



TMT4320 Nanomaterials, fall 2015

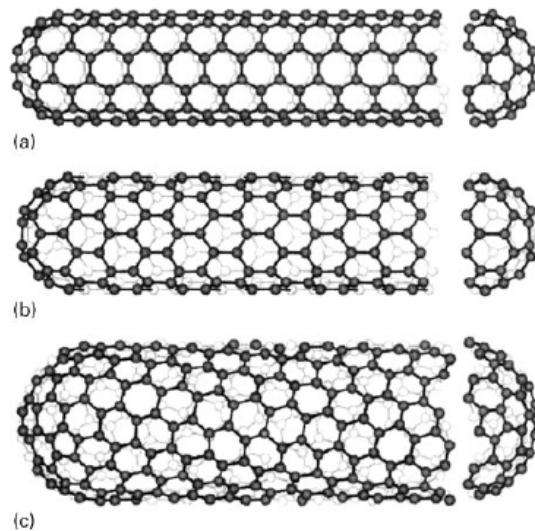
## EXERCISE 7 - SOLUTION

### PROBLEM 1

- a) A carbon nanotube can be defined in terms of a graphite sheet that is rolled up into a cylinder. The three different structures are armchair (a), zigzag (b) and chiral (c) (see figure below), which depends on the angle at which the graphite sheet is rolled up. The different structures can be observed by removing the end cap and looking at the pattern formed by the carbon atoms.

Armchair nanotubes are metallic. Zigzag nanotubes are metallic if  $n$  of the chiral vector  $(n, m)$  is an integer multiple of 3 (3, 6, 9, etc.) ( $m = 0$ ), otherwise semiconducting. Chiral nanotubes are metallic if  $n - m$  of the chiral vector  $(n, m)$  is an integer multiple of 3 (3, 6, 9, etc.), otherwise semiconducting.

In the metallic carbon nanotubes two mini-bands occupy the mid-gap state and quantum mechanical tunneling leads to electrical conductivity. Ballistic electron transport has been observed, meaning that electrical conductivity without phonon or surface scattering occurs. The semiconducting tube has a band gap between the conduction and valence band.



- b) Metal catalyst and residual impurities can be removed by heating in oxygen at  $\sim 400^\circ\text{C}$  and boiling in mineral acid. The carbon nanotubes are much more stable than the carbon particles, so the treatment will mostly only affect the soot and carbon particles. The problem with this method is that the both the acid and the heat treatment can destroy the structure of the carbon nanotube if care is not taken, and thereby alter its properties.

Metallic nanotubes can be separated from the semiconducting ones by electrophoresis. When an AC electric field with high frequency ( $>10$  kHz) is applied to carbon nanotubes dispersed in an electrolyte solution the negative ions surrounding the particles and tubes cannot move in response to the alteration of polarities of the electric field. An electric dipole therefore appears in the nanotubes and nanoparticles. The dipole will move towards the electrodes due to strong Coulomb forces. Since this attractive force depends strongly on the length of the dipole (dipole moment), the long nanotubes will have a much stronger dipole moment compared to the particles, and will therefore move towards the electrodes, leaving the particles behind. Differences in the dielectric constant between the metallic and semiconducting nanotubes cause them to move towards opposite electrodes.

Carbon nanotubes can also be sorted by length by precipitation from a non-solvent followed by centrifugation. Presence of the non-solvent causes the longest nanotubes to precipitate out first. Adding more solvent will cause shorter tubes to precipitate out.

Another method involves precipitation by evaporation of an octadecylamine solution. The latter is based on different preferences for charge transfer with the electron donating solvent.

The nanotubes can also be manipulated chemically, which means functionalizing them selectively depending on their conduction behavior and then separating the different phases for instance by differences in solubility in various solvents.

