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## **The bench synthesis of silver nanostructures of variable size and an introductory analysis of their optical properties**

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A laboratory practical was designed for use by both undergraduate and second level students to demonstrate the synthesis and characterisation of tuneable silver colloids. It clearly illustrates the novel optical properties of silver nanoparticles compared to the bulk metal. The synthesis is both rapid and repeatable, and can be conducted on the laboratory bench at room temperature.

### **Introduction**

For some time nanotechnology has been regarded as the next major scientific advance. References to nanoscience and nanotechnology are now ubiquitous throughout both scientific journals and popular science publications, as researchers dedicate more and more resources to the study and application of all things *nano*. This is particularly evident by the way that the controlled synthesis of nanoparticles (of various shapes and sizes) for use in a wide range of applications continues to progress and gather interest <sup>1-2</sup>. Therefore the development of a secondary school / undergraduate laboratory practical based on a simple synthesis and characterisation of nanoparticles is not only highly relevant as an example of modern chemistry, but also appealing to students.

A simple and rapid practical is proposed, which allows students to both synthesise silver nanoparticles (with size control) and monitor size changes using UV-Vis spectroscopy. The submitted practical has an added advantage that it may be geared

specifically to the educator's needs, depending on the availability of instrumentation, ability of students and time dedicated for the practical / lesson.

Bulk silver is easily identified; its very appearance (silver grey colour) often used as a descriptor; as materials progress to the nanoscale however it is not unusual for their set physical properties to change as the influence of quantum mechanics on the material increases. This is clearly evident with silver colloids; a colloid is a type of mixture that appears to be a solution but is actually a mechanical mixture. A colloidal system consists of two separate phases: a dispersed phase (internal phase), and a continuous phase (dispersion medium). In a colloid, the dispersed phase is made of tiny particles or droplets that are distributed evenly throughout the continuous phase. The dispersed-phase particles are sized between 1 nm and 100 nm in at least one dimension. With silver colloids, because the silver nanoparticles they contain are smaller in dimension than the wavelength of visible light, they interact with light in different ways as demonstrated in figure 1.



Figure 1. A sample set of the different coloured Silver colloids produced in the practical.

It is well established that the colour<sup>3-5</sup> of the (suspended silver nanoparticles) colloids varies according to the morphology of the nanoparticles. Therefore it is possible to estimate the size of the colloidal nanoparticles by just observing their colour.

### **Materials**

The water used in the practical should be of high purity such as Millipore grade (with > 18.2 M $\Omega$  resistivity) or distilled. Silver nitrate (purum p.a. > 99.0%), sodium borohydride (reagent Plus 99%) polyvinyl alcohol, (99+% hydrolyzed, typical M.W. 89000-98000 gmol<sup>-1</sup>), tri sodium citrate, (purum p.a.,  $\geq$  99.0%), hydrazine, (reagent grade, N<sub>2</sub>H<sub>4</sub> 50-60 %), crystal violet, (ACS reagent,  $\geq$  90.0% anhydrous basis),

malachite green, (indicator Riedel-de Haën), Rhodamine 6G, (Dye content ~95 %), were all purchased from Sigma Aldrich and used as received without further purification. Students should prepare or be supplied with the following stock solutions, 1% PVA w/v (aqueous), 0.001M sodium borohydride, 0.001M Tri Sodium Citrate, 0.1M Hydrazine, 0.001M Silver Nitrate and for 'junior' laboratory sessions solution 'A' ( which contains  $3 \times 10^{-3}$ M Silver Nitrate and  $2.5 \times 10^{-3}$  M Tri Sodium Citrate, 1:1 volume ratio). In 'senior' laboratory sessions students may prepare their own seed solution, as outlined in the experimental below and so do not require solution 'A'.

### **Hazards**

Silver nitrate is corrosive, causing burns when in contact with the skin and eyes. Sodium borohydride is flammable and toxic. Sodium citrate may cause irritation to the skin, eyes and respiratory tract. Hydrazine hydrate causes burns and is toxic. Hydrochloric acid and sodium hydroxide are corrosive causing burns when in contact with skin and eyes. Students should wear the appropriate personal protection equipment (goggles, gloves, and lab coat), and follow all laboratory safety precautions.

