

Quantum dots: introduction and applications

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Abstract

Semiconducting nano particles can synthesized using wet chemical techniques at low temperature and can be utilized in a lot of industrial fields. This report focuses on the synthesis of CdSe/CdS core-shell Quantum Dots which are a type of Semiconducting nano particles and there application in order to make QLED displays. We also talk about how the properties of the excitons inside these Quantum Dots vary, as the size of the shell is changed. As the shell thickness is increased the spatial distribution of the hole is shifted from the core towards shell which leads to change in the absorption spectrum and the excitation energy. When the electron and hole come together they release energy in the form of electromagnetic radiation controlling the size of quantum dot we can get the desired colours. The colours produced by Quantum Dots are much brighter from the already existing LEDs. Quantum Dots can also be used to increase the efficiency of solar systems by increasing the size of the spectrum of the light that can be absorbed by the solar system.

Keywords: Quantum Dots; Semiconducting nanoparticles ; synthesis ; Solar Cells ; Hartree Fock equations

1 Introduction

Quantum Dots(QD's) are semiconducting nanoparticles, they show exceptional optical,chemical and electronic properties which have hundreds of industrial applications. Core-Shell quantum dots provide an advantage over normal Quantum Dots and their properties can be altered and controlled by varying the thickness of core or the shell. This report is about how these nano particles can be synthesised, how the electrons and holes behave when the thickness of shell is varied,while keeping the thickness of the core same(1.75 nm) and finally we talk about the how these QD's can be used industrially.The radius of the Quantum Dots is roughly below the Bohr's exciton radius,which leads to the motion of the excitons being confined also known as Quantum Confinement. This further leads to the Qunatizations of the Conductance band(CB) and the Valence Band(VB)which is almost continuous for the Bulk Semiconductors.The synthesis of the QD's is done via chemically processes where the thickness of the shell can be varied by changing the amount of the compounds used. The thickness of the shell and the core can be determined by using Transmission electron Microscope.For the analysis of the wave functions of type-1 and type-2 excitons the Hartree Fock mean field approximation has been used, the equations obtained have been further solved using finite difference method. The Probability density function of the electron and the hole are used to calculate the excitation energy and the bonding energy.The applications of Quantum Dots are being researched immensely and these are the possible applications :

solar cells, LEDs, lasers, single-photon sources, quantum computing, cell biology research, microscopy, and medical imaging. This report will mainly focus on how we can use QD's in order to increase the efficiency of solar cell by increasing the amount of light absorbed by the cell.

2 Quantum Dots: a deeper look

Quantum Dots are semiconducting nanocrystalline materials with diameter in range of a few nanometers(2-10nm). They use **quantum confinement** in order to show unique properties.

2.1 Quantum Confinement

The spatial confinement of electron hole pair due to quantizations in quantum mechanics is known as quantum confinement. This is mainly shown by semiconductor materials as they already posses band gaps. Metals do not have band gaps due to which quantum confinement is less prevalent.

As the size is reduced, the delocalized energy states gets confined. The electron hole pairs gets confined as the diameter of the particle approaches the bohr radius. This results in increase in the energy gap.

In order to change and control the properties of these QDs we need to alter the band gap.

2.2 Energy band gap

QDs exhibit photo luminescence. When QDs are provided with energy the excitons get excited, these excitons emit radiation when they come to lower energy state. By controlling



Figure 1: Glowing Quantum Dots

the band gap we are able to emit radiation of particular wave length .

The energy band gap can also be utilized for absorbing radiations having particular wave length. This property can be utilized in order to increase the efficiency of solar cells by broadening of the spectra of light which can be absorbed by the solar cells.

