LABORATORY REPORT

CHEMISTRY 475-L03

Experiment #2

Growth Kinetics of Zinc Oxide Nanoparticles

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9 October 2035
Introduction

Zinc Oxide nanoparticles are receiving an increasing amount of attention in today’s research of nanophase materials and semiconductor. New materials which are artificially synthesized from these nanoparticles have been demonstrating advanced properties. The desired particle size is generally below 100nm because in this range, the unique quantum confinement effect, which will be discussed later, possessed by these nanoparticles will occur.1

In this lab, nanoparticles of ZnO is synthesized to observe its growth kinetics because ZnO is one of the few oxides that show quantum confinement effects within an experimentally accessible size range.2 Due to the wide bandgap (3.37 eV), relatively large exciton binding energy (60 meV) at room temperature and other properties, ZnO can be applied in gas sensors, ceramics, as well as electrical and optical devices2 such as transparent electronics, ultraviolet light emitter, surface acoustic varistors.3

ZnO nanoparticles can be prepared by precipitation of colloids sol–gel methods, thermal transport methods, pulsed laser deposition and so on.3 In this experiment, alcoholic solutions of Zinc ion and hydroxide are combined to from nanoscale particles of ZnO because Zn$^{2+}$ and OH$^-$ ions in a water solution will easily form precipitation. The reaction are as follows:

$$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O}$$ (1)

This reaction occurs spontaneously because small particles have big surface to volume ratio and is kinetically favored while large particles grown based on small particles are thermodynamically stable.4 The rate of this process can be explained by Ostwald ripening that the rate and particle size distribution decrease with the aging of ZnO nanoparticles.4

When ZnO, the semiconductor, absorbs the energy from a photon in the spectrometer, the electron in the valence band is excited to the conduction band, leaving a localized positively charged hole in the valence band. The Coulomb force between the electron and the hole leads to the formation of what is called an exciton.
As the particle grows from the point at which the nanoparticle is fairly small to the size of the natural exciton radius, quantum-size effects continue to take effect. Because energy is needed to confine the exciton in the potential well, in this case the sphere of ZnO particle, the absorption spectra will demonstrate a blue shift compared with that of bulk particles which is not affected by the exciton confinement. Suggesting by the equation of the effective-mass model\(^4\):

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

where \(E_g^*\) is the band gap energy for the particle, \(E_{g\text{ bulk}}\) is the bulk gap energy for ZnO, \(m_e^*\) is the effective mass of electrons and \(m_h^*\) is the effective mass of holes, the band gap energy decreases as the radius of the particle increases, therefore resulting in the red shift in the absorption spectra. The confinement diminishes as the particle grows bigger in size.

To monitor the growth kinetics of ZnO nanoparticles, a thermostated UV-Vis spectrometer is used to obtain the absorption spectra. The cuvette is held at a set temperature in the spectrometer. Spectrums are automatically recorded at a set time interval. The cutting-off wavelength \(\lambda_c\) is determined by the tangent of the peak\(^4\). The band gap energy can therefore be obtained by equation\(^4\)

\[
E_g^* = \frac{hc}{\lambda_c} \quad (3)
\]

By solving equation (2), the radius of the nanoparticle is readily accessible. The overall trend of the size of ZnO over time can be analyzed. The rate law used for this modeling is expressed by equation (4).

\[
\tilde{r}^3 = Kt \quad \text{where} \quad K = \frac{8\gamma DV_m^2 C_s}{9RT}
\]

And \(\tilde{r}\) is the average particle radius, \(C_s\) 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. Therefore a
linear relationship can be observed between radius cubed and experiment time. The diffusion coefficient calculated from eqn.4 can be compared to that obtained from the Stokes-Einstein model to evaluate the applicability of the rate law model:

\[
D = \frac{k_BT}{6\pi \eta \alpha}
\]  

(5)

Where \( \alpha \) is the hydrodynamic radius of the solute, \( \eta \) is the viscosity of the solvent, and \( k_B \) is Boltzmann’s constant.4

Objectives

1. To investigating the growth kinetics of ZnO nanoparticle formation based on quantum confinement theory.
2. To monitor the trend of particle size and band gap energy in the growth kinetics.

Experimental

Preparing ZnO colloid

0.0221 grams of grounded Zinc acetate dehydrate \([\text{Zn(CH}_3\text{CO}_2)\cdot 2\text{H}_2\text{O}]\) was dissolved in 50.0 ml of iso-propanol in a 100ml dried beaker under vigorous stirring at room temperature. 0.0065 grams of sodium hydroxide was dissolved in 50.0 ml of iso-propanol in another dried 100ml beaker under vigorous stirring at room temperature.

After one week’s period, the Zinc acetate and sodium hydroxide was fully dissolved in iso-propanol. Set the water bath to 67°C. Transfer 5 ml of Zinc acetate to an Erlenmeyer flask. Transfer 5 ml of NaOH to another Erlenmeyer flask. Put a rubber stopper on both of the flasks to avoid isopropanol vapor diffusing. Fill the thermostated cuvette with isopropanol.