Supplying the students with stock solutions of the proposed reagent concentrations significantly reduces the experimental risks. When preparing the sodium borohydride solution it is important to ensure that the volumetric flask is either left unstoppered or that the stopper is loosely fastened to avoid a build up of Hydrogen gas which can result in the failure of the vessel. Waste containers should be available for any waste solutions containing silver.

### **Experimental**

The synthesis methods proposed below are completely reliable, providing the practical is conducted with proper care (i.e. slow drop-wise addition of reagents where instructed and the use of properly cleaned glass ware). The prepared reagents, with the exception of sodium borohydride, will last several days to months if stored appropriately (e.g. photosensitive silver nitrate solutions should be stored in opaque vessels). As sodium borohydride decomposes in water (equation 1), it is necessary that the sodium borohydride solution should be freshly prepared the day of the

practical. It should be noted that the best results are achieved when all reagent solutions are freshly made.



### **Synthesis 'junior lab' – second level / 1<sup>st</sup> year undergraduate students**

The silver colloids were prepared by a two part process, consisting of nucleation and particle growth<sup>1-2</sup>. Initially a seed solution was prepared by the chemical reduction of silver nitrate ( $\text{AgNO}_3$ ) with sodium borohydride ( $\text{NaBH}_4$ ) in the presence of a stabiliser and capping agent, Tri Sodium Citrate (TSC). The seed solution was then added, with constant agitation, to a mixture of TSC and hydrazine ( $\text{H}_4\text{N}_2$ ) to produce a 'growth' solution. To this mixture set volumes of  $\text{AgNO}_3$  were added, producing the different colloids. The different volumes of excess  $\text{AgNO}_3$  that are added to the growth solution determine the colour, and therefore the size/shape, of the nanoparticles in the solution.

The principle behind this method is as follows: the seed solution that is added to the growth solution works like a sort of 'frame' or starting point. The excess  $\text{AgNO}_3$  that is added to the growth solution is also reduced by the TSC and  $\text{H}_4\text{N}_2$  to silver atoms which interact with the existing seed nanoparticles, to give a gradual growth of the seed particles, to form nanoparticles of different sizes and shapes<sup>6</sup>. (Please note; the green dispersion is most likely the product of the combined processes of particle growth (larger particles) and secondary nucleation (smaller particles), this accounts for the two distinct particle size ranges of the green colloid (figures 4 & 5b).

### **Seed production**

To 20 cm<sup>3</sup> of solution A (ensure that the solution is being stirred continuously) slowly add (preferably drop wise) 6 cm<sup>3</sup> 0.001M sodium borohydride. Best results are observed using a clean 100 cm<sup>3</sup> beaker as the reaction vessel. (Solution A is a 1:1 mixture of 0.003M  $\text{AgNO}_3$  and 0.0025M TSC)

### **Fabrication of coloured colloids**

To 5 cm<sup>3</sup> 1% PVA, first add 1 cm<sup>3</sup> of the seed solution, followed by the addition of 3 cm<sup>3</sup> 0.1M TSC, and 5 cm<sup>3</sup> 0.1M  $\text{H}_4\text{N}_2$  (again ensure this mixture undergoes constant

agitation). To produce the coloured colloids, set volumes of 0.001M AgNO<sub>3</sub> should be added to this ‘growth mixture’ as outlined in table 1, with best results observed using a clean 250 cm<sup>3</sup> beaker as the reaction vessel.

<b>0.001 M AgNO<sub>3</sub> (cm<sup>3</sup>) ( X cm<sup>3</sup>)</b>	<b>Colour</b>
<b>~ 0.40</b>	<b>Yellow</b>
<b>~ 1.00</b>	<b>Orange</b>
<b>~ 1.30</b>	<b>Red</b>
<b>~ 2.50</b>	<b>Purple</b>
<b>~ 6.00</b>	<b>Blue</b>
<b>~ 20.00</b>	<b>Green</b>

Table 1. Summary of volumes of 0.001 M AgNO<sub>3</sub> and the resulting colloids.

### **Synthesis senior lab – undergraduate students**

Again the silver colloids were produced using a two part process. Here the seed solution was once more prepared by the chemical reduction of AgNO<sub>3</sub> with NaBH<sub>4</sub> in the presence of polyvinyl alcohol (PVA)<sup>7</sup> a stabiliser and capping agent. It should be noted that this seed synthesis requires the student to show great care and patience with the addition of the reducing agent, in order to produce a suitable seed and hence coloured colloids.

