Nanotechnology

The Science of the Very

Small

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With thanks to:

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Overview of Nanoscience

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What is Nanoscience?

Nanoscience is the science of very small things. How small? Well before we answer that, see how good you are at thinking about the size of things. The quiz below consists of a lists of things of various sizes - can you rank them in order of size, starting with the biggest?

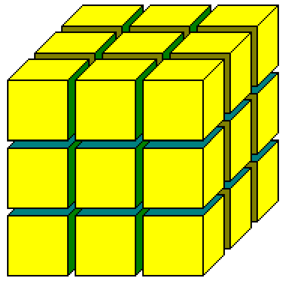
Rank #	Item
	Water Molecule
	Chicken Egg
	Red Blood Cell
	Bacteria
	Human Being
	Virus
	Atom
	Diameter of DNA
	Ant

So how did you get on? It's clear from the list that there are some very big things and some very small things. To help group things into similar sizes, we use a scale. For example, the milliscale is used to group things the size of things based around the size of millimetres - 1 thousandth of a metre. The microscale is the scale of one billionth of a metre, 0.000001 m. When we use a microscope, we can view things on this scale. The next scale down has recently come into view, with new sophisticated instruments and clever ways of making things at this scale - this is the nanoscale - things in the size range below 1 billionth and above 1 trillionth of a metre - one nanometre is 0.000000001 m or more conveniently 10 -9 m. At this scale, we start to see things like viruses, which are 100's of nanometres in size, DNA strands, which are a couple of nanometres wide. However, this scale is bigger than simple molecules such as water - which are only parts of nanometres and atoms which are smaller still.

Why is the nanoscale important?

Things of the nanoscale have always been there, but it's only in the last twenty or so years that scientists have developed the technology to see them clearly. Now that we can see them, we can start some clever science, and even make things on the nanoscale. Why would we want to? There are some very special properties about nanoparticles - two of the most important of which are surface area and shape.

Surface Area:



Imagine we have a cube that has a side of 3 cm. What is its surface area? When you work it out - the area of each side times the number of sides, you should get an area of 54 cm^2.

If we now cut the cube up, so that it contains 27 cubes, each with a side of 1 cm, what is the new surface area? When you work it out, you should find that the new surface area is 162 cm^2. In other words, just by chopping the cube up into smaller pieces, we have increased the surface area. Imagine we kept doing this, so that the cubes we formed would become smaller and smaller, ending up with sides of the size of a few nanometres. The resulting surface area would increase greatly, to approximately two thousand times the surface area of the original bulk material, so that the nanomaterial would have a much larger surface area. Many chemical reactions occur by molecule's surfaces interacting - thing of the hydrogenation of alkenes in chemistry. Therefore, the greater the surface area, the more reactive a substance generally is. And it is a LOT more reactive! Take something like aluminium metal. In bulk form, it corrodes very slowly to form aluminium oxide, and does not react much with water. Nanoscale aluminium reacts explosively with water, simply because the water is able to reach a lot more of the aluminium surface very quickly. In short, larger surface area means greater reactivity

Shape:

The next key thing about nanomaterials is their shape. Because we are dealing with molecules on the same size as proteins receptors, and various other biological substances, very small changes in shape mean that we can impact how these molecules interact with biological substances, in designing new ways to tackle viruses or new methods for sensing proteins of different types, for example in a diagnostic test for different diseases. For this reason, nanoscience is considered to be a hybrid of all the traditional sciences, as it brings together chemistry, biology and physics, with engineering in the manufacture of devices.

Making Nanomaterials

Now that we know what size nanomaterials are, how do we go about making them. There are two main approaches - one is called the top-down approach, the other is the bottom-up approach.

Top-Down

The top-down approach is a physics/engineering approach. It involves taking bulk material and carving out the nanomaterials, much like a sculptor would carve out a statue, only on a much smaller scale. The advantage of this technique is that you can create very precise shapes and structures using lasers or atomic sized needles. The disadvantage is that there is an enormous cost in the precision instruments that are required to make nanoscale materials. Computer chip companies like Intel would use an approach like this in generating nanoscale computer chips - you can find out more by looking up techniques such as "photolithography".