2.3 Excitons

The Hamiltonian of the system is given below

$$H^{ehp} = -\frac{\hbar^2}{2}\nabla_e\left(\frac{1}{m_e(r)^*}\right)\nabla_e - \frac{\hbar^2}{2}\nabla_h\left(\frac{1}{m_h(r)^*}\right)\nabla_h - \frac{e^2}{K|r_e - r_h|} + V_e(r) + V_h(r) \quad (1)$$

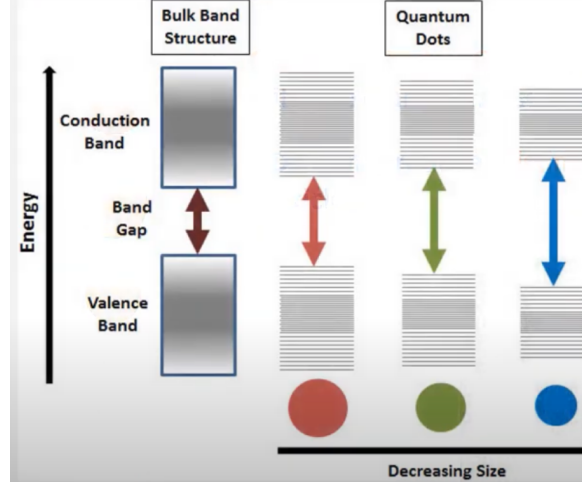


Figure 2: Band Gap

here the first term corresponds to the electron's kinetic energy and the second term corresponds to the hole's kinetic energy, the third term is the potential energy due to the Columbic attraction between the hole and electron, the fifth and the fourth term are the confinement potential of the hole and electron. K is the dielectric constant of the medium, m_e^* and the m_h^* are the electron and the hole's effective mass. The time independent Schrodinger wave equation for the system can be given as

$$H^{ehp}\Psi_{nlm}^{ehp}(r_e, r_h) = E_{nlm}\Psi_{nlm}^{ehp}(r_e, r_h) \quad (2)$$

the $\Psi_{nlm}^{ehp}(r_e, r_h)$ is the excitonic wave functions and the E_{nlm} is the excitonic energies. But, the equations given above requires computational power more than we currently have due to which Hartree Fock method is used to make approximations.

The final equations used for our analysis is given below,

$$\left[-\frac{\hbar^2}{2} \nabla_e \left(\frac{1}{m_e(r)^*} \right) \nabla_e - q_e \phi_h + V_e(r) \right] R_e(r) = E_e R_e(r) \quad (3)$$

$$\left[-\frac{\hbar^2}{2} \nabla_h \left(\frac{1}{m_h(r)^*} \right) \nabla_h - q_h \phi_e + V_h(r) \right] R_h(r) = E_h R_h(r) \quad (4)$$

where q_e and q_h represent charges, $R_e(r)$ and $R_h(r)$ are the **Radial Wave Function**, $\phi_e(r)$ and $\phi_h(r)$ are the columbic potential generated by electron and hole. The confinement potential for the electron given by R_1 and R_2 is calculated by difference of the electron affinity of the core and the shell and for the hole, it is calculated by reducing confinement potential of electrons with the difference of band gap between core and shell. The confinement potential outside dot is taken to be ∞ .

$$V_e = X_{CdSe} - X_{CdS} \quad (5)$$

$$V_h = E_{bg(CdSe)} - E_{bg(CdS)} - V_e \quad (6)$$

The confinement potential profile of QD's is represented as:

$$V_{e,h} = \begin{cases} 0 & r < R_1 \\ V_{e,h} & R_1 < r < R_2 \\ \infty & r > R_2 \end{cases}$$

Further the potential can be given by Poisson's equation,

$$\nabla_e K(r) \nabla_e \phi_e = q_e \rho_e \quad (7)$$

$$\nabla_h K(r) \nabla_h \phi_h = -q_h \rho_h \quad (8)$$

where $\rho_{e,h}$ is the charge density due to the electron and the hole respectively and can be given by:

$$\rho_e = \frac{1}{4\pi} q |R_e^{n,l}(r)|^2$$

$$\rho_h = \frac{1}{4\pi} q |R_h^{n,l}(r)|^2$$

here n is the principal quantum number and l is the azimuthal quantum number.

As we are only going to be looking on the s-s transitions, so **n=1 and l=0**.

3 Synthesis of CdSe/CdS quantum dots

3.1 Chemicals used

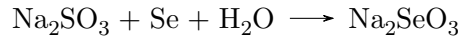
Selenium metal powder (Se), cadmium acetate dehydrate Cd (CH₃COO)₂·2H₂O, 2-mercaptoethanol (HOCH₂CH₂SH) also known as ME and potassium iodide (KI), , India. Sodium sulfite (Na₂SO₃), polyethylene oxide(PEO) (Mw = 5,00,000) and polyethylene glycol (PEG) (Mw = 200) , N,N-Dimethylformamide (DMF), chloroplatinic acid (H₂PtCl₆), Ti (IV) bis (ethyl -aceto -acetato)-diisopropoxide solution (2wt% in 1- butanol) also known as blocking layer, acetonitrile ,polyvinylidene fluoride (PVDF) (Mw = 1,00,000) , Double distilled (DD) water was also used.