### **Seed production**

To 2 cm<sup>3</sup> of PVA (1% w/v) add 2 cm<sup>3</sup> 0.001M AgNO<sub>3</sub> and mix well. To this mixture slowly add 2 cm<sup>3</sup> of 0.001M NaBH<sub>4</sub> drop wise ensure that the mixture undergoes constant agitation during the NaBH<sub>4</sub> addition. Best results are achieved overall when the resulting seed solution is a golden yellow, although this colour change is almost immediately evident it is also important that the student adds the full volume of NaBH<sub>4</sub> as failure to do so impinges the growth of further coloured colloids.

### **Fabrication of coloured colloids**

The production of the coloured colloids follows that of the ‘junior’ laboratory experimental outlined above in table 1.

## **Characterisation of the silver nanoparticles**

Characterisation of the silver nanoparticles can involve several techniques, dependent on availability of instrumentation, ability of students and time dedicated for the practical.

The authors used UV-Vis, dynamic light scattering (DLS) and electron microscopy, which were conducted using a Perkin Elmer, Lambda 900 Spectrometer, a Malvern nano series Zetasizer and 100CX Transmission Electron Microscope (TEM) or Hitachi SU 6600 FESEM (STEM) respectively. The results presented below are for colloids produced via the senior lab practical, it should be noted that almost identical results are achieved with colloids produced via the junior practical.

## **Results and discussion**

### **Colloid characterisation**

#### **The Tyndall effect – Has a colloid been prepared?**

The Tyndall effect, also known as Tyndall scattering, is the scattering of light by colloidal particles or particles in suspension. It may be demonstrated using a laser pointer and several clear and coloured solutions, e.g. deionised water and a selection of dye solutions as well as prepared colloids, to demonstrate the observed scatter is a result of the presence of nanoparticles and not simply due to pigment.

The student should shine the laser through the solutions. In non colloidal mixtures only the points where it enters and exits the liquid is evident; the path the laser travels through the media is absent. If the solution is colloidal, the path of the laser is clearly illuminated (figure 2).

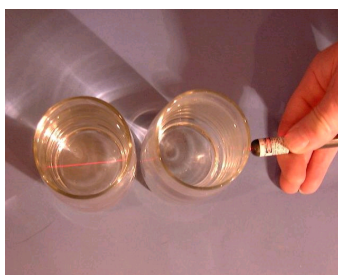


Figure 2. The glass on right contains only DI water, while glass on left contains silver colloid.

### **UV-Vis analysis**

The absorption spectrum of the 'seed' colloid, shown in Figure 3, indicates the production of the nanoparticles where the presence of a plasmon absorption band at ~400 nm is characteristic of silver nanoparticles<sup>8</sup>.

