A study of the interaction between nanoparticles and light: an experimental proof and visualisation of Mie theory in polymer composites

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ABSTRACT

An experimental proof of Mie theory has been developed using gold nanoparticles. The relationship between nanoparticle size and the ratio of scattering to absorption has been investigated, and nanoparticle – polymer composites have further been produced to provide a visualisation of Mie theory.

Keywords: Mie theory, nanoparticle, gold, polymer composite, dichroic

1 INTRODUCTION

Gold nanoparticles have long been utilised for their attractive colours. A well-known example is the Lycurgus cup, dated at the 4th century, which appears red when viewed in transmitted light and green in reflected light due to the presence of gold/silver/copper nanoparticles in the glass (Figure 1) [1]. About 1500 years later in the 1850s, the science behind gold nanoparticle colour was first explored with Michael Faraday's studies on the optical properties of gold colloids [2]. However the theory behind the observed colours was not truly understood until Gustav Mie published a mathematical description of the absorption and scattering of electromagnetic radiation by a spherical nanoparticle in 1908 [3]. This became known as Mie theory. The interaction between nanoparticles and light remains of significant interest to the nanotechnology community, as understanding this interaction allows us to predict the nanoparticle size, shape and material that is most suitable for various applications.

Metallic nanoparticles undergo localised surface plasmon resonance (LSPR) effects; the oscillation of nanoparticle conduction electrons upon resonance interaction with incoming electromagnetic radiation (Figure 2). LSPR greatly enhances the absorption and scattering of light by nanoparticles described by Mie theory. The size, shape and composition of the particles determine the frequency at which the electron oscillation and incoming light are resonant, and hence the wavelength of the LSPR absorption/scattering and the colour that is displayed. For example, spherical gold nanoparticles with diameters of 20 nm undergo LSPR resonance at approximately 520 nm which gives a red coloured colloid [5]. Increasing the size of the particles results in a red-shift in the LSPR absorption and a change in colour from red to purple to grey.

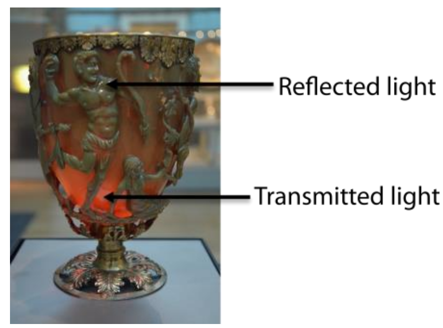

Figure 1: Photograph of the Lycurgus cup with white light placed inside at bottom. Reproduced from Wikimedia Commons, CC BY-SA 2.0 [4].

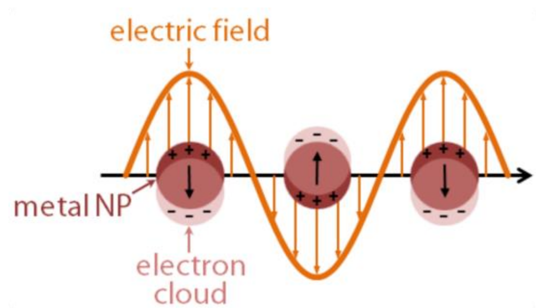

Figure 2: Schematic illustration of localised surface plasmon resonance.

Mie theory also describes how nanoparticle size determines the ratio of LSPR scattering to absorption. First shown computationally by Jain and co-workers for spherical gold nanoparticles [6], increasing nanoparticle size results in an increase in scattering and a proportional decrease in absorption. We present an experimental proof of this relationship between size and the scattering:absorption ratio for gold nanoparticles.

2 EXPERIMENTAL

A series of gold nanoparticle colloids with narrow size distributions were synthesised in aqueous solution. Following characterisation, the particles were incorporated into acrylic polymers which were then dried onto glass slides. The details of this methodology are proprietary and are not presented here.

