Lab Week 1 – Module γ₃

Materials as "particle in a box" models:
Synthesis & optical study of CdSe quantum dots

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OBJECTIVES

- ✓ Introduce the particle-wave duality principle
- ✓ Introduce the concept of quantum mechanical particles
- ✓ Electrons/photons interactions
- ✓ Introduce quantization and "particles in a box"
- ✓ Study the relationship between nanoparticle size and optical properties of CdSe quantum dots
- ✓ Gain experience in wet chemical synthesis and optical characterization methods

Questions

At the end of this laboratory experience you should be able to answer the following questions:

1) What is the concept of "box" in quantum mechanics?

2) Why an electron in a box can appear as a colored object?

3) Why the size of a CdSe nanoparticle can determine the optical properties of such a particle?.

From 3.012
Notes

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Photos of light absorption and emission, from MIT labs of Prof. Mayes, Stellacci and Bawendi.

BACKGROUND

Particle in a box: a way for visualizing quantum mechanics

One of the most immediate consequences of the physical principles of quantum mechanics is the presence of discrete energy levels in real systems.

The goal of modules β1, β2, and β3 is to provide students with a visual proof of this event, in order to make the understanding of the coming lectures in 3.012 easier.

Let us first refresh some key concepts of modern physics:

Particle Wave duality
Every physical entity behaves at the same time as a particle and as a wave.
Thus one has to describe physical objects as particle and waves at the same time.

Light for example can be described as a wave or as a flux of particles called photons. Photons are particles whose energy can be directly related to their wave properties via the relation $E = h\upsilon = \dfrac{hc}{\lambda}$, where $h = 6.626184$ Js is the Planck constant; and υ is the oscillation frequency, while λ is the wavelength.

One concept to keep in mind in order to understand the following discussion is that photons interact with other particles is a very peculiar way, in fact these particle appear (via an emission mechanism) and disappear (via an absorption mechanism) commonly. In particular, the interaction of a photon with an electron leads to the disappearance of the photon and to an energy gain for the electron that equals the energy of the photon that disappeared. Similarly photons can "appear" when a particle loses energy.

Because of this property we can use photons as very simple and versatile means of providing energy to other particles.

Because of this property we can use photons as very simple and versatile means of providing energy to other particles. In particular photon-electrons interactions are the cause of colors in materials.
Color theory is a complex science, indeed the color of a material is determined by the various types of interactions that photon and electron have (absorption, reflection, scattering, non-linear absorption and conversion, and emission). In this lab we will try to understand the two main forms of interactions (that happen to be the easiest to understand ☺) absorption and emission.

Absorption is the disappearance of a photon of a given energy (i.e. color) with the simultaneous gain of the same amount of energy for one electron in a material. The probability of this event is called the absorption cross section.

Emission is the appearance of a photon of a given energy (i.e. color) with the simultaneous loss of the same amount of energy for one electron in a material. The probability of this event is called the emission (or fluorescence) quantum yield.

In order for both these phenomena to happen the electron need has to be able to "exist" in two different states whose energy difference equals the energy of the absorbed/emitted photons.

(This may sound complex, but it is not, also is really nice to see, I promise!)

Particle in an infinite well
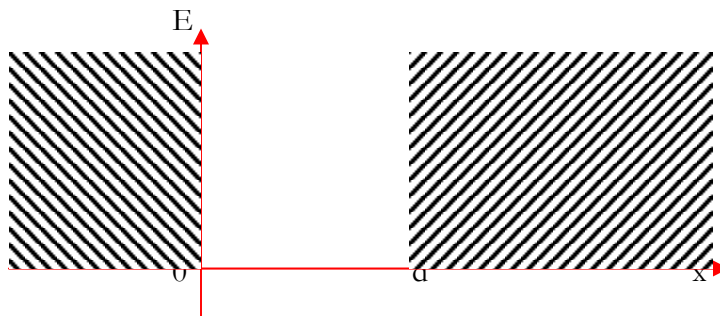
Let us consider now a particle confined in one dimension (x) in between two infinite energy barriers. A physical way of representing such situation is to define a potential

$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 < x < d \\ \infty & x > d \end{cases}$$

(in any potential the origin can be chosen freely, thus the 0 value of V in the region where the particle is confined was chosen for the sake of making the calculation easier. Any other number would be equally acceptable, leading to the same results.)

