ABSTRACT

Recent detection of excitonium has generated interest in excitons that are reigning photonic material science since last 50 years. In low dimension materials such as quantum dots, rods or sheets, the sizes are of few exciton radii in three, two and one axes respectively, and exciton binding is greatly influenced by such a confining potential on the boundary at which the crystalline order suddenly changes or vanishes. The size resolved binding energy of exciton in semiconducting Cadmium Selenide is here taken as a marker of the onset of nanophase, and calculations are reported using available data on quantum confinement.

Key words: nanophase, quantum dot, exciton, exciton binding energy, quantum confinement.


1. INTRODUCTION

Recently Prof Peter Abbamonte with physics research group at Illinois, the University of California (Berkley) announced the discovery of a new form of matter known as excitonium. This material is made up of a kind of boson, a composite particle of zero or integral spin that leads to phases of a superfluid, superconductor and an insulating electronic crystal [1]. Though it is a different development from exciton formation in semiconductors, Peierls phases and exciton condensation share the same symmetry and similar observables a super lattice and the opening of a single-particle energy gap. The content of excitonium is exciton, yet alive in material science. We may put it in the way that excitonium is a condensate made
up of excitons, a quirky quantum-mechanical pairing of electron and hole where the hole acts like a positively charged particle, attracting the electron.

The first appearance of exciton dates back to the late 1920s, when a narrow photoemission lines were observed in the spectra of organic molecular crystals by A. Kronenberger and P. Pringsheim and I. Obreimov and W. de Haas and interpreted by the Russian theorist Yakov Frenkel, who introduced excitation waves in crystals in 1931, and “exciton” in 1936 [2-5].

An exciton in organic molecular crystals was a Coulomb-correlated electron-hole pair belonging to the same crystal cell with the crystal potential acting as a perturbation to the Coulomb interaction. The binding energy of this later on called ‘Frenkel exciton’ is the energy of its ionisation to a non-correlated electron hole couple.

Excitons in semiconducting crystals came in the end of 1930s when Gregory Hugh Wannier and Sir Nevil Francis Mott observed that the rate of electron and hole hopping between different crystal cells much exceeds the strength of their Coulomb coupling with each other. The binding energy of these later on called Wannier-Mott excitons have values of hundredth of that for Frenkel excitons and their sizes of the order of tens of lattices constants [6-7] in bulk. These resemble hydrogen atom but have larger radii, finite life times and different binding energies.

Since 1980s onwards, nanotechnology and nanoscience have invented smart materials in nanometer range of sizes that are quite different from bulk ones [8-10]. The band engineering by means of the high-precision growth methods allows the creation of a number of electronic and optoelectronic devices. There have been found new fundamental effects in nanomaterials, like the integer and fractional quantum Hall effects, Coulomb blockade, light-induced ferromagnetism, etc.

The large size of Wannier-Mott excitons as in bulk semiconductors makes them strongly sensitive to nanometer-scale variations of the band edges positions due to miniaturization of host sizes. The energy spectrum and wave-functions of quantum confined excitons can be strongly different from those of bulk excitons. The study of Wannier-Mott excitons in such confined systems as quantum wells, quantum wires and quantum dots whose sizes are a few Bohr excitonic radius, has attracted scientists worldwide. In this communication we compute size dependence of excitonic binding energy in CdSe semiconductor and show how only having a nanometer size is not sufficient for particulate to be taken as smart materials.

2. THEORY
The Wannier-Mott excitons in semiconductor structures can be conveniently described within the effective mass approximation which incorporates effect of the periodic crystal potential into effective masses in the band, and allows a free particle description having a parabolic dispersion dependent on the crystal material. It is further modified by coulomb interaction energy in medium and quantum confinement energy.

The electron-hole pair motion and Coulomb interaction in a crystal having a relative permittivity \( \varepsilon_r \) may be described by a radial wave-function of relative electron-hole motion satisfying the Schrödinger equation as for the electron-hole state in a hydrogen atom type Hamiltonian:

\[
H = \left[ -\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r} \right]
\]
Here the exciton reduced mass is \( \mu = \frac{m_e m_h}{m_e + m_h} \) with the used masses themselves being the effective ones of the electron and the hole in the band, forming the exciton. The Hamiltonian takes care of central Coulomb potential energy and kinetic energy. The solution wave-function of the 1s-state of exciton with energy eigen value and the dielectric constant in the denominator, one can estimate that the exciton binding energy in semiconductor.

In smart materials, however, confinement of exciton leads to modification in the value so obtained. The quantum size effects in semiconductor QD greatly influence the states of the correlated electron-hole pairs (excitons) that are present in QD even at room temperature, and lead to important changes in the optical properties of QDs as compared to those of the corresponding bulk materials; the transitions between Wannier excitonic states are linked to those changes [11–14].

The range of spatial confinement is best described through the Bohr radius of exciton in the material. In the case of 3D confinement, the minimum energy to create an exciton (electron-hole pair) in a semiconductor particulate of size \( r \) is given, in SI units, as below [15, 16]:

\[
E_{\text{min}} = E_g + \Delta E_{\text{con}} - \frac{f e^2}{4\pi \varepsilon_0 \varepsilon_r r}
\]

The value of the second term is given by

\[
\Delta E_{\text{con}} = \frac{\hbar^2 \pi^2}{2\mu r^2}
\]

Here \( E_g \) is the band gap of the bulk semiconductor and \( \Delta E_{\text{con}} \) is the separation of energy level caused by size confinement; \( \varepsilon_0 \) and \( \varepsilon_r \) are the permittivity of vacuum and the relative permittivity of the material. In this formula, the second energy term is due to size confinement and the third term represents energy due to Coulomb attraction between electron and holes in semiconducting medium of nanoparticle.

