Growth kinetics of nanocrystalline ZnO particles from colloidal suspensions

Objective:

• To investigate the absorbance of zinc oxide nanoparticles during preparation and hence determine the growth kinetics.
• To model the absorbance of ZnO nanoparticles as a function of particle size and other parameters.

Duration:

It should take a 3 hour lab session to prepare the colloid and analyze it thoroughly and approximately 3 hours to model the absorbance and investigate the effect of the different parameters.

Background

There are many examples of quantum state semiconductor systems including TiO₂, ZnO, CdS, PbS, CdSe, and ZnS. Nanoparticles of these materials have different optical properties from the bulk material including an enlarged band gap.

ZnO nanoparticles absorb at a shorter wavelength than bulk particles. This is especially useful in the cosmetics industry, where nanosize particles that absorb in the UV but are transparent in the visible make highly efficient and non-allergenic sunscreens. ZnO also fluoresces in the visible (about 500 nm) and in the UV (380 nm). The fluorescence again depends on the particle size so in theory a tunable fluorescent particle could be produced which would be of particular interest as a phosphor material in display applications.

In a semiconductor such as ZnO, light is only absorbed if it has a frequency (and hence energy) that is greater than the energy required to excite an electron from the valence band to the conduction band of the material. This promotion of the electron to the conduction band creates a positively charged hole in the valence band. There is a strong attraction between the negatively charged electron and the positively charged hole,
causing them to orbit each other. They form a stable species called an exciton. In bulk semiconductors, the electron and hole orbit each other at a distance that depends on the semiconductor's dielectric constant. When semiconductor particles are synthesized with dimensions smaller than the natural exciton radius (called the Bohr radius) quantum size effects occur. For instance, ZnO nanoparticles smaller than 20 nm absorb light at a shorter wavelength than bulk particles. This is because energy is now required to confine the exciton within the nanoparticle. In fact only particular (discrete) exciton energies are allowed. Exciton confinement induces quantization of energy. For this reason semiconductor nanoparticles are also called quantum dots.

The position of the exciton transition of a colloidal system depends on the particle size and shape, solvent or adsorbate refractive index, and the interparticle distance. For ZnO particles about 3nm in diameter, the absorbance maximum ($\lambda_{\text{max}}$) is around 365nm. For smaller colloids, a slight (few nanometer) blue shift is expected, whereas for larger colloids, red-shifting of this band is observed. The peak width gives information about the polydispersity of the colloidal solution, with broader peaks indicating a greater distribution in particle size.

In the experiment you will be investigating the growth kinetics of ZnO particle formation. This method produces a final particle size of about 3-4 nm depending on the temperature of the water bath. The particle size at different times in the experiment will be estimated from the cut-off wavelength in the UV-Vis spectrum. The size as a function of time will then be plotted to determine the growth kinetics. Finally, a model of the absorption process will be developed and the effect of different parameters such as particle size, refractive index of the solvent and damping frequency will be investigated.

HAZARDS: Using isopropanol at this temperature can cause harmful vapours so the procedure should be carried out in a well-ventilated room and safety glasses worn at all times. Care must be taken when handling hot liquids.
Lab Documentation

**Preparing Zinc Oxide Colloid**

1. Dissolve 0.2 mmol of zinc acetate \([\text{Zn(CH}_3\text{CO}_2)_2\cdot2\text{H}_2\text{O}]\) in 16 mL of 2-propanol in a 50 mL conical (or Erlenmeyer) flask under vigorous stirring at 65 °C.
2. Pour the zinc acetate solution into a 200 mL conical flask and dilute with 168 mL of chilled 2-propanol and chill entire contents to 0 °C.
3. Prepare a solution of 0.02M NaOH in 2-propanol by dissolving a known amount of NaOH in 2-propanol at 65 °C.
4. Add 16 mL of NaOH solution to zinc acetate solution at 0°C over 1 minute under constant stirring.
5. Immerse suspension in a water bath at 65 °C for 2 hours.
6. Remove 4 mL aliquots after 0, 1, 3, 5, 10, 15, 30, 60, 90, 120 minutes and measure the absorbance spectrum.
7. While waiting for samples start answering the questions at the end of this section.
8. Dispose of solvents in the organic waste containers provided in the fumehood.