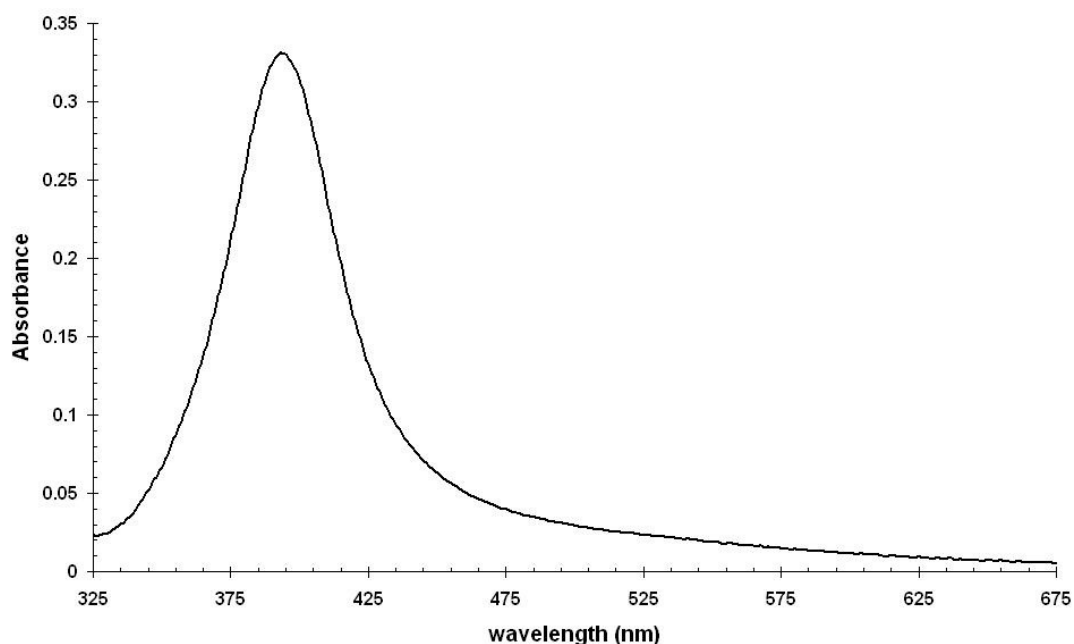


Figure 3. UV-Vis spectrum of stable aqueous colloidal Ag Seed solution, with  $\lambda$  max of 393 nm.  
 $[\text{Ag}^+] = 0.001\text{M}$  ( $2.0 \text{ cm}^3$ ),  $[\text{PVA}] = 1\% \text{ wt/wt}$  ( $2.0 \text{ cm}^3$ ),  $[\text{NaBH}_4] = 0.001\text{M}$  ( $2.0 \text{ cm}^3$ )

Such plasmon bands are the result of the unique physical properties of the nanoparticles themselves. When an external electro-magnetic field such as light is applied to a metal, the conduction electrons move collectively so as to screen the perturbed charge distribution in what is known as plasmon oscillation. The Surface Plasmon Resonance (SPR) is therefore a collective excitation mode of the plasmon localized near the metal surface. In the case of a metal nanoparticle, the surface plasmon mode is 'restricted' due to the small dimensions to which the electrons are confined, i.e. the surface plasmon mode must conform to the boundaries of the dimensions of the nanoparticle <sup>9</sup>. Therefore, the resonance frequency of the surface plasmon oscillation of the metal nanoparticle is different from the plasmon frequency of the bulk metal. Surface interactions can alter the optical properties and influence the spectral profile of the light scattered by the SPR of the metal nanoparticles. This feature can be employed as an indicator in sensing interactions. Among the metal nanoparticles known to exhibit SPR, silver nanoparticles have an especially strong SPR. Particle size may be determined using Mie theory, which solves Maxwell's equations <sup>10</sup> and in turn describes the extinction spectra (extinction = scattering + absorption) of spherical particles of arbitrary size <sup>5,11-12</sup>.