After the temperature inside the cuvette is calibrated to 63.8°C, conduct the blank test. Set the acquisition range of the UV-Vis spectrometer as from 200 nm to 820 nm in wavelength. Set the runtime to 4000 seconds and cycle time to 50 seconds.

After the temperature of the Zinc acetate and NaOH solution is calibrated to 65°C, quickly poured the two solution to a beaker and stir the mixture. Quickly fill the
cuvette with the mixed solution and cap the cuvette to avoid isopropanol vapor diffusing.

**Data collection and cut-off wavelength determination**

Start collecting data. After finished the 4000 seconds running, export all the data to Igor. Load all the waves in one graph named absorbance vs wavelength for comparison.

Select curve fit region. This region, from 350 nm to 356 nm in the wavelength, is selected because the curves are best fitted with a line and they are most paralleled to each other in this region. Do curve fitting in the selected region with the function of a line. Use programming language to fit each curve automatically.

Determine the cut-off wavelength. The cut-off wavelength is measured from where the tangent, the slope of the peak, crossed the wavelength axis. This value of intercept is the required cut-off wavelength.

Slow down the curve fitting process by inputting “sleep/t 5” in the command so that each curve fitting can be observed and the preciseness of the fit can be evaluated for future adjustment in the fitting region.

Obtain a graph of cut-off wavelength vs time by running the program designed (see appendix).

**Data processing and particle radius determination**

Note that the radius is related to the cut-off wavelength shown in eqn(2), we can therefore substitute in the constant and cut-off wavelength to solve for the answer to this equation. Because the radius $r$ is a nonzero variable, $r^2$ can be multiplied to both sides of the equation and change it into a quadratic equation

$$
(E_g - E^* - rac{0.124e^4}{h^2(4\pi\varepsilon_0)^2} \left( \frac{1}{m^*m_e} + \frac{1}{m^*h m_e} \right)^{-1}) r^2 - \frac{1.8e^2}{4\pi\varepsilon_0} r + \frac{\hbar^2 \pi^2}{2} \left( \frac{1}{m^* m_e} + \frac{1}{m^* h m_e} \right) = 0 \tag{6}
$$

The function quadratic(a, b, c) was created to compute the radius. (see appendix).
Results and discussion

The concentration for Zn\(^{2+}\) in the total 100 ml isopropanol solution is

\[
c = \frac{m_{Zn(CH_3CO_2)H_2O} / M_{Zn(CH_3CO_2)H_2O}}{V} = \frac{0.0221/219.50}{0.1} = 1.007mM
\]

The concentration for OH\(^-\) in the total 100 ml isopropanol solution is

\[
c = \frac{m_{NaOH} / M_{NaOH}}{V} = \frac{0.0065/39.9971}{0.1} = 1.625mM
\]

Both the concentration is slightly higher than the suggested value of 1 mM and 1.6 mM, which will have some impact on the final results. The actual temperature inside the cuvette is 63.8 °C

Coefficient a, b and c for the quadratic equation (6):

\[
E^*_{g} = \frac{hc}{\lambda_e} = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^8}{\lambda \times 10^{-9}} J
\]

\[
E^*_{g \text{ bulk}} = 3.4 \times 1.602 \times 10^{-19} = 5.4468 \times 10^{-19} J
\]

\[
- \frac{0.124e^4}{\hbar^2 (4\pi\varepsilon_0)} \left( \frac{1}{m^* m_e} + \frac{1}{m^* m_e} \right)^{-1} = - \frac{0.124 \times (1.602 \times 10^{-19})^4}{\hbar^2 (4\pi \times 3.7 \times 8.854 \times 10^{-12})^2} \left( \frac{1}{0.24 m_e} + \frac{1}{0.45 m_e} \right)^{-1}
\]

\[
= -6.1789 \times 10^{-21} J
\]

\[
a = E^*_{g \text{ bulk}} - E^*_{g} - \frac{0.124e^4}{\hbar^2 (4\pi\varepsilon_0)} \left( \frac{1}{m^* m_e} + \frac{1}{m^* m_e} \right)^{-1}
\]

\[
b = \frac{-1.8e^2}{4\pi\varepsilon_0} = -1.224 \times 10^{-28} J \cdot m
\]

\[
c = \frac{\hbar^2 \pi}{2} \left( \frac{1}{m^* m_e} + \frac{1}{m^* m_e} \right) = 3.8848 \times 10^{-37} J \cdot m^2
\]
It can be seen from Fig.1 that as the nanoparticle grows bigger, the wavelength corresponding to the maximum absorption increases.

Note that some absorbance value get larger than 1.0 especially when the ZnO particle gets bigger. This suggests that the concentration of ZnO nanoparticle is too high and most of the UV light is being absorbed. The original solution need to be diluted to get more accurate absorbance spectra.