**Particle Size Determination**

The particle size can be determined experimentally from the absorption spectra using the effective mass model derived by Brus\(^2\).

\[
E^* \approx E_{g}^{\text{bulk}} + \frac{\hbar^2 \pi^2}{2r^2} \left( \frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0} \right) - \frac{1.8e^2}{4\pi \varepsilon_0 r} - \frac{0.124e^4}{\hbar^2(4\pi \varepsilon_0)^2} \left( \frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0} \right)^{-1}
\]

(1)

where \(E_{g}^{\text{bulk}}\) is the bulk band gap (for ZnO, \(E_{g}^{\text{bulk}} = 3.4\) eV), \(\hbar\) is Planck's constant (\(\hbar/2\pi\)), \(r\) is the particle radius, \(m_e^*\) is the effective mass of electrons, \(m_h^*\) is the effective mass of holes, \(m_0\) is the free electron mass, \(e\) is the charge on an electron, \(\varepsilon_0\) is the permittivity of free space and \(\varepsilon\) is the relative permittivity. The particle size is obtained from the band gap inferred from the optical absorption spectra. The band gap, \(E_g\), can be determined from the cut-off wavelength \((E_g = h\nu/\lambda_c)\). The particle size obtained from this method is slightly larger than that determined by other techniques such as TEM or XRD (by about 1nm) possibly due to the absorbance being related more to the size distribution of particles. An example of the absorption spectra obtained is shown in Figure 1. The cut-off wavelength should be determined from the intersection of the tangent of the peak with the wavelength axis.
Growth Kinetics

Ostwald ripening

Initially, a solution will contain a large number of small particles or crystals. Because of surface tension (and surface to volume ratios), small particles are much more soluble than large particles. The small particles will be precipitated onto larger particles. The small particles therefore act as nutrients for bigger particles and the average particle size will increase. The rate of this process, called Ostwald ripening, decreases as the particles grow and the particle size distribution becomes narrower.

This spontaneous process occurs because larger particles are more energetically favored than smaller particles. While the formation of many small particles is kinetically favored, (i.e. they nucleate more easily) large particles are thermodynamically favored. This is because small particles have a larger surface area to volume ratio than large particles and are consequently easier to produce. Molecules on the surface are energetically less stable than the ones already well ordered and packed in the interior. Large particles, with their greater volume to surface area ratio, therefore represent a lower energy state. Hence,
many small particles will attain a lower energy state if transformed into large particles and this is what we see in Ostwald ripening.

The rate law can be derived\(^1\) from the Gibbs-Thomson equation and Fick's law, but the main result is:

\[
\bar{r}^3 = Kt
\]

where

\[
K = \frac{8\gamma V_m^2 C_\infty}{9RT}
\]

\[(2)\]

where \(r\) is the particle radius, \(C_\infty\) is the equilibrium concentration at a flat surface, \(\gamma\) is the interfacial energy, \(V_m\) is the molar volume of the solid, \(D\) is the diffusion coefficient, \(R\) is the gas constant and \(T\) is the temperature (K). Hence a plot of particle size cubed versus time should be linear if the particle growth follows Ostwald ripening.

The Stokes-Einstein model for ionic diffusion can be compared to the Ostwald model by comparing the diffusion coefficient obtained from the graph and from the equation below.

\[
D = \frac{kT}{6\pi \eta a}
\]

\[(3)\]

where \(a\) is the hydrodynamic radius of the solute and \(\eta\) is the viscosity of the solvent and \(k\) is Boltzmann's constant.