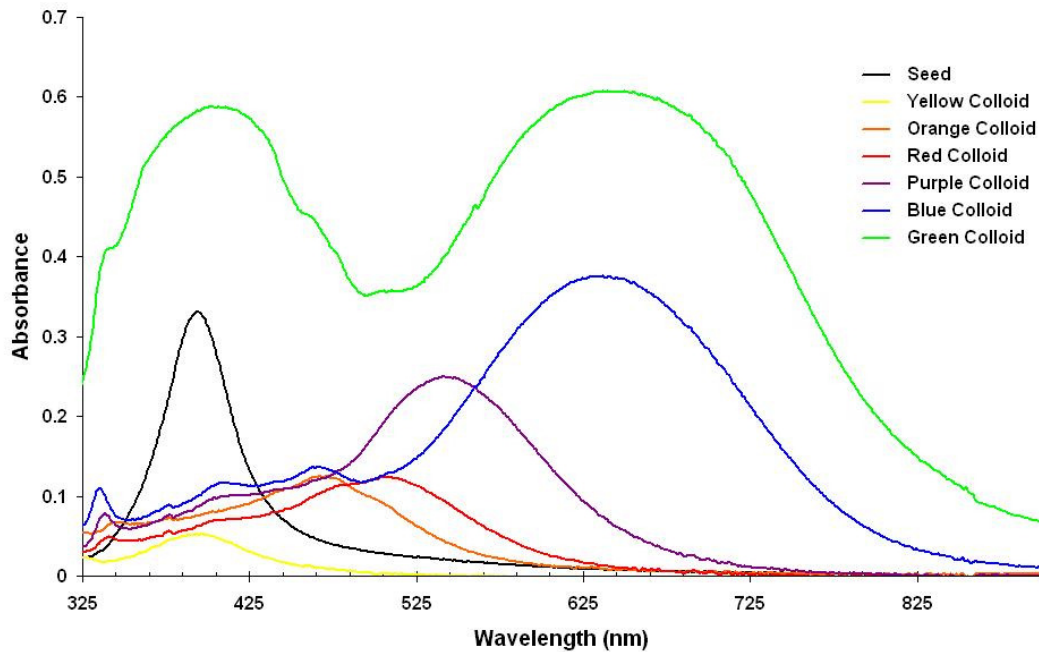


Figure 4. UV-Vis spectra of aqueous coloured Ag colloids. General make up of colloids [PVA] = 1% wt/wt ( $1.0 \text{ cm}^3$ ), seed solution ( $1.0 \text{ cm}^3$ ), [TSC] = 0.1M ( $3.0 \text{ cm}^3$ ),  $[\text{H}_4\text{N}_2] = 0.1\text{M}$  ( $5.0 \text{ cm}^3$ ) +  $[\text{AgNO}_3] = 0.001\text{M}$  ( $X \text{ cm}^3$ ). Please note that the value of X is stated in Table 1.

The excitation spectra of the different coloured colloids, which are presented in figure 4, are clearly influenced by the nanoparticles' properties. It should be noted that for smaller particle size ranges such as the yellow colloid, a narrower/sharper absorbance band is observed. In contrast the blue colloid with a wider particle size range has clearly broader peaks. The  $\lambda$  max of the spectra also shifts position with changes in the nanoparticles size and shape.

The different nature of each colloid is also highlighted in the UV-Vis spectra of the green colloid where two distinct absorbance peaks are observed as a result of the interaction of two species (type) of nanoparticles i.e. the larger blue nanoparticles and the smaller yellow nanoparticles, (these are the most likely species contributing to the green as the peaks are seen to have similar  $\lambda$  max's – Yellow 445 nm, Blue 670nm, Green band 1, 405 nm, band 2, 648 nm). The other colloids exhibit just one distinct band that can display a shoulder. However this could be attributed to band broadening due to the wider particle size range.

## Dynamic light scattering, DLS

Size analysis by DLS utilises the Brownian motion that particles, emulsions, and molecules in suspension undergo as a result of bombardment by solvent molecules. If the particles are illuminated with a laser, the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles as smaller particles are “hit” more frequently by the solvent molecules and move more rapidly. Analysis of these intensity fluctuations yields the velocity of the Brownian motion and hence the particle size using the Stokes-Einstein relationship<sup>13-14</sup>.

$$D = k_B T / 6\pi\eta r \quad (2)$$

Where D is the diffusion constant ( $m^2s^{-1}$ ),  $k_B$  is Boltzmann's constant ( $JK^{-1}$ ), T is the absolute temperature (K),  $\eta$  is the viscosity of the solvent ( $kgm^{-1}s^{-1}$ ) and r is the particle radius (m). The typical graphical output of the zetasizer is shown below (figure 5a), whereas figure 5b is a graphical presentation of a combination of the size distributions of the different colloids.

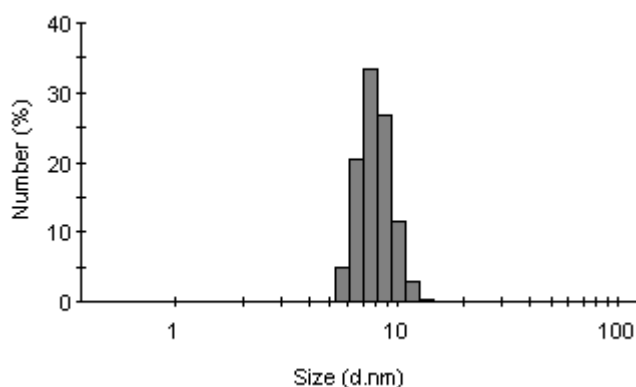


Figure 5a. Distribution of particle diameters within the 'seed' Ag colloid.

