

# Nanocomposites: From ancient masterpieces to value-adding nanotechnology

Andrea N. D. Kolb

School of Chemical & Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington  
(email: [andrea.n.d.kolb@gmail.com](mailto:andrea.n.d.kolb@gmail.com))

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## Introduction

Composites comprising metal nanoparticles (NPs) and glass, porcelain, gum arabic or gelatine have been known and investigated for hundreds of years.<sup>1</sup> For example, the Lycurgus Cup from the 4<sup>th</sup> century AD (Fig. 1), exhibited in the British Museum in London, is considered a masterpiece of the early glass industry. This work became famous for its dichroic effect that depends on the angle of the light shining on it; the cup appears red in transmitted light and green in reflected light.<sup>2</sup> As we know today, the effect arises from nanoparticulate gold–silver–copper alloys that are dispersed in the glass matrix of the cup.<sup>3</sup> Another famous use of nanoparticulate gold is the colourant “Purple of Cassius”. Since the late 1600s, it has been used on a large scale as a decoration for factory-made ceramics,<sup>4</sup> and although pure gold, the colourant is available in shades of pink to maroon.



**Fig. 1.** The Lycurgus Cup (from Wikimedia Commons)

## Optical properties of nanoparticles

The unusual colours of metal NPs arise from localised surface plasmon resonance (LSPR), which depends on the size, shape and dielectric function of the particle, and the refractive index of the surrounding medium.<sup>5</sup> This phenomenon is a result of the interaction of the electric field of light with the NP, which is accompanied by the absorption of a photon of energy by the particles. The gain in energy induces a dipole on the particle by collectively separating free conduction electrons (dense electron cloud) from the positively charged metal core. The separation of the electrons is confined to the boundaries of the metal particle due to the attractive forces of the positive core. The

separating and restoring of the electron cloud results in an oscillation that is also called a “plasmon” of a NP. The oscillation resonates with frequencies in the visible and the near infrared region of the electromagnetic spectrum and creates a characteristic LSPR band (Fig. 2).<sup>6</sup> In simple terms, the dense electron cloud can be regarded as animated fans in a stadium who constantly perform a Mexican Wave. The steady performance creates a wave that travels continuously through the spectators. In the case of electrons, the collective oscillation is permanent and results in non-fading, distinctive colours. This makes gold NPs, for example, a highly effective colourant with a molar extinction coefficient that is approximately 2–5 orders of magnitude greater than that of conventional dyestuffs.<sup>7,8</sup>

In the case of 20 nm AuNPs, the LSPR band occurs at approximately 520–525 nm, which translates to a ruby red.<sup>9</sup> Smaller particles (10 nm) have a blue-shifted LSPR band and larger particles (30–100 nm) have a red-shifted band. Therefore, spherical AuNPs of 10–100 nm exhibit colours that range from red to pink, purple and lilac. Anisotropic particles, such as rods, ‘dog-bones’, plates, triangles, cubes and branched structures, possess both a transverse and a longitudinal axis which interact with the electric field of the incident light. Both interactions resonate with optical frequencies and occur as two separated LSPR bands. As a result, AuNPs of precise shape, dimension and length-to-width ratio can offer a powerful approach to engineering AuNPs with a wide colour gamut (Fig. 3).

## Use of nanoparticles for the production of nanocomposites

Since the early 1900s, nanogold has been applied knowingly to produce nanocomposites. In the 1940s, for instance, nanogold–skin composites were produced by staining keratinous skin cells with AuNPs.<sup>10</sup> This staining technique uses an Au<sup>3+</sup> precursor to impregnate the cells where it is reduced to Au<sup>0</sup> (AuNPs). The nanogold–skin composite is pink, deep red, reddish purple or purplish black, where the different colours represent different structural components of the skin. The reddish purple originated from very fine AuNPs and the deep purplish black was associated with rather coarse AuNPs.<sup>10</sup> In the 1950s, nanogold–wool composites were produced using a gold staining technique.<sup>11</sup> Like human hair, wool is a keratinous fibre with a complex and variable chemical and physical structure. The distribution, colour and colour intensity of the AuNPs showed that the gold deposition in the fibre was asymmetric, which helped to elucidate the bilateral inner structure of wool fibres.<sup>11</sup> In the 1970s, this staining technique was used commonly to produce a variety of metal–wool composites which were studied by