3.2 Apparatus Required

Sodium sulphide (Na₂S) fused flakes, FTO glasses of sheet resistance 8/sq, two neck flask , glass rod

3.3 Experimental Procedure

We start by mixing *Se* (0.063 gm) along with *Na₂SO₃* (0.304 gm) along with DD water, inside of a two neck beaker. The solution was mixed rigorously to produce *Na₂SeO₃* .



This solution is refluxed until it becomes transparent. Now, *Cd(CH₃COO)₂·2H₂O* (0.1066 gm) is dissolved along with 50 ml of DD water at 40 C, this will be called **Cadmium Solution**. Another solution with DD water and *Na₂S* is prepared.

The *Na₂SeO₃* obtained is added into the **Cadmium Solution** and in one of the beakers

we add 2-mercaptoethanol(0.3 ml) drop wise. The 2-mercaptoethanol acts as a capping agent. Thus one of the solution obtained has capped QD's and one has uncapped QD's. Both the solutions are orangish in colour and show photo luminescence under UV light.

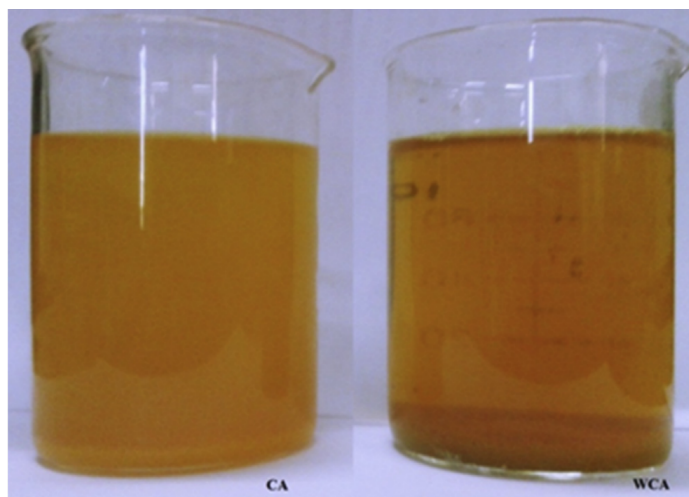


Figure 3: Quantum Dots

3.4 Synthesis of CdSe/CdS core shell quantum dots

The prepared QD's are analysed by X-ray diffraction and Transmission Electron Microscope.

The miniflex X-Ray diffraction instrument recorded the 2θ angles between 20° and 70° . The obtained diffraction graph is shown in fig.2, three peaks can be observed at $2\theta = 26.17^\circ, 43.72^\circ$ and 50.47° . Which corresponds to the (111), (220) and (311) crystal planes of the crystal structure. The particle size is estimated using the Debye-Scherrer