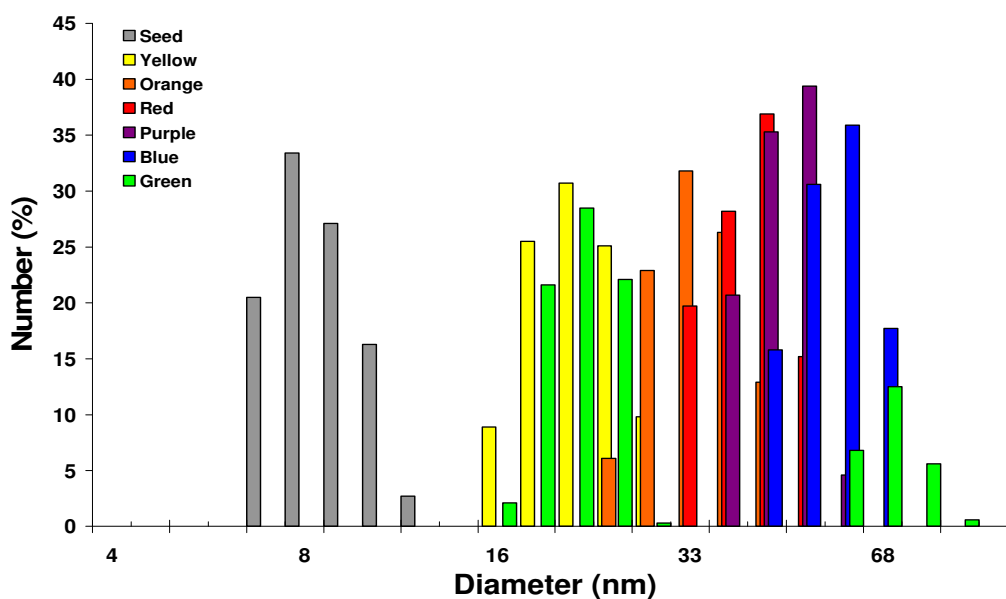


Figure 5b. Distributions of particle diameters of the seed and coloured Ag colloids.

Colour	UV-Vis $\lambda$ max	DLS	
		Particle Size Range	Average Size Range
Seed	393 nm	5 – 14 nm	8 – 9 nm
Yellow	445 nm	6 – 28 nm	10 – 13 nm
Orange	473 nm	11 – 38 nm	19 – 20 nm
Red	495 nm	11 nm – 60 nm	20-23 nm
Purple	555 nm	15nm – 50 nm	31-33 nm
Blue	670 nm	37 nm – 105 nm	58-60 nm
Green	405 nm & 648 nm	11 – 250 nm	91.1 % 20- 21 nm & 8.9 % $\geq$ 60 nm

Table 2. Summary of Colloids UV-Vis  $\lambda$  max's and DLS results.

### Electron microscopy.

An image of the nanoparticles, (Figure 6) was obtained from the interaction of the coating and the beam of electrons transmitted through the coating. Before analysis, the colloidal samples (prepared in the same manner as outlined in Figure 2 and Table 1) were diluted in ethanol and sonicated for 30 mins, before being cast onto the TEM grid (Agar scientific, holey carbon 200 mesh (Cu)) by drop coating. The average diameters of the nanoparticles were determined, using Zeiss axiovision software<sup>15</sup> and correlated well with the DLS results.