Bottom-Up approach

The bottom-up approach is a chemistry approach and involves making nanomaterials from simple molecules, assembling them together into the shape you want. A key feature of this is what's called molecular self assembly - where molecules are arranged together and mixed in sequence so they add together and "self-assemble" into the desired arrangement. As an example, imagine we wanted to make a protein sensor discussed above. We would have some sort of surface, a platform that is going to hold our device - with a metal strip onto it. the first step would be to dip this into a solution containing long alkane chains - maybe 15 carbons, that have an alcohol (-OH) or thiol (-SH) group on the end. These are like velcro to the metal, and stick on. At the other end, there would be a group that we could easily replace in a simple chemical reaction - so all we have to do is put out platform with alkane chains into a beaker and add in whatever we wanted to stick on the end - after it reacts, we can use the combined device as a sensor. For example, the group at the end might give off light when there is no protein attached, but not give off light when there is - so we could see very easily it there was protein present in the sample we were analysing. Self-assembly is very cheap, and can make large quantities, although sometimes the actual chemistry in the lab is a bit harder than I am making it sound on paper!

Characterising Nanomaterials

So now we have made our nanomaterials, how do we go about telling what size they are? What is their shape - do they have a smooth surface or bumpy? One of the great inventions in science was the optical microscope, by Robert Hooke in the seventeenth century. This allowed scientists to see down to the microscale for the first time. Which of the following do you think can be viewed easily by the human eye or the microscope?

Tick if could be viewed by eye or optical microscope	Item
	Water Molecule
	Chicken Egg
	Red Blood Cell
	Bacteria
	Human Being
	Virus
	Atom
	Diameter of DNA
	Ant

Of course, some things are just too small to be viewed by the microscope. Visible light is of a size of 300 - 800 nm, so it cannot resolve (or see) below this size. The answer was to use electrons instead of light, and the scanning electron microscope was born. This acts in a way not unlike the optical microscope, except instead of light waves, electron waves are used. This allows us to see down to about 10 nm. The next breakthrough was in 1986, when scanning probe microscopy was discovered by scientists at IBM. Using an instrument with a needle that had very fine tip, a couple of atoms wide, they were able not only to see atoms and molecules, but actually move them around. There is a very famous image of an IBM logo made of helium atoms on a solid surface. The scientists behind the development of this technique won a Nobel prize, their work opening up a new world to us, just as Hooke's microscope did in the 17th century. The reason these instruments can resolve down to nanometre level and below is that their tip is so fine, they can probe surfaces of a similar size.

Nanophobia

As with any new technology, there is always an unknown risk. It is the job of scientists to quantify this risk, and say whether it is significant. With my own students, I give them a chemical risk sheet for a "dangerous chemical" which says that it is toxic, and can cause all sorts of nasty diseases and problems. The chemical is sodium chloride - common salt. It is not dangerous to most people because the exposure is very low - but a small number of people need to consider this toxicity information, as they may be dealing with large quantities of it. Unfortunately this point is lost on a lot of media reports, and in truth scientists need to do a better job of getting a clear message out. Nanotechnology has enormous potential to do a lot of good for human kind, and indeed it is essential for technologies such as modern solar cells to work. There are recent reports that sunscreens, which contain nanoparticulate titanium dioxide or zinc oxide, which blocks out harmful UV radiation, are being sold as "Nanofree". The reason nanoparticles are included in sunscreens (and a lot of cosmetics) is that they are so small, they don't appear white, as they do in bulk form, so it is cosmetically advantageous to have a clear sunscreen than a milky white one. These have been tested, to show that they pose no danger, as the nanoparticles, although small, are too large to penetrate the dermal layer. However, this is lost on media, which unfortunately can often base articles on pseudo-science. There is an important job for scientists to do in quantifying any risk that may be involved, and then make a call on whether it is safe to use such materials.

NanoIreland

Ireland punches well above its weight in nano-research, given the size of the country (pun partly intended!) There are large research institutes in Trinity College Dublin - the CRANN centre and in UCC - the Tyndall Institute. In my own institution, DIT, we have the Focas Institute. My own research is based around nanoparticulate titanium dioxide, which is used as a self cleaning surface to kill off bacteria and other infectious material in hospital environments. The concept is that these materials are incorporated into paints and other surfaces in hospitals. They are continually activated by visible light from the room lights, which initiates reactions at the surface of the nanomaterial and and bacteria that are present, destroying the bacteria.