- c) Zigzag: (3,0)  
Armchair: (2,2)

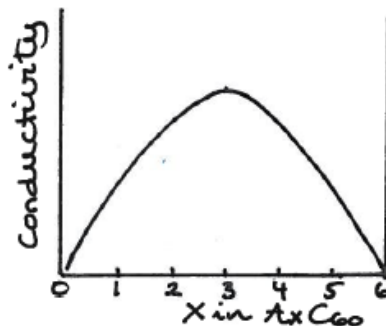
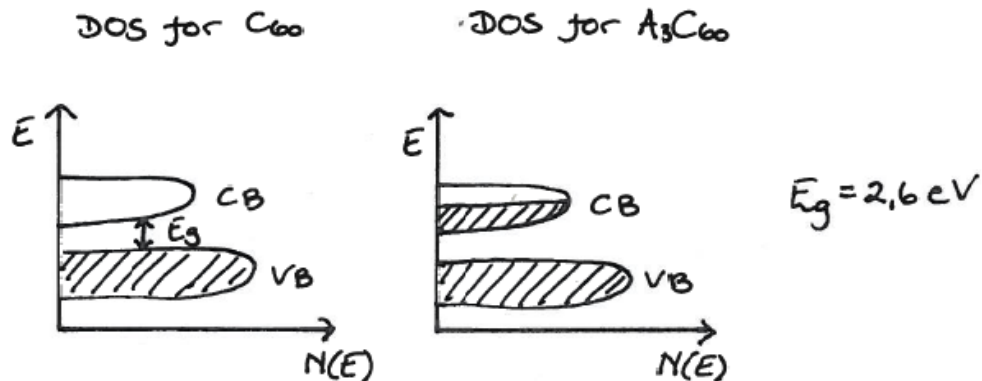
For help, draw hexagons on a sheet of paper and roll it up to produce “nanotubes” with different chiral vectors.

The smallest carbon nanotubes that have been identified experimentally have chiral index (3,3), (4,3), or (5,1). They were grown inside single-wall carbon nanotubes with the diameter of 1.0-1.2 nm, and the chiral indices were experimentally assigned beyond a doubt by an aberration-corrected high-resolution transmission electron microscopy (HR-TEM). In contrast to a theoretical prediction, the (3,3) nanotube is rather unstable and extremely sensitive to the electron beam and, therefore, may not survive alone without the protection of outer nanotube. The cap structure of (3,3) nanotube is also well-explained by a half-dome of  $C_{20}$  fullerene, which consists of six pentagons only. [Reference: L. Guan *et al.*, *Nano Lett.*, 8 (2), 459, 2008.]

- d) The  $C_{60}$  molecule

- i. A  $C_{60}$  molecule consists of 60 carbon atoms that are bound together in the form of 5-6 bonds (join of a hexagon and a pentagon) or 6-6 bonds (join of two hexagons). The 5-6 bonds are 1.45 Å and have the character of a single bond, while the 6-6 bonds are 1.38 Å and have the character of a double bond. The electronic properties of the  $C_{60}$  molecule are that of an electron acceptor. It can accept up to 6 electrons to form a hexa-anion  $C_{60}^{6-}$ . It is easy to reduce, but difficult to oxidize. The  $C_{60}$  molecule is non-polar and is therefore insoluble in polar solvents such as acetone or ethanol. It is weakly soluble in hydrocarbons such as pentane or hexane, while it dissolves best in aromatic solvents such as benzene, toluene and 1-chloronaphthalene. Due to the molecule's electron acceptor properties, it is possible to graft groups of molecules to

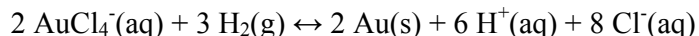
- the surface of the  $C_{60}$  molecule and thereby alter its properties.  $C_{60}$  is a good electrophilic reagent and can therefore host nucleophilic addition reactions. A large number of derivatives of  $C_{60}$  have been produced, mainly to modify its solubility.
- ii. If a large number of  $C_{60}$  molecules are packed into a solid material, they will pack according to an FCC structure at room temperature. In the tetrahedral and octahedral interstitial sites cations can be placed to form fullerides. The most well-known fullerides have the formula  $A_3C_{60}$  and are metallic. Here, alkali metals ionize and donate their electrons to the conduction band of the  $C_{60}$  network. For Rb and K these materials become superconducting at very low temperatures. Once the alkali metal has donated its electron to the  $C_{60}$  network it no longer contributes to the conductivity of the material.
- iii. As  $x$  increases in  $A_xC_{60}$ , the conductivity will increase up to  $x = 3$  and then decrease again, so maximum conductivity will be for  $x = 3$ . This can be explained by the degree of filling of the conduction band. As  $x$  increases the conduction band of  $C_{60}$  starts to fill. When the degree of filling is low the mobility is high since there is more room for the electrons to move, but the number of charge carriers is low. As the degree of filling increases, the number of charge carriers increases and the conductivity will therefore increase. However, as the degree of filling reaches more than 50 % filling of the conduction band, the mobility starts to decrease as there will be less space in the conduction band. Although a higher value of  $x$  provides more charge carriers, the mobility will decrease and hence the total conductivity decreases. For  $x = 6$  the conduction band is full and there is no space for the electrons to move, hence there will be no electronic conductivity. Please see figures below for illustration (CV = conduction band, VB = valence band, DOS = density of states).