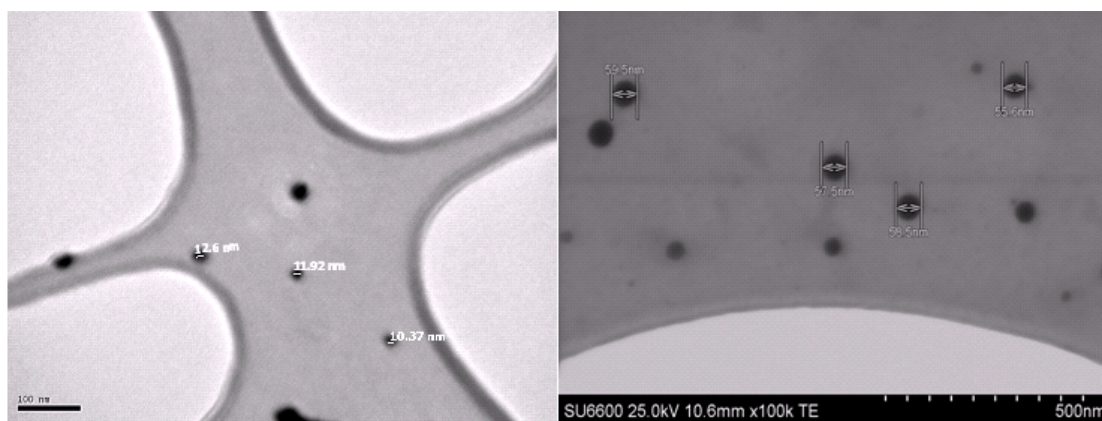


Figure 6. On the left a TEM image of silver nanoparticles (yellow colloid) with an average diameter range of 10 – 13 nm, and on the right a STEM image of silver nanoparticles (blue colloid) with an average diameter range of 58-60 nm

### Effect of ions on colloids stability

Steric stabilisation and electrostatic stabilization are the two main mechanisms for colloid stabilisation. Electrostatic stabilisation is based on the mutual repulsion of like electrical charges. Different phases generally have different charge affinities, so that a charge double-layer forms at any interface. Small particle sizes lead to enormous surface areas (hundreds of  $m^2/g$ ), and results in this effect being greatly amplified in colloids. This can be better explained by the DLVO theory <sup>14</sup>.

The Deryagin-Landau-Verwey-Overbeek (DLVO) theory suggests that the stability of a particle in solution is dependent upon its total potential energy function  $V_T$ . This theory recognizes that  $V_T$  is the balance of several competing contributions:

$$V_T = V_A + V_R + V_S$$

$V_S$  (the potential energy due to the solvent) usually only makes a marginal contribution to the total potential energy over the last few nanometers of separation. More important is the balance between  $V_A$  and  $V_R$ ; these are the attractive and repulsive contributions.

DLVO theory suggests that the stability of a colloidal system is determined by the sum of these Van der Waals attractive ( $V_A$ ), and electrical double layer repulsive ( $V_R$ ) forces that exist between particles as they approach each other due to the Brownian motion they are undergoing. This theory proposes that an energy barrier resulting from the repulsive force prevents two particles approaching one another and adhering together. Therefore if the particles have a sufficiently high repulsion, the dispersion will resist flocculation and the colloidal system will be stable. However if a

repulsion mechanism does not exist then flocculation or coagulation will eventually occur. To maintain the stability of the colloidal system, DLVO theory states that the repulsive forces between the particles must be dominant.

The stability of many colloids of both natural and man-made origin can be improved by the presence of macromolecules or polymers, (e.g. fatty acids in milk are stabilised by the presence of casein). This is steric stabilisation. Polymers increase viscosity in the colloids, altering the sedimentation behaviour. This coupled with their high molecular weights results with only a small concentration being necessary to achieve this.

PVA is a well known and commonly used random block copolymer stabiliser. Only part of the macromolecule adsorbs to the particle allowing the rest to solvate and to expand away from the interface, preventing other particles from approaching. PVA is widely used for polymer nanocomposites. Due to the water solubility of PVA the nanoparticles can be produced in an aqueous medium making the preparation process non-toxic.

Therefore, the deliberate addition of ions to the colloidal system demonstrates the need of a stabiliser. With the addition of an acid or base (dilute HCl or NaOH), the colloids appearance changes as the larger particles aggregate in an uncontrolled manner. This first results in the colloid undergoing a colour change. If the concentration of ions is sufficient, the silver nanoparticles will aggregate completely to produce bulk silver; a black precipitate.

## **Motivation**

Continuing interest in the controlled synthesis of metal nanoparticles has resulted in the development of numerous experimental protocols for the production of defined nanostructures<sup>1-2, 6</sup>. Consequently, this growing area of research is highly relevant to students and educators alike. This has led to a number of educational publications describing the synthesis of both semiconductor<sup>16-17</sup> and metal<sup>6, 18-20</sup> nanoparticles.

Here the authors describe a rapid, simple and robust methodology that may be carried out on bench, with comparatively mild reagents and without the need of ventilation<sup>6</sup> or heating apparatus<sup>18</sup>, allowing for the experiments use in both undergraduate and second level laboratories.

## **Student results**

Both second level and undergraduate students may perform this practical; in both cases a clear explanation of the Tyndall effect and an understanding of the localised plasmon resonance of metal particles on the nanoscale are required.