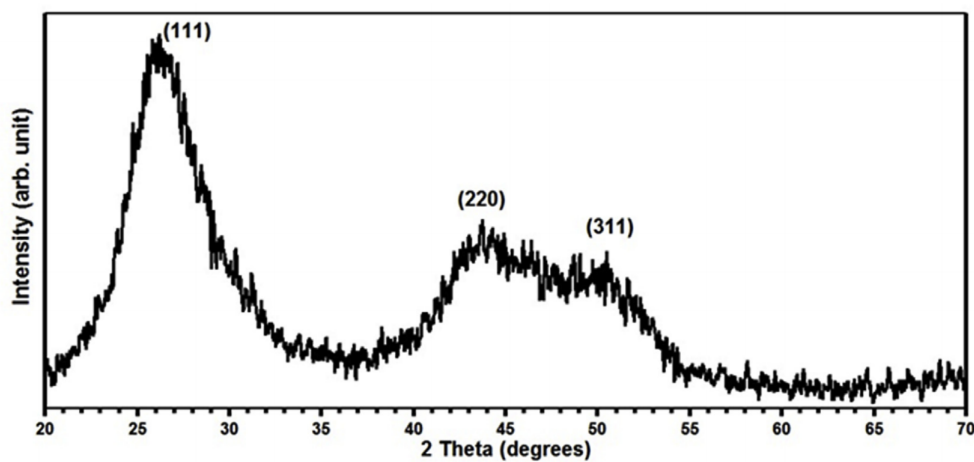


Figure 4: X-ray Diffraction Spectrum

equation given below

$$D = \frac{K\lambda}{\beta \cos(\theta)}$$

where λ is the wavelength of the X-ray Radiation, θ is the Bragg's diffraction angle, K is a dimensionless shape factor whose value equals to 0.94 for cubic structure and β is FWHM of the peaks in radians.

This gives us the average diameter of the core shell diameter as **3 nm**.

The High resolution transmission electron microscopy (HRTEM) are shown below, they

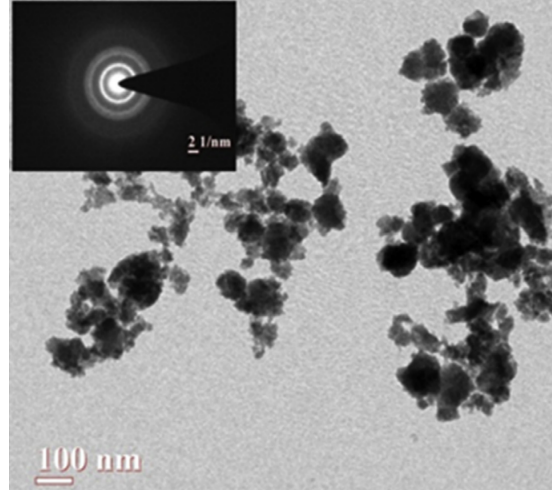


Figure 5: HRTEM image with bigger scale

provide us with much greater insight towards how the real QD's look. The fig.4 has marked the QD's in which the core and shell are clearly visible. The average particle size obtained from this method is 4 ± 0.2 nm . There is a 1nm difference in the particle size obtained from HRTEM and XRD, this is due to time delay in sample preparation and carrying out the measurements.

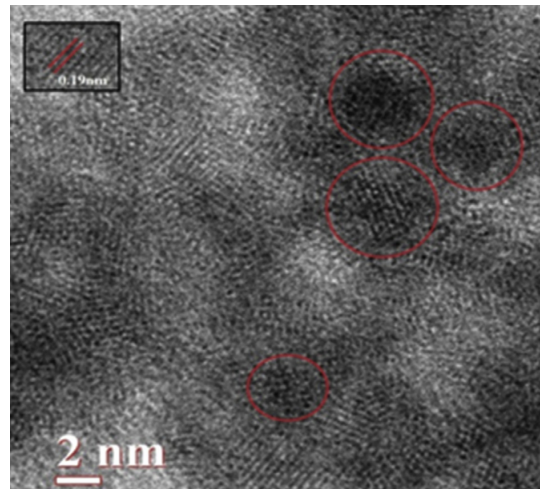


Figure 6: HRTEM image(zoomed in)

4 Simulation

We have used Finite difference method in order to solve the 4 equations given above and the algorithm uses a conditional loop in order to calculate the exact value of wave functions of electron and hole.

4.1 Algorithm

The below flowchart shows how the algorithm calculates the wave function of the electron and hole using the Poisson's equation and Schrodinger equation.