**Questions**

1. Explain how the band gap can be determined from the absorption spectra.
2. Determine the particle size using the above assumptions and band gap.
3. Plot the particle size cubed as a function of time and determine the slope.
4. Estimate the diffusion coefficient in equation 2 from the slope of the graph and by finding the values of the constants from the literature. Make the approximation that \(C_\infty = \text{equilibrium concentration} \ [1.63 \times 10^{-7} \text{ mol L}^{-1}]\).
5. Compare the value of \(D\) found from the graph to the value calculated from the Stokes-Einstein model for diffusion.
Lab Documentation

Constants

- \( E_g^{bulk} = 3.4 \text{eV}, \quad \varepsilon = 3.7 \)
- \( m_e^* = 0.24, \quad m_h^* = 0.45, \)
- \( C = 1.63 \times 10^{-7} \text{M} \)
- \( v = 0.24 \text{mJ} \text{m}^{-2} \)
- \( \gamma = 0.24 \text{mJ} \text{m}^{-2} \text{T} \quad \text{T} = 65 \text{°C} = 338 \text{K} \)

From CRC Handbook

- \( V_m = 14.338 \times 10^{-6} \text{m}^3 \text{mol}^{-1} \)
- \( k = 1.38 \times 10^{-23} \text{J} \text{K}^{-1} \)
- \( \eta \text{ at } 50 \text{°C} = 1.04 \times 10^{-3} \text{N s m}^{-2} \)
- \( a = 0.51 \text{nm} \)

**Modeling**

The absorbance of a dilute solution of small particles can be calculated from Mie Theory:

\[
A = \frac{CNl}{2.303} \tag{4}
\]

where \( C \) is the absorption cross section, \( N \) is the number of particles per unit volume and \( l \) is the optical path length (cm). The absorption cross section is dependent on the dielectric properties of the particle and the surrounding medium and in the limit where the circumference of the particle is less than the wavelength of light the cross section can be expressed as:

\[
C = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon''}{(\varepsilon' + 2\varepsilon_m)^2 + \varepsilon''^2} \tag{5}
\]

where \( R \) is the radius of the particle, and \( \varepsilon_m \) and \( \varepsilon \) are the dielectric permittivity for the medium and for the sphere respectively. For the medium this is constant but for the sphere the dielectric permittivity contains real and imaginary parts:

\[
\varepsilon = \varepsilon' + i\varepsilon'' \tag{6}
\]

For a semiconductor sample this data must be collected from plots of reflectivity. A table of data for ZnO is included at the end of the laboratory notes.

The Drude theory of the dielectric properties of metallic particles predicts a size dependence of the dielectric permittivity. For semiconductor particles no such theory
exists and hence the real dielectric constants have to be used. The Drude model may be later used to investigate metallic colloids such as gold or silver.

**Questions**

1. Look up the values of the constants in the above equations.
2. Using the table of dielectric data for ZnO, plot the model spectra for a range of particle sizes. Note that the data is for bulk zinc oxide (R>6nm).
3. What happens to the shape and position of the absorption maximum? How is this justified?
4. Using the final particle size found from the experiment, plot the absorption spectrum and relate it to the experimental data. What is the difference between the experimental spectrum and the zinc oxide model and how can it accounted for?
5. What effect would changing the solvent to ethanol have on the absorption spectrum and why?

**Constants**

Mean free path, Fermi velocity and number of conduction electrons can be found easily from solid state textbooks. However, they will be reproduced here. You are expected to look these values up to check they are correct and justify any assumptions you have to make.

$$\varepsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$$

$$m_e = 9.11 \times 10^{-31} \text{ kg} \quad e = 1.6 \times 10^{-19} \text{ C}$$

Dielectric constants for following solvents at 65 ¡C:

- Water: 1.7588
- Ethanol: 1.7994
- Isopropanol (25¡C): 1.8906

**References**


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Notes for Demonstrators:
The water bath should be turned on at least an hour before the laboratory session to allow the temperature to stabilise. The sodium hydroxide solution can be prepared in advance to reduce the amount of time students spend preparing solutions. Isopropanol should be kept in the fridge to again reduce the time students spend cooling solutions down. Quartz cells must be used in the UV-Vis.
This lab was originally developed using 1L of isopropanol but was scaled down to 200mL. The amount prepared may depend on analysis requirements and can be scaled appropriately.

CAS Numbers
Zinc acetate 557-34-6
Isopropanol 67-63-0
Sodium hydroxide 1310-73-2