electron microscopy.<sup>12</sup> The gold staining technique was a simple tool to learn about the histology of the substrate to which the AuNPs were attached. In more recent years, the focus in studying nanocomposites has turned from the concentration of the substrate component to the nanoparticle component of the composite and its unusual physicochemical properties. It has been realised that nanocomposites possess new or enhanced properties that exploit the natural synergy between the components. In the last decade, nanocomposites have been developed for application in the paper, textile and energy industries.

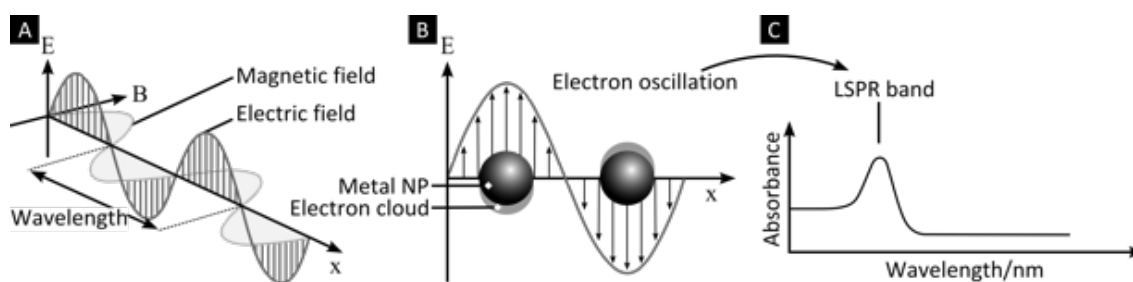
Nanocomposites can be produced using a chemical reaction to synthesise NPs in the presence of a substrate, which can include a variety of materials.<sup>1,13</sup> For example, both vegetable and bacterial cellulose were used as substrates in the production of nanocomposites comprising NPs of Au and Ag.<sup>14,15</sup> Such violet and grey nanogold–cellulose composites may find application in security paper production, while nanosilver–cellulose composites with antibacterial activity may be used for biomedical applications.<sup>14,15</sup>

In 2011, nanogold–wool composites for high value textiles and fashion apparels were reported.<sup>16</sup> The nanocom-

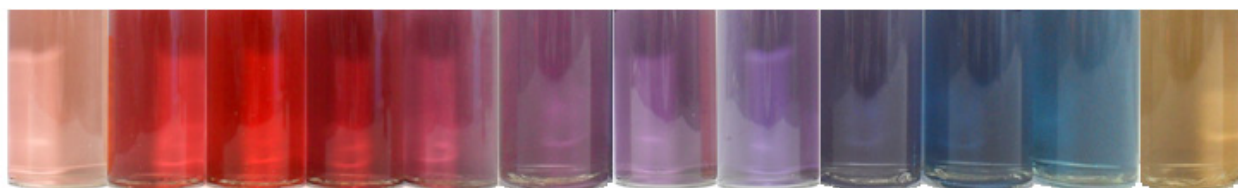
posite exhibited different colours, including deep purple (Fig. 4), which are associated with the LSPR properties of the AuNPs. The porous nature of wool and the affinity of gold for sulfur contained in the cystine amino acids were used to control the size of the AuNPs and to chemically bind them to the surface and within the wool fibre matrix. Because the AuNPs are chemically bound to the cystine, they do not wash or rub out and are also stable to UV light.<sup>16</sup>