This data set is abandoned for the reason that its cut-off wavelength starts at around 370 nm and end at 383 nm. The starting radius calculated is 600 nm, which is highly above the reasonable range of a nanoparticle. Possible explanation for this deviation in data can be the moisture in the isopropanol solution. Water can be introduced into the system by hydrated Zn(CH$_3$CO$_2$)$_2$ $\cdot$2H$_2$O, NaOH water absorbance, incomplete dried container or cuvette, accidental water spark from the thermostatic water bath and so on.

The following part of the analysis is based on the sample data set provided by Professor Joseph V. Diverdi.
Figure 2. Absorption spectrum for ZnO nanoparticle growth at the temperature 65 °C. 229 curves are collected and plotted in this graph over a time period of 6840 seconds.

In figure 2, due to quantum confinement effects, systematic red shift with the aging of particle is observed. As the nanoparticle grow, the particle size distribution get narrower. Therefore the peak width of larger particles is narrower.

Figure 3. The determination of cut-off wavelength using a line curve fit. Points with absorbance from 0.2 to 0.1 were selected to do the curve fitting because the curve between these two points are most straight and paralleled to each other.
Figure 4. The cut-off wavelength versus experiment time at temperature 65 °C. 229 cut-off wavelength values are obtained by computing the intercept of the tangent line of the peak. The cut-off wavelength ranges from a minimum 329.949 nm to a maximum 358.379 nm.

It can be seen in Fig.4 that the cut-off wavelength increases over time except for the beginning part, which indicates that smaller energy is needed to confine the extinction in the sphere of ZnO. The band gap energy for the particles decreases too. Therefore, the increasing space of confinement indicating the growth of ZnO can be observed from the trend. Several points at the beginning didn’t comply with the overall trend because the curve fitting range.

Figure 5. The particle radius versus experiment time at temperature 65 °C. The particle radius are obtained by solving the quadratic equation (6).
Given that $r^3 = Kt$, $K$ is equal to the coefficient $a$ in the curve fitting equation. According to eqn.5, the diffusion coefficient can be calculated.

$$D = \frac{9RTK}{8\gamma V^2_n C_m} = 3.89 \times 10^{-6} \text{m}^2\text{s}^{-1}$$

The Stokes-Einstein diffusion coefficient calculated by eqn.6 is $1.04 \times 10^{-9} \text{m}^2\text{s}^{-1}$ at 65 °C. Significant magnitude difference is shown between these numbers.

**Acknowledgement**

I would like to thank Professor Joseph V. Diverdi for providing the sample ZnO growth Igor packet.

**References**


### Appendix

Functions programmed in the Igor procedure:

```plaintext
#pragma rtGlobals=1  // Use modern global access method.

function plot()  
    wave absorbance;  
    variable i;  
    for(i = 0; i < dimsize(absorbance, 1); i += 1)  
        AppendToGraph absorbance[i];  
    endfor  
end

function test()  
    wave absorbance, temp, intercept, W_coef, radius, radius_cube;  
    variable i;  
    for (i = 0; i < dimsize(absorbance, 1); i += 1)  
        // copy selected column to one-d wave  
        temp = absorbance[p][i];  
        // curve fit wave  
        // CurveFit/X=1/NTHR=0/Q line temp[x1, x2] /D  
        CurveFit/X=1/NTHR=0/Q line temp[75, 78] /D  
        // place result in desintation wave  
        intercept[i] = -W_coef[0] / W_coef[1];  
        // compute the radius  
        variable energy_star = 6.626e-34 * 3.0e8 / intercept[i] * 1e9; // J  
        variable energy_bulk = 5.45e-19 // J  
        variable k0 = 7.01e30 // kg^-1  
        variable k1 = 3.85e-37; // J m^2  
        variable k2 = -1.12e-28; // J m^1
```
variable k3 = -6.15e-21; // J
variable a = energy_bulk - energy_star + k3;
variable b = k2;
variable c = k1;
radius[i] = quadratic(a, b, c);
radius_cube[i] = radius[i]^3;
doupdate;
sleep/t 5;
endfor
end

function find_point(my_wave, my_y)
    variable my_y;
    wave my_wave;
    variable i;
    for (i = dimsize(my_wave, 0); i > 0; I -= 1)
        if (abs(my_wave[i] - my_y) < 0.05)
            return i
        endif
    endfor
    return 0;
end;

function quadratic(a, b, c)
    variable a, b, c;
    variable radical = b^2 - 4 * a * c;
    if (radical < 0)    // both roots are complex
        return NaN;
    endif
    variable root1 = (-b + sqrt(radical)) / (2 * a);
    variable root2 = (-b - sqrt(radical)) / (2 * a);
    if ((root1 < 0) && (root2 < 0)) // both roots are negative
        return NaN;
    endif
    if ((root1 > 0) && (root2 < 0))     // one root is positive, the other negative
        return root1;
    endif
end
if ((root1 < 0) && (root2 < 0)) // one root is positive, the other negative
    return root2;
endif

// both roots are positive
if (abs(root1 - root2) < 0.001 * abs((root1 + root2) / 2))
    return (root1 + root2) / 2;    // the roots are so close to be indistinguishable
endif

if (root1 > root2)    // return the larger root
    return root1;
else
    return root2;
endif
end