3 RESULTS AND DISCUSSION

Gold nanoparticles in solution have been synthesised and used to experimentally demonstrate Mie theory. Systematically increasing the size of the gold nanoparticles has resulted in an increase in scattering processes and a corresponding decrease in absorption. The experimental relationship between nanoparticle size and the ratio of scattering to absorption compares well to that produced using Mie theory calculations.

We have further incorporated these gold nanoparticles into polymers to create solid state composites that provide a visualisation of Mie theory. When the composites are viewed against a dark background the light scattered by the particles is seen as an orange/brown colour (right of Figure 3). With an increase in nanoparticle size the scattered colour is seen to increase in intensity, consistent with the increase in the scattering:absorption ratio predicted by Mie theory and demonstrated experimentally in this work. Additionally, when the composites are viewed in transmitted light there is the typical colour change from purple to grey commonly associated with an increase in gold nanoparticle size (left of Figure 3).

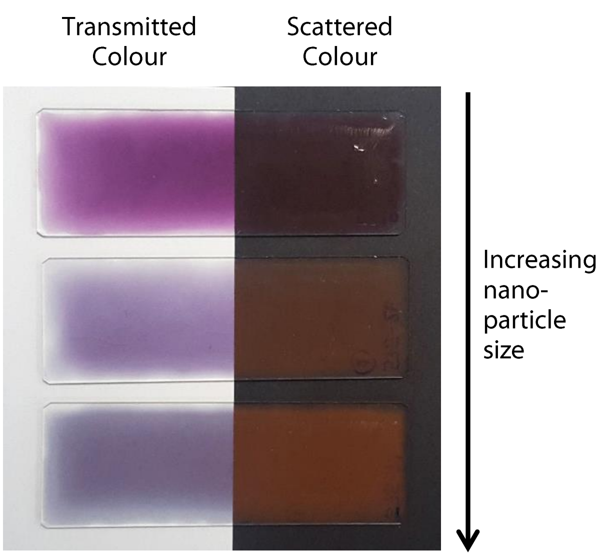

Figure 3: Gold nanoparticle – polymer composites dried onto glass slides.

The change in colour of each sample between transmitted and reflected light is an example of the dichroic effect also seen in the Lycurgus cup. The encapsulation of this effect in polymer composites has a range of potential applications in the areas of security and design. Furthermore, the composites could be used as a teaching tool to aid in understanding of gold nanoparticle physics and Mie theory.

4 CONCLUSION

We have experimentally demonstrated that the ratio of scattering to absorption increases with increasing gold nanoparticle size, and shown that this relationship compares well to Mie theory results. By further incorporating gold nanoparticles into polymer composites we have produced a means of visualising Mie theory.

REFERENCES

[1] D. Barber and I. C. Freestone, "An investigation of the origin of the colour of the Lycurgus Cup by analytical transmission electron microscopy," Archaeometry 32, 33, 1990.

[2] M. Faraday, "The Bakerian lecture: experimental relations of gold (and other metals) to light," Philos. Trans. R. Soc. Lond. 147, 145, 1857.

[3] G. Mie, "Beiträge zur Optick trüber Medien, speziell kolloidaler Metallösungen," Ann. Phys. 330, 377, 1908.

[4] Photo licenced under the Creative Commons Attribution-Share Alike 2.0 Generic license. https://commons.wikimedia.org/wiki/File:Lycurgus_cup,_one_of_the_finest_examples_of_Roman_glassware_made_in_the_4th_century_AD,_British_Museum,_London_(14233393147).jpg (accessed 12/02/2019).

[5] J. Turkevich, G. Garton and P. Stevenson, "The color of colloidal gold," J. Colloid. Sci. 9, 26, 1954.

[6] P. K. Jain, K. S. Lee, I. H. El-Sayad and M. A. El-Sayad, "Calculated absorption and scattering properties of gold nanoparticles of different size, shape, and composition: applications in biological imaging and biomedicine," J. Phys. Chem. B 110, 7238, 2006.