A particle (in this specific case an electron) is described by its wavefunction $\psi(\mathbf{r}, t)$, a function defined in all places in space ($\mathbf{r}$) and time (t). The values of this function are complex numbers and are related to the probability of finding that particle in that given position of space ($\mathbf{r}$) at that given time t.

In our case we will concentrate on a one dimensional problem, thus we will substitute $\mathbf{r}$ with x, moreover we will assume that the wavefunction can be divided in two parts one that depends on time but not on space and the other that depends on space and not time, $\psi(x,t) = \varphi(x)\xi(t)$

In this case the spatially varying part of the equation has to obey the time independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\varphi(\mathbf{r})+V(\mathbf{r})\varphi(\mathbf{r})=E\varphi(\mathbf{r}) \ \ in \ 3 \ D$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial^2 x}\varphi(x)+V(x)\varphi(x)=E\varphi(x) \ \ in \ 1 \ D$$

where $\hbar=\dfrac{h}{2\pi}$, V is the potential energy of the system and E is the total energy of the particle.

The existence, for $x>d$ and $x<0$, of an infinite potential (i.e. a very large barrier) prevents the particle from ever being in those regions of space. Being the wavefunction a measure of the probability of finding the particle in a region of space, we have to impose $\varphi(x)=0$ for $x>d$ and $x<0$.

For 0<x<d the time independent Schrödinger equation becomes (being V(x)=0)

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial^2 x}\varphi(x)=E\varphi(x)$$

This is a classical wave equation whose general solution is
$\varphi\left(x\right)=\ Ae^{\ ikx}\ +\ Be^{\ -ikx}$ with A and B being complex number.

In order to prove that this is the correct solution and to find the possible values of k it is enough to substitute this function back in the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial^2 x}\left(Ae^{ikx}+Be^{-ikx}\right)=E\left(Ae^{ikx}+Be^{-ikx}\right) \ ---> \ \frac{\hbar^2 k^2}{2m}\left(Ae^{ikx}+Be^{-ikx}\right)=E\left(Ae^{ikx}+Be^{-ikx}\right)$$

$$\frac{\hbar^2 k^2}{2m}=E$$

To summarize, by simply looking at the potential we have defined the wavefunction as:

$$\varphi(x)=\begin{cases} 0 & x<0 \\ Ae^{ikx}+Be^{-ikx} & 0<x<d \\ 0 & x>d \end{cases}$$

This result just states that a particle cannot be outside insurmountable walls. Even in the classical case this would be true.

One of the key properties of wave functions in that they are continuous, thus we have to impose that $\varphi(0)=\varphi(d)=0$.

This means that: $\varphi(0)=A+B=0 \ --> \ A=-B$ thus $\varphi(x)=2iA\sin(kx)$

Similarly, $\varphi(d) = 2iA\sin(kd) = 0$. This second equation is true **only** for certain values of k, specifically $k = \dfrac{n\pi}{d}$.

By using these values of k in the expression of the total energy of the system we have:

$$E = \frac{\hbar^2 n^2 \pi^2}{2md^2}$$

Thus the only energy values that this particle can have are the ones expressed in the equation above.

The main consequences are that (1) the particle cannot have zero energy, (2) the particle can have only discrete states.