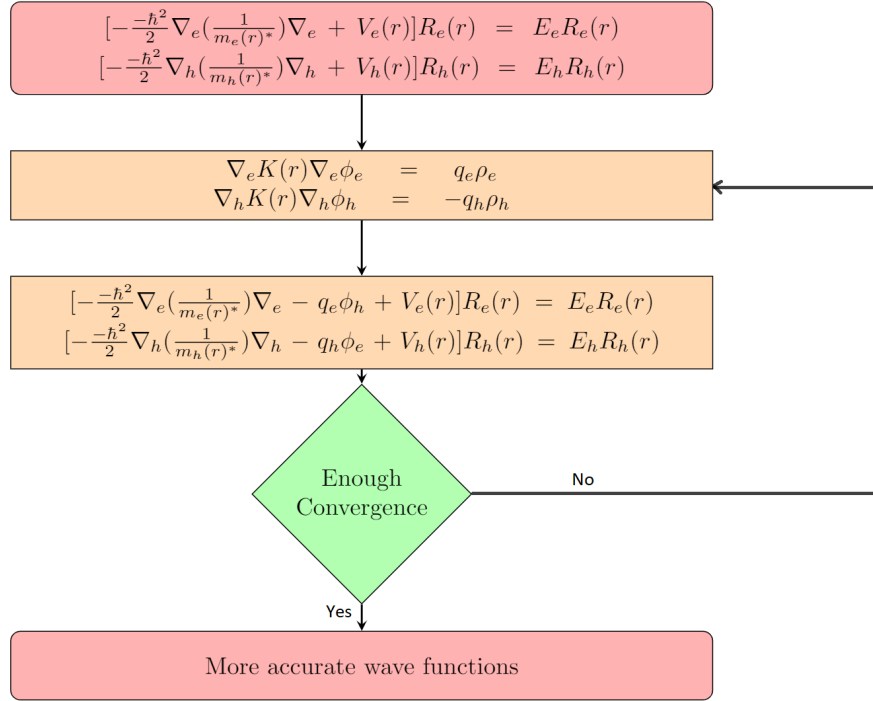


Figure 7: Flowchart of Algorithm

4.2 Solving the Schrodinger wave equation

Note - We are solving the equation for 1D space.

The Schrodinger wave equation is solved using Finite Difference method. The whole space is broken down into n points and the derivatives are calculated at each point.

As we are only doing the simulation for 1D the equation becomes an ordinary differential equation.

$$[-\frac{\hbar^2}{2}\frac{d}{dr}(\frac{1}{m_e^*})\frac{d}{dr} - q_e \phi_h + V_e(r)]R_e(r) = E_e R_e(r) \quad (9)$$

For now let's take $\phi_h = 0$,

$$\left[-\frac{\hbar^2}{2} \frac{d}{dr} \left(\frac{1}{me^*}\right) \frac{d}{dr} + V_e(r)\right] R_e(r) = E_e R_e(r) \quad (10)$$

Using Finite difference method -

$$\frac{\Delta R_e}{\Delta r} = \frac{R_{e(i+1)} - R_{e(i-1)}}{2d} \quad (11)$$

where $d = r_{i+1} - r_{i-1}$ Similarly

$$\frac{\Delta^2 R_e}{\Delta r^2} = \frac{R_{e(i+1)} - 2R_{e(i)} + R_{e(i-1)}}{d^2} \quad (12)$$

we will substitute these values of differences inside equation (9)

$$\left[-\frac{\hbar^2}{2} \frac{1}{me^*} \frac{R_{e(i+1)} - 2R_{e(i)} + R_{e(i-1)}}{d^2} + V_e(r_i)\right] R_e(r_i) = E_e R_e(r_i) \quad (13)$$

When we put different values of $i = 0, 1, 2, \dots, n$. We get n equations these equations can be represented using matrix notations.

$$-\frac{\hbar^2}{2m_e^* d^2} \begin{bmatrix} -2 & 1 & 0 & \dots & 0 \\ 1 & -2 & 1 & \dots & 0 \\ \dots & \ddots & \ddots & \ddots & \ddots \\ 0 & 0 & 0 & 1 & -2 \end{bmatrix} \begin{bmatrix} R_{e(1)} \\ R_{e(2)} \\ \ddots \\ R_{e(n)} \end{bmatrix} + \begin{bmatrix} V_1 & 0 & 0 & 0 & 0 \\ 0 & V_2 & 0 & 0 & 0 \\ \ddots & \ddots & \ddots & \ddots & \ddots \\ 0 & 0 & 0 & 0 & V_n \end{bmatrix} \begin{bmatrix} R_{e(1)} \\ R_{e(2)} \\ \ddots \\ R_{e(n)} \end{bmatrix} = E \begin{bmatrix} R_{e(1)} \\ R_{e(2)} \\ \ddots \\ R_{e(n)} \end{bmatrix}$$

If we had not taken ϕ_h to be zero it could be represented in a similar method.