Links to further information and resources:

- Nano Sense - http://nanosense.org/ A full suite of learning materials, including teacher and student materials, for introducing the topic of nanotechnology.
- Video Lab Manual for Nanotechnology experiments: http://mrsec.wisc.edu/Edetc/nanolab/
- Nanotech Project: http://www.nanotechproject.org/ - see http://www.nanotechproject.org/topics/nano101/ for introduction to topics
- Article on nanomedicine: A Supramolecular Approach to Medicinal Chemistry: Medicine Beyond the Molecule, D. K. Smith (RSC Higher Education Award Winner 2005) http://pubs.acs.org/doi/abs/10.1021/ed082p393
- Contextualising Nanotechnology in Chemistry Education: http://www.rsc.org/publishing/journals/RP/article.asp?doi=b801289j
- List of Links: http://research.uiowa.edu/nniui/links.html

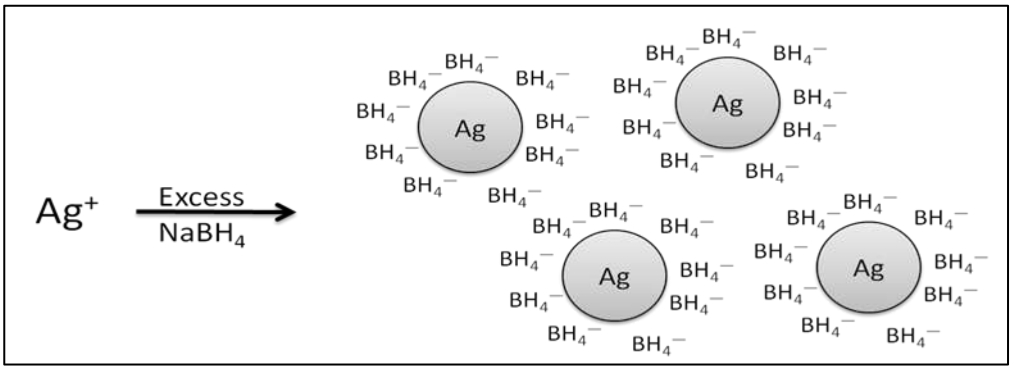
Making Nanoparticles

This laboratory experiment involves the synthesis of silver nanoparticles. Silver nanoparticles have a wide range of potential uses, and there has been a dramatic increase in the amount of research carried out over the last ten years. Principal interests include the development of anti-bacterial surfaces and clothing, especially for hospital environments. It has also been added to cleaning appliances such as washing machines, as an antibacterial reagent as well as plasters, and even socks! Other research is involved in conductive sensors for pollutants and conductive paints.

There are lots of ways to make silver nanoparticles, but they usually all follow the same two-step process. The first step makes nanosilver "seeds" – very small particles about 18 nm in diameter. These seeds take the form of a silver colloid, which, because of their size look like a yellow solution. In this experiment, the seeds have been made in advance, but their preparation is very simple. They are prepared by reducing Ag^+ ions using fresh sodium borohydride. This gives a yellow colloidal solution. The second step involves growing the nanoparticles – adding more silver to the seeds so they become a little larger. In order to control the growth of the nanoparticles, a capping reagent is added which stops the growth of the particles and prevent them becoming too big, and hence falling out of solution.

Step 1: Preparation of Seeds (prepared in advance of practical)

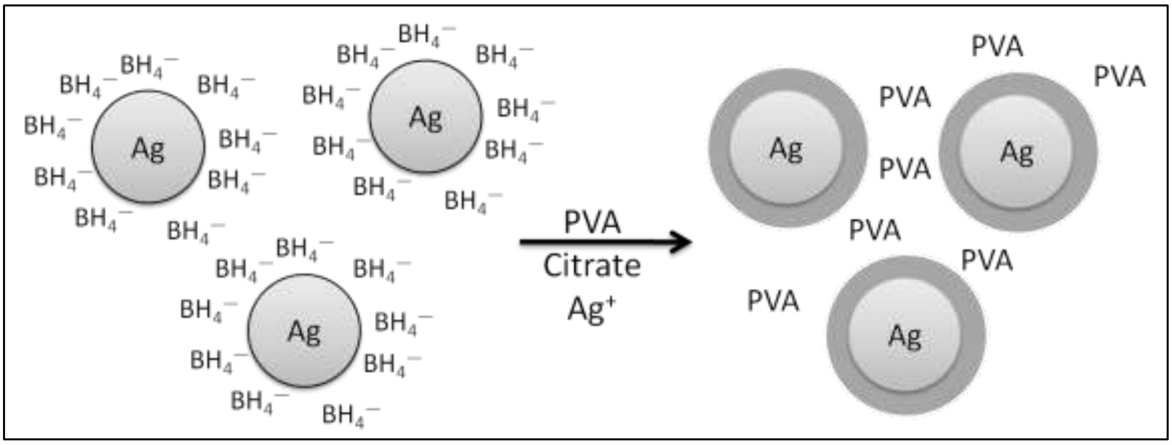
$$AgNO_3 + NaBH_4 \rightarrow Ag_{seeds}$$