Table 1 First 10 energy levels for a particle in a infinite well of varying width. The mass on the electron used to compute these values was: 9.10953 10^{-31} Kg.

| Quantum number		Energy (E)					
n	d (Å)=	2	6	10	14	18	22
	1	9.400836866	1.044537	0.376033	0.191854	0.11606	0.077693
	2	37.60334747	4.17815	1.504134	0.767415	0.464239	0.310771
	3	84.6075318	9.400837	3.384301	1.726684	1.044537	0.699236
	4	150.4133899	16.7126	6.016536	3.069661	1.856955	1.243086
	5	235.0209217	26.11344	9.400837	4.796345	2.901493	1.942322
	6	338.4301272	37.60335	13.53721	6.906737	4.17815	2.796943
	7	460.6410064	51.18233	18.42564	9.400837	5.686926	3.80695
	8	601.6535594	66.8504	24.06614	12.27864	7.427822	4.972343
	9	761.4677862	84.60753	30.45871	15.54016	9.400837	6.293122
	10	940.0836866	104.4537	37.60335	19.18538	11.60597	7.769287
ΔE_{2-1}	eV	28.2025106	3.133612	1.1281	0.575561	0.348179	0.233079
	nm	43.96246379	395.6622	1099.062	2154.161	3560.96	5319.458

If the electron in the well would be considered as a particle in a classical way then any photon that would interact with the electron would be absorbed. In reality the electron is also a wave and thus it can have only specific energies. As a consequence the electron can interact with a photon (absorbing it) only if the energy of such photon equals the energy difference between the state the electron is in (typically n=1) and one of the other states of the system.

Quantum Dots

Quantum dots are semiconductor nanocrystals having dimensions typically between ~1-10 nm [1-7]. Because of their very small size, quantum dots exhibit different optoelectronic behavior than bulk semiconductors of the same composition. In particular, the confined dimensions result in a quantization of the bulk electronic bands and a widening of the gap (called a blue shift) between the valence band and conduction band, which is size dependent.   Thus a quantum dot can be seen in analogy to the "particle in a box" model above (or "particle in a sphere" model), where ΔE_{2-1} increases with decreasing d.

Bulk   **Quantum well**   **Quantum wire**   **Quantum dot**

10 – 100 Å
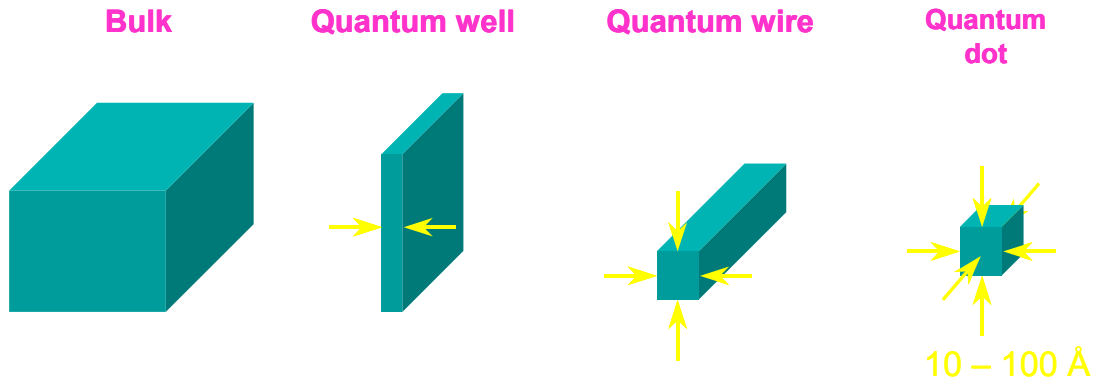
The practical consequence of quantized energy states in semiconductor nanocrystals is seen when light interacts with these materials to create excitons, or electron-hole pairs. When an exciton is created, it has a natural associated length scale, called the exciton Bohr radius, due to the electron-hole Coulombic attraction [1,3,7]. The length scale is defined through the electron and hole wave functions, which give the probability of finding an electron/hole at a given position. Quantum confinement occurs when the nanocrystal dimensions are smaller than the exciton Bohr radius (about 5.6 nm for CdSe) [1].
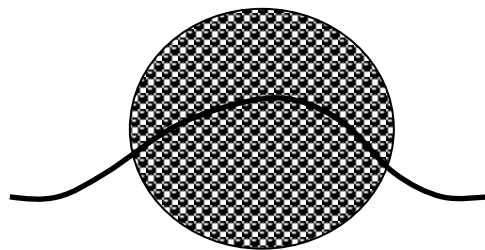
As a consequence, absorption/excitation occurs for specific discrete values of the incident photon energy. Upon relaxation of the excited state through electron-hole recombination, the emitted photons also exhibit well-defined energies. Note that the emission peaks occur at slightly lower energy compared to the absorption peak (also known as a red shift).