## PROBLEM 2

a) There are many methods to produce gold nanoparticles. Here are some examples:

1. Reduction of  $\text{AuCl}_4^-$  in aqueous solution by gaseous  $\text{H}_2$ :



$\text{AuCl}_4^-$  is so strongly oxidizing ( $E^\circ = +1.002 \text{ V}$ ) that weaker reducing agents such as carboxylates or alcohols are usually sufficient. A stabilizer is necessary to stop further growth of the gold nanoparticles.

Benefits: Easy method, many reducing agents can be used.

Limitations: Control of nanoparticle size (especially compared to reverse micelle methods).

2. Reduction of  $\text{AuCl}_4^-$  in reverse micelle. Starting from an aqueous solution of  $\text{AuCl}_4^-$ , the tetrachloroaurate ions are transferred to an organic phase by vigorously mixing the aqueous solution with a solution of tetraoctylammonium bromide (TOAB) dissolved in toluene. After adding dodecanethiol to the organic phase, an aqueous solution of  $\text{NaBH}_4$  is subsequently introduced into the mixture with rapid stirring. Colloidal gold (1-3 nm) is formed in the organic phase and subsequently isolated by vacuum evaporation or by precipitation with methanol. Once the products are isolated as dry powders, stable colloidal suspensions can be reconstituted in any number of nonpolar or weakly polar solvents, including toluene, pentane, and chloroform, but not alcohol or water. The result is alkanethiol-stabilized colloidal Au nanoparticles that are stable almost indefinitely in nonpolar solvents

Benefits: Control of particle size, stability of nanoparticles in many solvents.

Limitations: Has to use organic solvents instead of water as reaction solvent.

b) There are many methods to produce barium titanate ( $\text{BaTiO}_3$ ) nanoparticles. Here are some examples:

1. Precipitating a mixedmetal alkoxide precursor,  $\text{BaTi}(\text{O}_2\text{C}(\text{CH}_3)_6\text{CH}_3)[\text{OCH}(\text{CH}_3)_2]_5$  with  $\text{H}_2\text{O}_2$  in diphenyl ether solution with oleic acid as stabilizer. The addition of  $\text{H}_2\text{O}_2$  effectively initiates a hydrolysis reaction. Condensation occurred as the solution was heated at  $100^\circ\text{C}$ , resulting in Ba-O-Ti linkages, but with particle growth constrained by the presence of the oleic acid stabilizer. This method resulted in 6-12 nm monodisperse, crystalline particles that did not require calcination.

Benefits: Monodisperse nanoparticles, direct formation of the oxide, relatively low synthesis temperature for an oxide.

Limitations: Has to produce the bimetallic alkoxide precursor prior to synthesis, stability of precursor in air/water atmosphere, much organic reactants.

2. Pechini synthesis from  $\text{BaCO}_3$  and  $\text{Ti}(\text{O}^i\text{Pr})_4$  precursors, citric acid as chelating agent and ethylene glycol as polymerization agent. A complex is formed and after drying the gel is calcined/annealed at  $700\text{-}1000^\circ\text{C}$  to obtain single-phase  $\text{BaTiO}_3$  with product sizes 50-340 nm.

Benefits: Elimination of the requirement that the metals involved form suitable hydroxo complexes.

Limitations: Lack of control over particle size, shape, and morphology. Mainly spherical particles are produced. A high temperature calcination step is necessary. Agglomerates are formed.

- c) Gold (Au) and barium titanate ( $\text{BaTiO}_3$ ) are two very different types of materials. Au is a metal while  $\text{BaTiO}_3$  is an insulator. Au nanoparticles contain only one element (Au), while  $\text{BaTiO}_3$  contain three (Ba + Ti + O). This makes it more difficult to obtain  $\text{BaTiO}_3$  than Au since all three element atoms have to be put together correctly to make  $\text{BaTiO}_3$ . Other phases can form instead of  $\text{BaTiO}_3$  such as  $\text{BaO}+\text{TiO}_2$ ,  $\text{BaTi}_2\text{O}_4$  and so on.