Finally we use the **eig()** function of MATLAB in order to get the values of eigen values and eigen vectors of the matrices.

Note - Similarly we can solve the same equation for the hole.

4.3 Solving the Poisson's equation

After calculating the density of charge carriers we solve poisson equation using FDM and this gives us the value of ϕ_h and ϕ_e . Which is used as the input into the loop again and we get the more accurate values of the wave function.

$$\rho_e = \frac{1}{4\pi} q |R_e^{n,l}(r)|^2$$

This gives us the electron density

$$\nabla_e K(r) \nabla_e \phi_e = q_e \rho_e \quad (14)$$

The above equation can be solved by again dividing the space into n parts and writing the equation again

$$K_i \left(\frac{\phi_{i+1} - 2\phi_i + \phi_{i-1}}{d^2} \right) = \rho_{e(i)} \quad (15)$$

A for loop is used in order to implement this and the final value is obtained inside a vector. This vector is diagonalised and inputted into the equation number (9).

4.4 MATLAB code

```
% QUANTUM DOT
% this will for CdSe and CdS for now but we want for the whole thing

clear all;
clc;
close all;
%% constants
m_e = 1;
h = 1;
V_e_shell = 0.29; % confinement potential inside the quantum dot
V_core = 0 ;
V_hole_shell = 0.45;
e_charge = -1;
hole_charge = 1;
K_shell = 8.9;
K_core = 9.3;

%% space%
%z = linspace(-2e-9,2e-9);
d= 0.05e-9;
z= -2e-9:0.05e-9:2e-9;
core_size = 1.75e-9; % radius of the core
shell_size = 1e-9; % thickness of the shell
m_e_core = 0.13*m_e; % effective mass of electron in shell
m_e_shell = 0.21*m_e; % effective mass of electron in core
m_h_shell = 0.80*m_e; % effective mass of hole in shell
m_h_core = 0.45*m_e; % effective mass of hole in core

n = size(z);
%% defining the potential term for electron

V_e = zeros(n);
V_e((core_size < z ) ) = V_e_shell;
V_e((-core_size > z ) ) = V_e_shell;%% why is the right side cindition not working
V_e = diag(V_e);

%% effective mass of electron

m_e = zeros(n);
m_e((core_size <= z )) = m_e_shell;
m_e((-core_size >= z )) = m_e_shell;
m_e(-core_size < z & z<core_size) = m_e_core;
% coz we will requier the diagonal
m_e= 1./m_e;
```

```

m_e = diag(m_e);

%% KINETIC ENERGY term for ELECTRON
[dont_matter y] = size(z);
K_e = eye(y,y)*(-2);
a=ones(y-1,1);
K_e = K_e + diag(a,1) + diag(a,-1);

% %% HAMILTONIAN for ELECTRON
% H_e = (K_e*(-h^2)*m_e)./(4*d) + V_e;
%
% %% WAVE FUNCTION of ELECTRON
% [eig_vec_e , eig_val_e] = eig(H_e);

%% defining the potential term for hole

V_h = zeros(n);
V_h((core_size < z ) ) = V_hole_shell;
V_h((-core_size > z ) ) = V_hole_shell;%% why is the right side cindition not working
V_h = diag(V_h);

%% effective mass of hole

m_h = zeros(n);
m_h((core_size <= z )) = m_h_shell;
m_h((-core_size >= z )) = m_h_shell;
m_h(-core_size < z & z<core_size) = m_h_core;
% coz we will requier the diagonal
m_h= 1./m_h;
m_h= diag(m_h);

%% KINETIC ENERGY term for HOLE
[dont_matter s] = size(z);
K_h = eye(s,s)*(-2);
b=ones(s-1,1);
K_h = K_h + diag(b,1) + diag(b,-1);

%% DIELECTRIC constant

K_r = zeros(n); % n is a [1 81] matrix
K_r((core_size <= z )) = K_shell;
K_r((-core_size >= z )) = K_shell;
K_r(-core_size < z & z<core_size) = K_core;
% am gonna make all the matrices column