We can see that as the silver ions are reduced to nanoparticles by the borohydride, the remainder of the excess borohydride ions wrap around the nanoparticles and keep them from clumping together and falling out of solution. A ratio of 2:1 $NaBH_4$:$AgNO_3$ results in a stable nanoparticle colloid.

Step 2: Growth of nanoparticles

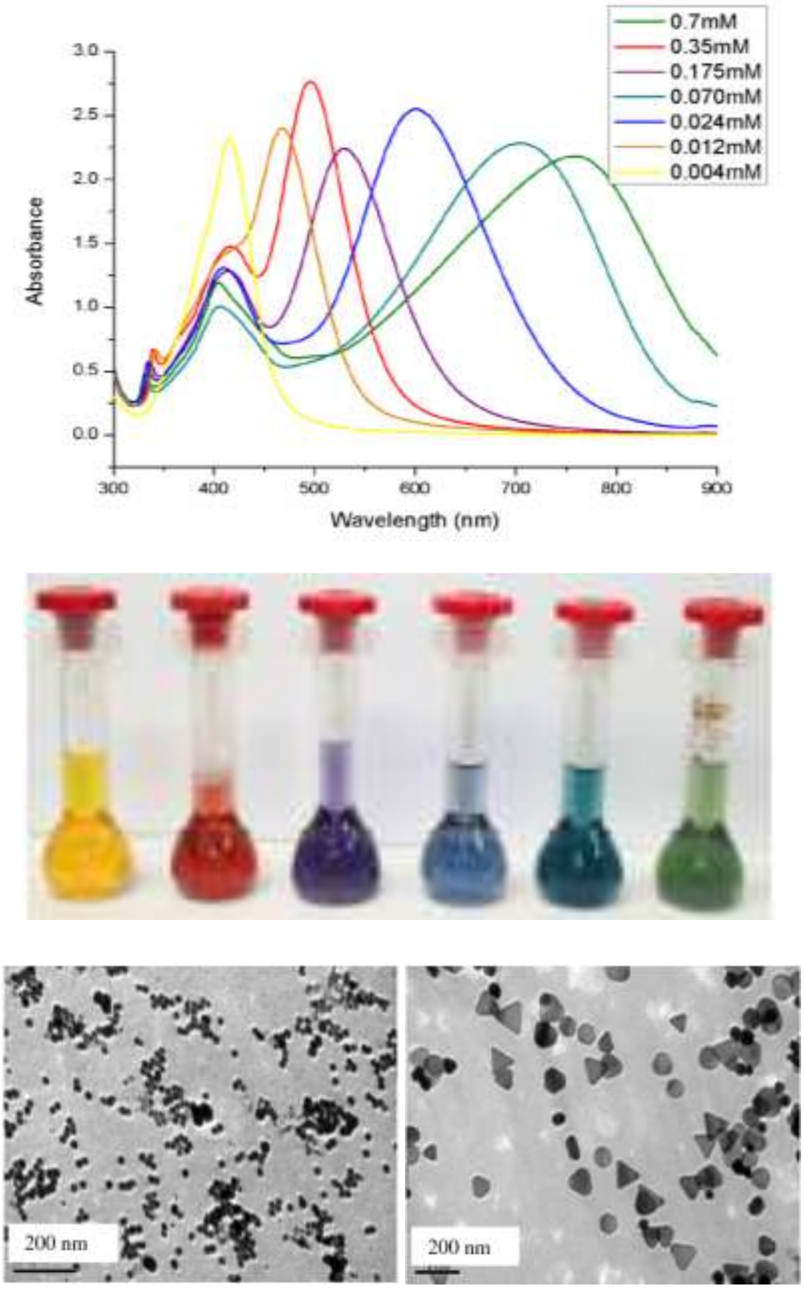
In the second step, a polymeric material polyvinylalcohol (PVA) is added to the seed solution, along with more silver nitrate. The PVA is used to increase the viscosity of the solution to keep the nanoparticles separate as they grow. The other reagents are required to reduce the silver ion to silver which adds to the seed in creating larger nanoparticles. The particles shown in the illustration are spherical, but it is common to observe triangular shaped particles growing from the spherical seeds.