$\text{BaTiO}_3$  typically needs a much higher synthesis temperature than Au to form a single-phase crystalline material since the length the atoms have to diffuse to get into the crystalline atomic positions is longer than in a single-phase material such as Au.

Gold precursors such as  $\text{AuCl}_4^-$  is stable in aqueous solutions, while  $\text{Ti}^{4+}$  ions easily hydrolyze and have to be stabilized by additives or the use of alkoxides.

In addition, Au nanoparticles is typically made by reducing an gold ion or gold-containing complex ion to  $\text{Au}^0$ , while  $\text{BaTiO}_3$  is an ionic compound consisting of  $\text{Ba}^{2+}$ ,  $\text{Ti}^{4+}$  and  $\text{O}^{2-}$  ions, so reduction synthesis is not applicable for  $\text{BaTiO}_3$ .

### PROBLEM 3

- a) The sedimentation times are calculated using equation 1.

$$t(d = 1000 \text{ nm}) = \frac{9h\eta}{2\left(\frac{d}{2}\right)^2(\rho_p - \rho)g}$$

$$= \frac{9 \cdot 0.10 \text{ m} \cdot 2.923 \times 10^{-4} \text{ N s/m}^2}{2\left(\frac{1000 \times 10^{-9} \text{ m}}{2}\right)^2 (19.3 - 0.6548) \times 10^3 \text{ kg/m}^3 \cdot 9.807 \text{ m/s}^2} = 2877.4 \text{ s} = 48.0 \text{ min}$$

$$t(d = 100 \text{ nm}) = 287738.6 \text{ s} = 4795.6 \text{ min} = 79.9 \text{ h}$$

$$t(d = 5 \text{ nm}) = 115095432.8 \text{ s} = 1918257.2 \text{ min} = 31971.0 \text{ h} = 3.6 \text{ years}$$

- b) The average Brownian motion lengths of the three gold nanoparticles within the sedimentation time are calculated using equation 2.

$$x(d = 1000 \text{ nm}) = \left( \frac{RTt}{3\pi\eta \frac{d}{2} N_A} \right)^{1/2}$$

$$= \left( \frac{8.314 \text{ J/mol K} \cdot 298.15 \text{ K} \cdot 2877.4 \text{ s}}{3\pi \cdot 2.923 \times 10^{-4} \text{ N s/m}^2 \cdot \frac{1000 \times 10^{-9} \text{ m}}{2} \cdot 6.023 \times 10^{23} \text{ mol}^{-1}} \right)^{1/2} = 9.27 \times 10^{-5} \text{ m} = 92.7 \text{ } \mu\text{m}$$

$$x(d = 100 \text{ nm}) = 2.93 \times 10^{-3} \text{ m} = 2932.4 \text{ } \mu\text{m}$$

$$x(d = 5 \text{ nm}) = 0.262 \text{ m} = 262277.7 \text{ } \mu\text{m}$$

- c) The average Brownian motion length can most easily be compared with the sedimentation distance by expressing the percentage the Brownian motion length is of the sedimentation distance:

$$d = 1000 \text{ nm: } \frac{9.27 \times 10^{-5} \text{ m}}{0.010 \text{ m}} \cdot 100\% = 0.093\%$$

$$d = 100 \text{ nm: } \frac{2.93 \times 10^{-3} \text{ m}}{0.010 \text{ m}} \cdot 100\% = 2.932\%$$

$$d = 5 \text{ nm: } \frac{0.262 \text{ m}}{0.010 \text{ m}} \cdot 100\% = 262\%$$

We clearly see that the thermal forces (Brownian motion) no longer are negligible for the 5 nm nanoparticles, but rather become very significant. At 1000 nm diameter the thermal forces are very small and we can safely assume that equation 1 is ok to use.

- d) The sedimentation time of particles can be shortened by using a centrifuge. The dispersion containing nanoparticles is put into a tube which is inserted into a centrifuge. The centrifuge spins around and because of the centripetal acceleration nanoparticles that are heavier than the liquid will be collected at the bottom of the tube.

There are different types of laboratory centrifuges which vary in the volume of dispersion that can be centrifuged and the rotary speed. Bench-top centrifuges are often used to separate larger volumes of dispersions, while floor-stand ultracentrifuges can obtain very high speeds and are often used to separate very small nanoparticles or organic samples.