale blue transmitted colour is not observable in the absorption spectrum except for a small shoulder in the spectrum at ~600-700 nm.

TEM analysis has shown that the Cu_2O particles formed are cubic in shape (Figure 5). The cubes are relatively monodisperse and show truncated or curved corners.

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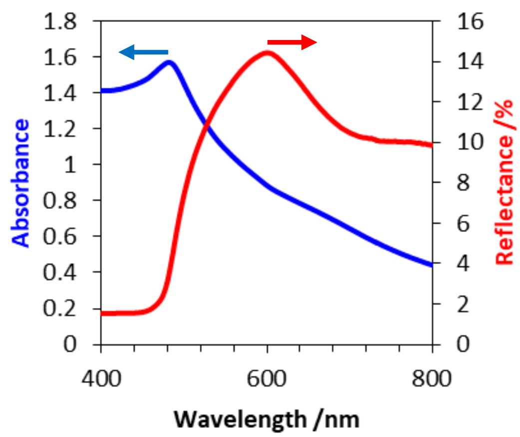

Figure 4: UV-vis absorption and reflectance spectra of Cu_2O particles.

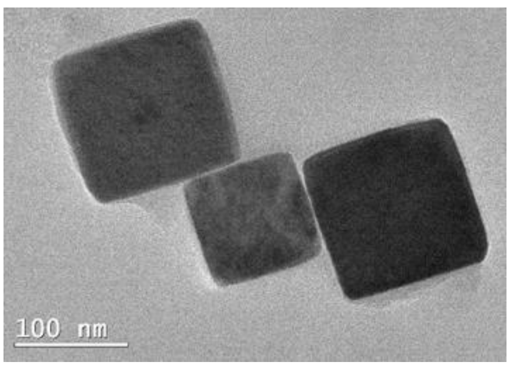

Figure 5: TEM micrograph showing Cu_2O particles with cubic morphologies.

4 CONCLUSIONS

We present cuprous oxide particles in solution that display the dichroic effect. By careful control of the methodology we have produced a solution that appears bright yellow in reflected light but pale blue in transmitted light. Characterisation has confirmed that Cu_2O particles have formed and has determined the size and shape of the particles.

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