The experiment may be adjusted to suit the allocated laboratory time period. Variations of the practical have been successfully conducted in the Dublin Institute of Technology in laboratory sessions ranging from 2 – 3 hours, with over 500 students (groups of 20 -30 working in pairs) successfully completing it to date.

The most common factor for initial failure to produce the coloured colloids was the use of ‘dirty’ glassware where the students had neglected to ensure that the glassware was properly cleaned (and rinsed) prior to the practical (this had the benefit of clearly demonstrating to the students the importance of laboratory housekeeping).

The undergraduate students had already gained some useful knowledge that they were able to correctly apply when they were asked to characterise the colloids using UV-Vis spectroscopy. Students reported finding the experiment “somewhat challenging yet interesting and enjoyable”.

## **Supplemental Material**

Instructions for students and technical notes (including a complete risk assessment and introductory power point presentation) for the instructor are available at, <https://www.dropbox.com/sh/9zf0cwe077xqhwo/mR0XZZGAFU>

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## **References**

1. D.M. Ledwith, A.M. Whelan, J.M. Kelly, *J. Mater. Chem.*, 17, 2007, 2459–2464

2. D. Aherne, D.M. Ledwith, M. Gara, J.M. Kelly, *Adv. Funct. Mater.*, 18, 2008, 2005–2016
3. A. Shkilnyy, M. Souce, P. Dubois, F. Warmont, M.L. Saboungi, I. Chourpa, *Analyst*, 134, 2009, 1868 – 1872.
4. M.E. Abdelsalam, S. Mahajan, P.N. Bartlett, J.J. Baumberg, A.E. Russell, *J. Am. Chem. Soc.*, 129, 2007, 7399 – 7406
5. K.L. Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, *J. Phys. Chem. B*, 2003, 107, 668-677.
6. A.J. Frank, N. Cathcart, K.E. Maly, V. Kitaev, *J. Chem. Educ.*, 2010, 87, 1098-1101
7. P.K. Khanna, N. Singh, S. Charan, V.V.V.S. Subbarao, R. Gokhale, U.P. Mulik, *Mater. Chem. Phys.*, 2005, 93, 117-121.
8. T. Li, H.G. Park, S. Choi, *Mater. Chem. Phys.*, 2007, 105, 325-330.
9. Z.H. Mbhele, M.G. Salemane, C.G.C.E. van Sittert, J.M. Nedeljkovic, V. Djokovic, A.S. Luyt, *Chem. Mater.*, 2003, 15, 5019-5024.
10. C.F. Bohren, D.R. Huffman, *Absorption and scattering of light by small particles*, New York; Chichester: Wiley, (1983)
11. Y. Kunieda, K. Nagashima, N. Hasegawa, Y. Ochi, *Spectrochim. Acta, Part B*, 64, 2009, 744–746.
12. E. Filippo, A. Serra, D. Manno, *Sens. Actuators, B*, 2009, 138, 625–630.
13. P. Atkins, J. de Paula, *Atkins' Physical Chemistry*, 7th ed., Oxford University Press, Oxford; New York, (2002), 845.
14. [http://www.malvern.com/LabEng/industry/colloids/dlvo\\_theory.htm](http://www.malvern.com/LabEng/industry/colloids/dlvo_theory.htm) (accessed September 2011)
15. <http://www.zeiss.com/c12567be0045acf1/ContentsFrame/cbe917247da02a1cc1256e0000491172> (accessed December 2011)
16. K. Winkelmann, T. Noviello, S. Brooks, *J. Chem. Educ.* 2007, 84, 709.
17. E. M. Boatman, G. C. Lisensky, K. J. Nordell, *J. Chem. Educ.* 2005, 82, 949.
18. C. D. Keating, M.D. Musick., M. H. Keefe, M. J. Natan, *J. Chem. Educ.* 1999, 76, 949.
19. A. D. McFarland, C.L. Haynes, C. A. Mirkin, R.P. Van Duyne, H.A. Godwin, *J. Chem. Educ.* 2004, 81, 544A.

**20.** S. D. Solomon, M. Bahadory, A.V. Jeyarajasingam, S.A. Rutkowsky,  
*J. Chem. Educ.* 2007, 84, 322.