Characterising Nanoparticles

Bulk silver has a silver-grey colour, but as we make the particle size smaller, the materials have different colours, depending on their size. This is because as the particles become smaller than the wavelength of visible light (300 – 800 nm), they interact with light in a different way. They also become small enough to become a suspension in solution – or what is called a colloid. (Milk is an example of a colloid – very small particles suspended in solution which has the appearance of a white liquid).

Much work has gone into determining how the colour of silver nanoparticles varies according to size. It has been found that as particle size increases, the colour of the nanoparticles change from yellow (an absorbance around 400 nm) through to green (an absorbance around 800 nm). Therefore, we can estimate the size of the nanoparticles just by looking at their colour. Using more advanced instrumentation such as electron microscopy, we can get a image of what shape the particles are and how big they are. Some examples for silver nanoparticles are shown overleaf.



Nanoparticle Characterisation: Top – UV/visible spectra show how the nanoparticle absorbance changes depending on particle size, allowing estimation of the particle size based on λ_{max}; Middle – colours of silver nanoparticles from seeds to the right to largest particles on the left; Bottom – electron micrograph images of colloid seeds on the left (yellow solution) and larger nanoparticles on the right (green solution).

Image Credits: John Kelly, Aine Whelan, Deirdre Ledwith (TCD) for coloured solutions and Suresh Pillai, Vinod Etacheri, Reenamole Georgekutty, Michael Seery (DIT) for micrographs – used with permission.

A colour copy of this sheet is available separately.

Station 1: Synthesis

Using the silver seed solution provided, add other chemicals provided, add the following reagents in the order indicated while stirring the solution:

- 1 cm^3 1% polyvinyl alcohol (PVA)
- 1 cm^3 silver colloid seed solution
- 3 cm^3 0.001M *tri*-sodium citrate
- 5 cm^3 0.1M hydrazine
- + **X** cm^3 0.001M silver nitrate dropwise

As you add the silver nitrate, note the colour of the solution, until a total volume of about 20 mL has been added.

Amount of 0.001 M Silver Nitrate (cm^3)	**Colour of resulting solution**
~0.4	
~1.0	
~1.3	
~2.5	
~6.0	
~20	

Station 2: UV/vis Absorption Spectra

Place a cuvette containing one of the colloids into the UV/vis spectrometer. It may be necessary to dilute the darker solutions – if so, dilute them with water. Note the absorption maximum and sketch the shape of the curves. Repeat for a second colour and note how they differ.

Colour 1:

Absorption Maximum

Sketch of Graph

Colour 2:

Absorption Maximum

Sketch of Graph

Station 3:
Tyndall Effect & Particle Aggregation

Using a laser pointer, shine the light first through some deionised water and secondly through some of the colloidal solutions containing nanoparticles. Is there any difference between the how the laser light interacts with the two solutions. Note any observations and comment on what may be causing this difference.

Some 6 M HCl is available in a burette. Add some this to one of your colloidal solutions and note what happens. Can you explain what is occurring in this case?

Formal Synthesis Procedure and Technical Notes

With thanks to Aoife Power, DIT

The following chemical substances are used in this experiment. Good laboratory practice should be observed, including wearing of personal protective equipment (lab coat, glasses, gloves).