Additionally in 2011, silver NPs (AgNPs) were used to colour merino wool fibres and fabrics (Fig. 5).<sup>17</sup> The AgNPs were produced by the reduction of  $\text{Ag}^+$  to  $\text{Ag}^0$  with trisodium citrate (TSC) directly on the wool fibre surface. The TSC simultaneously acts as a capping agent for the NPs and as a AgNP–wool linker. The nanosilver–wool composites exploit the LSPR properties of the AgNPs and are coloured in hues of yellow/orange, red/brown and brown/black depending on particle size. The coloured fibres and fabrics are anti-microbial, anti-static and durable, which makes them attractive candidates for applications in upholstery and carpets.<sup>17</sup>

The term “nanocomposite” is also commonly used to describe a material that consists of a substrate and pre-



**Fig. 2.** Schematic illustration of LSPR of a metal NP. A: Electromagnetic field of light. B: LSPR occurs when the free conduction electrons of the NP interact with the electric field of the incident light of a suitable frequency. This induces a dipole by collectively separating the electrons from the positively charged metal core. This steady process of separating and restoring within the boundaries of the metal NP causes an oscillation of the separated, localised electrons (electron cloud). C: The oscillation of the surface electrons resonates with optical frequencies of light in the visible region and creates colours different from those of the respective bulk material.



**Fig. 3.** The many colours of nanoparticulate gold include shades of red, lilac, blue, turquoise and brown; from A.N.D. Kolb, PhD Thesis, Victoria University of Wellington, 2014.



**Fig. 4.** Purple nanogold–wool composites produced with AuNPs. Reproduced with permission from ref. 16. © 2011 Johnston and Lucas.



**Fig. 5.** Nanosilver–wool fibre composites produced with yellow AgNPs. Reproduced with permission from ref. 17. © 2011 American Chemical Society.

synthesised NPs which have been deposited onto the substrate in a separate work step. For over 15 years now, synthetic polymers, such as polyethylene (PE) and polyvinylalcohol (PVA), have been functionalised with metal NPs. The nanoparticle–polymer composites are produced by solvent-evaporation,<sup>1</sup> extrusion,<sup>1</sup> electrospinning,<sup>18</sup> or emulsion polymerisation.<sup>19</sup> Flexible nanosilver–PE composites appear yellow or red depending on the polarisation direction of the incident light. This makes them a potential colour filter to enhance the brightness and energy efficiency of light-emitting diodes (LEDs).<sup>20</sup> Composites comprising PVA and gold nanorods (AuNRs) with tuneable dimensions are also envisaged for the fabrication of thin film optical filters.<sup>21</sup>

In early 2011, the colouration of wool fabrics with anisotropic AgNPs of different colours was reported.<sup>22</sup> Colloidal AgNPs of different sizes and shapes were synthesised by the reduction of  $\text{Ag}^+$  to  $\text{Ag}^0$  with TSC in the presence of poly(vinylpyrrolidone) and  $\text{H}_2\text{O}_2$ . The AgNPs were blue (nanoprisms), red (thin nanodiscs) and yellow (thick nanodiscs), and the LSPR properties of the AgNPs deposited on the wool were essentially identical to those of

the colloidal AgNPs (Fig. 6).<sup>22</sup> However, AgNPs are not stable to UV light and exposure is accompanied by an unattractive colour change over time.