```

```

K_r = K_r';

%% LOOP for implementing the algorithm

phi_h = zeros(n)';
rh_prev = zeros(n(1,2));

% Boundary conditions are already fulfilled as they are 0
for i= 2:(n(1,2))-1
    phi_h_diag = diag(phi_h);

    H_h = (K_h*(-h^2)*m_h)./(d^2) + V_h + phi_h_diag;

    [eig_vec_h , eig_val_h] = eig(H_h);

    if(fix(rh_prev*1e7)/1e7 == fix(eig_vec_h*1e7)/1e7 ) %% have used fix in order to eq
        break;
    end

    rh_prev = eig_vec_h;

    psi_h_net = eig_vec_h(:,1).^2; % ground state
    h_dens = ((1/4)*pi)*psi_h_net;

    for i= 2:(n(1,2))-1
        phi_h(i,1) = (-0.5)*((d^2*h_dens(i,1)/K_r(i,1))- phi_h(i+1,1) - phi_h(i-1,1));
        %      K_r(i,1).*(phi_e(i+1,1)-2*phi_e(i,1)+ phi_e(i-1,1)) = e_dens(i,1);
    end

end

%% final Re for electron

phi_e = zeros(n)';
re_prev = zeros(n(1,2));

```

```

% Boundary conditions are already fulfilled as they are 0
for i= 2:((n(1,2))-1)
    phi_e_diag = diag(phi_e);

    H_e = (K_e*(-h^2)*m_e)./(d^2) + V_e + phi_e_diag;

    [eig_vec_e , eig_val_e] = eig(H_e);

    if(fix(re_prev*1e7)/1e7 == fix(eig_vec_e*1e7)/1e7 )
        break;
    end

    re_prev = eig_vec_e;

    psi_e_net = eig_vec_e(:,1).^2; % ground state
    e_dens = ((1/4)*pi)*psi_e_net;

    for i= 2:((n(1,2))-1)
        phi_e(i,1) = (-0.5)*((d^2*e_dens(i,1)/K_r(i,1))- phi_e(i+1,1) - phi_e(i-1,1));
        % K_r(i,1).*(phi_e(i+1,1)-2*phi_e(i,1)+ phi_e(i-1,1)) = e_dens(i,1);
    end

end

%% plot

eig_vec_e_f = eig_vec_e.^2;

subplot(2,2,1);
plot(z,eig_vec_e(:,4))
grid on
ylabel("Radial Wave function of electron(nth energy state)")
xlabel("r")

subplot(2,2,2);
plot(z,eig_vec_h(:,4))
grid on
ylabel("Radial Wave function of hole(nth energy state)")

```

```

xlabel("r")

subplot(2,2,3);
plot(z,phi_e)
grid on
ylabel("Potential due to electron")
xlabel("r")

subplot(2,2,4);
plot(z,phi_h)
grid on
ylabel("Potential due to hole")
xlabel("r")

```

4.5 Results and discussion

We can observe the different values of wave functions of electron and hole by using this algorithm. We have kept the core radius same = 1.75 nm and the size of shell is varied to show how the wave function changes. Now as the thickness of the shell is increased we can