![Exciton states in nanoparticle](http://www.iaeme.com/IJARET/index.asp)
3. CALCULATIONS

Semiconductor nanocrystals when subjected to band gap excitation undergo charge separation in s and p levels represented in CdSe nanocrystals as

\[ \text{CdSe} + h\nu \rightarrow \text{CdSe} (e_p + h_p) + \text{CdSe} (e_s + h_s) \]

Their recombination is called exciton decay and is represented, for s kind, and similarly for p kind, as

\[ \text{CdSe} (es + hs) \rightarrow \text{CdSe} + h\nu \]

Resulting spectral frequency in ground state transition is informer of binding energy. Here a calculation is done for variation in binding energy with size particle. Using data of band gap [17], dielectric constant and effective masses of hole and electron [18], we have

\[ E_{\text{min}} = E_g + \frac{a}{\mu r^2} - \frac{b}{\varepsilon_r r} \]

Here \( a \) and \( b \) are constant appearing in the formulation, for \( f=1.8 \), with values

\[ a = 5.493 \times 10^{-68} \text{J}^2 \text{s}^2 \]
\[ b = 4.158 \times 10^{-29} \text{J} \]

Bulk CdSe is hexagonal Wurtzite structure with in-plane lattice constants 43 nm and out-of-plane 70.1 nm. The exciton Bohr radius in this system is 550 nm with a binding energy of 12 meV and high frequency dielectric constant 6.25. The spin–orbit coupling energy is 0.42 eV. Thus, in CdSe, the first term is 6.2 eV, the second term is \( 3.890/r^2 \text{ eV nm}^2 \) (figure 2) and the third term is \( -0.2304/r \text{ eV nm} \) (figure 3). The exciton ground state energy is \( E_b \) less than \( E_g \). This gives the binding energy in eV for \( r \) in nm for CdSe-QD. Effective mass of electron used is 0.13 times electron rest mass and that of hole is 0.38 times [18]. The value of reduced mass turns out to be 0.097 times the rest mass of electron.

The first term is bulk band gap. The second term is confinement energy shown in eV as a function of size in nm in figure 2.

![Figure 2](http://www.iaeme.com/IJARET/index.asp)  

**Figure 2** Confinement energy of exciton

The third term is plotted in figure 3. Its significance lies in indicating the sources of binding energy of exciton:

\[ E_{\text{cout}} = -\frac{0.2304 (\text{eV nm})}{r (\text{nm})} \]
Quantum Dot Confined CDSE Semiconductor

**Figure 3** Size resolved Coulomb interaction in nanoparticle

Figure 4 shows the minimum exciton energy (in eV), at various sizes (in nm) of nanoparticle which exhibits a dip of function minimum of 6.195 eV. This is 5 meV below the bulk value of band gap.

**Figure 4** Size-resolved exciton minimum energy

Figure 5 shows the surface plot of minimum exciton energy against the bulk band gap and size. The band gap changes are usual in strained crystals, for instance, due to applied hydrostatic pressures.

**Figure 5** $E_{\text{mid}}(E_g, r)$ surface in CdSe semiconductor
4. RESULT AND DISCUSSION

There are two competing contribution to minimum energy of exciton in nanosizes of Cadmium Selenide considered in the work, confinement of exciton to leading to level splitting and new band gap and Coulomb interaction in dielectric medium. The energy of confinement is a positive contribution and the Coulomb term is a negative one to the ground state exciton, both increasing in moduli as the particulate size decreases.

The dominance of confinement can be analyzed with sizes in the plots shown. The confinement energy, for example, is 79 meV at a size of 7 nm, while the Coulombic contribution at the same size is about -33 meV. At a size of 3nm, the confinement energy is 432 meV against the Coulomb interaction energy of only -76 meV. Confinement and Coulomb energies add together to vanish at 16 nm which size belongs to an intermediate confinement region. A grading is possible on the scale of size in units of Bohr radius (4.9 nm for CdSe). Strong confinement is observed below 16 nm size which is about thrice the Bohr radius. If the size of particulate be 1 nm, 2nm, 4 nm, 8nm, etc., the exciton binding energy has respective values of 230 meV, 115 meV, 57.5 meV, 29 meV, etc. the binding energy rises sharply in strong confinement region.

In some cases of strained materials, the bulk band gap is modulated. Its effect on ground state exciton energy may be viewed in the figure 5.

5. CONCLUSIONS

The bulk cadmium Selenide has a binding energy of exciton less than 14 meV. As the size is reduced, it starts increasing at a size of weak interaction greater than 16 nm. Strong confinement is observed by steep rise in exciton binding energy below the size of 16 nm which is about three excitonic radii. There is a steep increment in band gap also in the region of strong confinement in quantum dot sizes.

REFERENCES

Quantum Dot Confined CDSE Semiconductor