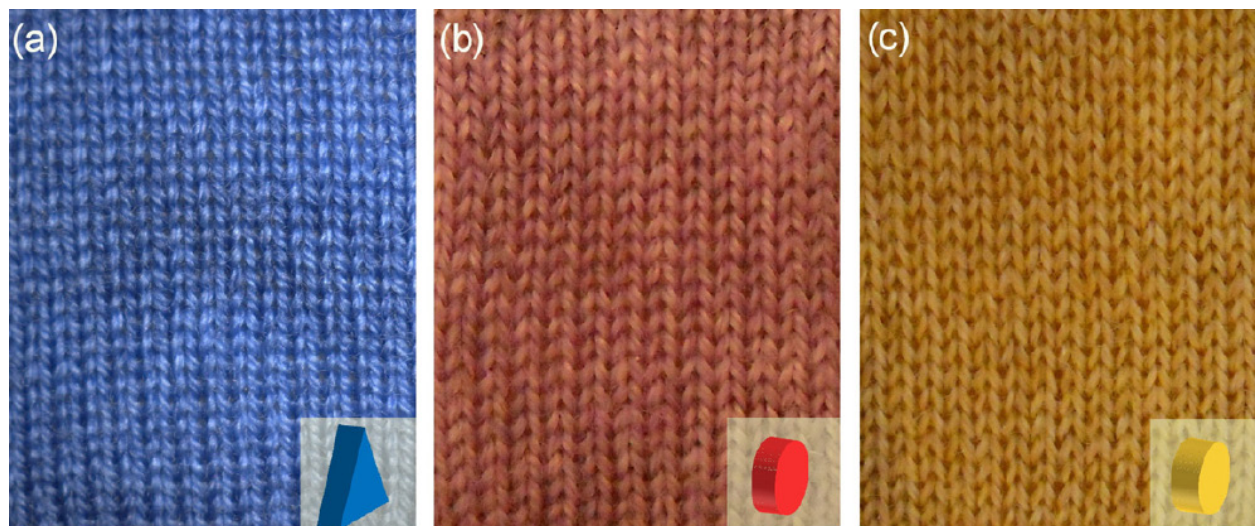
In 2013, the colouration of cotton and silk fabrics with pre-synthesised AuNRs of different colours was reported.<sup>23</sup> The optical properties of AuNRs originate from two LSPR bands and can be precisely engineered by tailoring the longitudinal band. This approach resulted in AuNR–cotton and AuNR–silk composites that were brownish red, green and purplish red. The believed electrostatic AuNR–fabric interaction provided the AuNR–cotton composites with commercially acceptable wash fastness whereas the AuNR–silk composites failed the requirements. Furthermore, the AuNRs provided the composites with very good UV protection and anti-bacterial properties.<sup>24</sup>

The two examples of nanocomposites described above<sup>22,23</sup> were produced by binding pre-synthesised plasmonic NPs to a substrate where the binding was associated with electrostatic interactions. This type of bond is relatively weak and offers opportunity for improving the overall fastness.

Strong covalent bonds are achieved through specific wet-chemical approaches, such as the direct attachment of pre-synthesised carboxyl-functionalised microparticles (MPs) to amine-containing wool by an amide bond.<sup>25</sup> The reaction was assisted by the use of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide and *N*-hydroxysuccinimide as this combination supports amide bond formation under mild reaction conditions. The MP–wool composite showed moderate durability to solvent washing and poor laundering performance. Additionally, the covalent attachment of a reactive chemical entity to the wool surface after surface-bound lipid removal was investigated. This method provided a proof-of-principle for durable nanocomposites with wool as the substrate.<sup>25</sup> Both methods appear to be elegant and potential approaches for the production of more wash fast nanocomposites via a covalent NP–substrate bond.

## Outlook

Nanocomposites consisting of precious metal NPs and materials have come a long way from Roman times to



**Fig. 6.** Nanosilver–wool fabric composites produced with (a) blue, (b) red and (c) yellow AgNPs. Reproduced with permission from ref. 22. © 2011 Elsevier.

the present research in nanotechnology. Using plasmonic NPs as colourants for textile fibres presents an interesting approach to manufacturing finished, value-added products. This approach could be useful in the long-term success of the wool industry.

The latest research shows that even nature produces nanocomposites with AuNPs. The discovery that Eucalyptus trees mine gold from a depth of 30–50 m and deposit it through their leaves may be a new technique for gold site exploration.<sup>26</sup>

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