Substance	Hazardous properties including physical hazards	Risk phrase	Target organs
Silver Nitrate (*as powder)*	**Skin Contact**: May cause skin irritation or burns. **Skin Absorption**: May be harmful if absorbed through the skin. **Eye Contact**: May cause eye irritation. **Inhalation**: May be harmful if inhaled. Material may be extremely destructive to mucous membranes and upper respiratory tract. **Ingestion**: May be corrosive if swallowed. Poison	**R 23/24/25/26 R 35/41**	various
Sodium Borohydride (*as powder)*	**Skin Contact:** Causes burns. **Eye Contact:** Causes burns. **Inhalation:** May be harmful if inhaled. Material is extremely destructive to the tissue of the mucous membranes and upper respiratory tract. **Ingestion:** Toxic if swallowed.	**R- 15-24/25-34 S- 22-26-36/37/39-43-45**	various
Poly Vinyl Alcohol (*as powder)*	**Skin Contact:** may cause skin irritation. **Eye Contact:** may cause irritation. **Inhalation:** May be harmful if inhaled. Material may be irritating to the upper respiratory tract. May be harmful if inhaled. **Ingestion:** may be harmful if swallowed.	**Not Hazardous according to Directive 67/548/EEC**	
tri Sodium Citrate (*as powder)*	**Skin Contact:** may cause skin irritation. **Eye Contact:** may cause irritation. **Inhalation:** May be harmful if inhaled. Material may be irritating to the tissue of the mucous membranes and upper respiratory tract. May be harmful if inhaled. **Ingestion:** may be harmful if swallowed.	**Not Hazardous according to Directive 67/548/EEC**	
Hydrazine Hydrate	**Skin Contact:** Causes burns. **Skin Absorption:** Toxic if absorbed through skin. Readily absorbed through skin. **Eye Contact:** Causes burns. **Inhalation:** Toxic if inhaled. Material is extremely destructive to the tissue of the mucous membranes and upper respiratory tract. **Ingestion:** Toxic if swallowed.	**R- 45-23/24/25-34-43-50/53 S- 53-26-36/37/39-45-60-61**	various

The following solutions should be prepared in advance of the practical/demonstration. PVA can take 2 – 3 hours to dissolve.

Preparation of Seed Solution:

1. Prepare a *fresh* solution of sodium borohydride (0.001 M) and store in an ice bath/cool area until ready to use. The top of the flask should be left loose to allow any evolving gas to escape easily. It may be easiest to prepare 0.01 M solution in 100 mL flask (0.038 g in 100 mL) and take 10 mL of this and make it up to 100 mL to give the final 0.001 M solution.
2. Prepare the silver ion solution by adding silver nitrate (0.005 g) and of tri-sodium citrate (0.0075 g) to 100 mL of distilled water.
3. Add 6 mL of the borohydride solution slowly to the solution containing silver nitrate and *tri*-sodium citrate to give a yellow colloidal solution. This solution should remain stable for several weeks or longer.

Preparation of other solutions:

1. Prepare a 1 %(w/v) solution by dissolving, for example, 1 g of PVA into 100 mL of water. Dissolution can be slow, and may require heating and stirring for about 2 hours.
2. Prepare a solution of *tri*-sodium citrate (TSC) (0.001 M) by dissolving, for example, 0.026 g of TSC into 100 mL of water.
3. Prepare a solution of hydrazine hydrate (0.1 M). This will depend on the concentration of stock available to you, but concentrated hydrazine hydrate is typically ~15.5 M. Therefore to prepare 0.1 M, make 1.6 mL of concentrated solution up to a 200 mL solution.

Preparation of different nanoparticle sizes:

Using the silver seed solution provided, add other chemicals provided, add the following reagents in the order indicated:

- 1 cm^3 1% polyvinyl alcohol (PVA)
- 1 cm^3 silver colloid seed solution
- 3 cm^3 0.001M *tri*-sodium citrate
- 5 cm^3 0.1M hydrazine
- + **X** cm^3 0.001M silver nitrate dropwise

Some Useful References on Silver Nanoparticles in the Laboratory

Synthesis and Study of Silver Nanoparticles, ***Journal of Chemical Education, 2007, 84(2), 322 – 325:*** describes another synthesis procedure of the seed solution and tests the stability of this by looking at the amount of borohydride used and looking at ways to promote/prevent aggregration. Step by step video instructions for this procedure are also available at the website: http://www.mrsec.wisc.edu/Edetc/nanolab/silver/ which includes information on how to make "stained glass" using nanosilver.

Synthesis of Silver Nanoprisms with Variable Size and Investigation of Their Optical Properties, ***Journal of Chemical Education, 2010, 87(10), 1098 – 1101:*** interesting alternative procedure along with explanation on the chemical processes involved as the nanoparticle grows – for example the role of the sodium citrate.

See also:

Contextualising Nanotechnology in Chemistry – paper by Christine O'Connor and Hugh Hayden, DIT in Chemistry Education Research and Practice. Available at: http://dx.doi.org/10.1039/b801289j