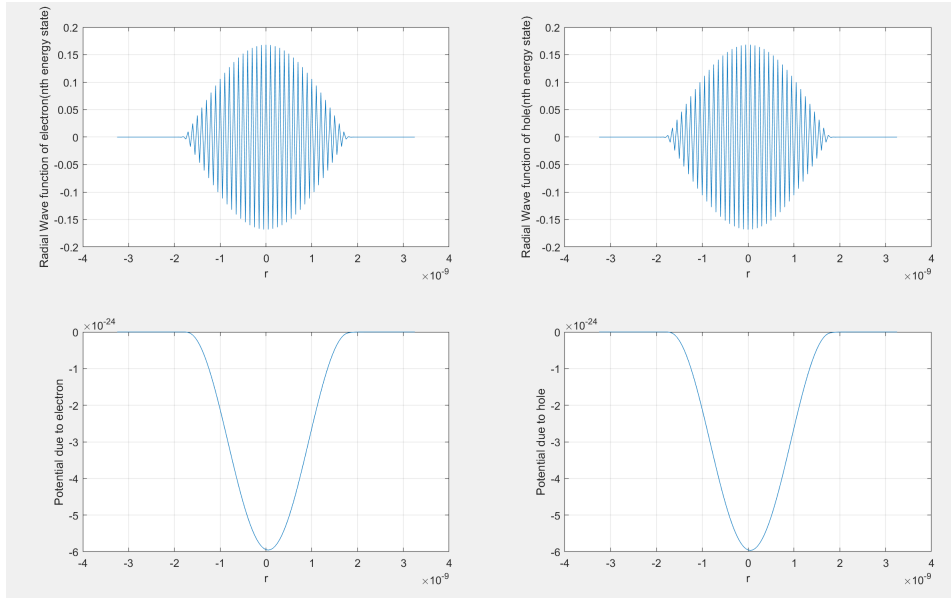


Figure 8: Ground state($radius_{core} = 1.75nm$ and $thickness_{shell} = 1.5nm$)

observe that the charge carriers which were originally mainly isolated inside the core, gets delocalized and can be found in shell too.

The graphs given below show this as the thickness of the shell increases from 0.25nm to 1.5nm the ground state wave function of the hole gets mpore distributed towards the shell.

The wave functions produced from our method is of immense importance as they can be

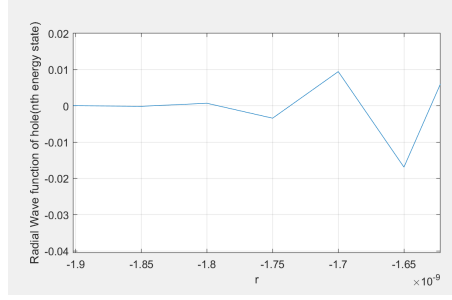


Figure 9: Hole wave function ($radius_{core} = 1.75nm$ and $thickness_{shell} = 0.25nm$)

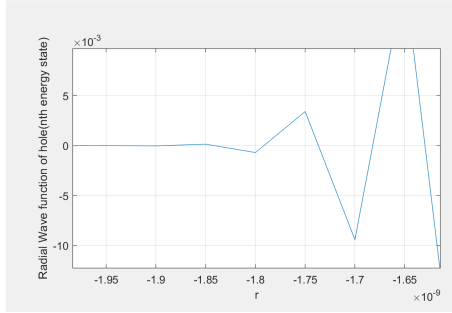


Figure 10: Hole wave function ($radius_{core} = 1.75nm$ and $thickness_{shell} = 1.5nm$)

used to calculate properties which have immense practical importance.

5 Applications in Solar Cell Efficiency

Solar Power is a renewable source of energy, which causes no pollution. It has the potential of resolving the power crisis that we face today. Due to this silicon solar cells have been under research with objective of improving their efficiency.

5.1 Problem with Solar Cells

The light from the Sun which is able to penetrate the environment and reach Earth has a spectrum which extends from IR to UV. One of the problem with Solar Cells is that common materials used to make solar cells can not absorb radiation from the whole spectrum. Only those photons which have greater energy than the band gap of the material are absorbed, the photons which have much greater energy are not able to produce excitons and end up contributing to the thermalization of the material, which further leads to the loss of energy.

5.2 Solution: Quantum Dots

As we can control the wave functions of QDs by changing the thickness of the core and shell , we can control the absorption energy which can be utilized in increasing the efficiency of the solar cells

Quantum Dots are used in order to use the whole spectrum of the Solar light. The up

conversion QD's are used for the low energy photons and the down conversion QD's are used for the high energy photons.

6 Conclusion

In the present work we explored a simple chemical route to prepare CdSe/CdS core-shell QDs, we further studied the properties and structure of the synthesised QD's using HRTEM and XRD. It was observed that the average size of the QD is 3nm. The second part of the report was about mathematical analysis of the Excitons in the QD. The radius of the core was taken to be 1.75 nm and the radius of the shell was varied from 0.25-3.25nm. As the thickness of the shell is increased we find that the RDF of the hole moves from core to shell. This change in spatial distribution leads to change in different properties and the type 1 exciton becomes type 2 excitons. Apart from these two types of excitons we also observe pseudo type 2 exciton which show dual absorption. Finally we see how the production of exciton in the QD can be used to modify the Solar Cell and how this leads to more Current and Voltage generated from the Solar Cell. This resolves the problem that normal Solar Cells face by increasing the bandwidth of the spectrum of Sun light which can be absorbed by the Solar Cell.

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References