Graph removed for copyright reasons.

ZnSe quantum dots absorption and emission spectra. C.A. Smith, H.W.H. Lee, V.J. Leppert, S.H. Risbud, Applied Physics Letters **75**, 1659 (1999).

Because of their narrow, intense fluorescence spectra which are tunable though size, there is strong technological interest in quantum dots for optoelectronic applications. For example, one area of strong R&D is quantum dot fluorescent labels/tags for biological assays and sensors, to replace fluorescent organic molecules [4]. High quality QDs exhibit less nonradiative decay than organic dyes, providing higher fluorescence quantum efficiency. QD efficiency is higher than bulk semiconductors as well, due to the localization of electron-hole pairs imposed by the QD surface.

The quality (intensity and sharpness) of the fluorescence spectra from quantum dots is affected by a number of variables:

- Size
- Size distribution
- Phase/chemistry
- Interparticle distance
- Surface termination

CdSe Dots

CdSe is a II-VI semiconductor with a bulk band gap of ~1.7 eV, with a corresponding emission of λ=760 nm. For CdSe quantum dots, emission wavelengths can range from 450-650 nm, depending upon size, covering much of the visible spectrum range. CdSe nanocrystals form in the hexagonal wurtzite structure, which exhibits four-fold coordination for both Cd and Se atoms [8]. CdSe can also form in the zinc blende structure, a variant of the diamond cubic structure, which also has four-fold coordination.
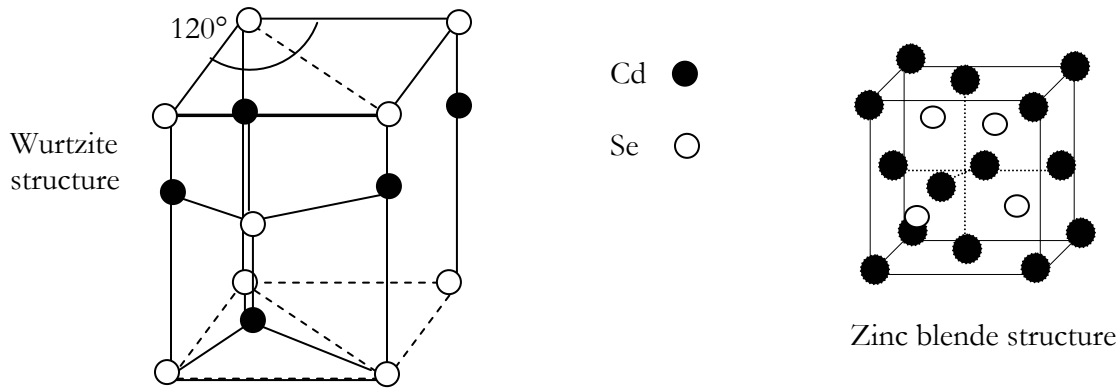
In CdSe, the Cd 5s orbitals constitute the LUMO, while Se 4p orbitals constitute the HOMO. The first excited hole-electron pair for CdSe has been identified as the $1S_{3/2}1S_e$ [1,3]. Other discrete transitions are also sometimes observable in the absorbance spectra for CdSe nanocrystals. CdSe nanocrystals tend to be prolate spheres, with an aspect ratio of 1.1-1.3, where the long axis corresponds to the c-axis of the wurtzite structure [7].

SYNTHESIS OUTLINE

The synthesis procedure, adapted from M. Bawendi's group, requires the preparation of three separate solutions which are ultimately combined to nucleate and grow the CdSe nanoparticles.

Reagents and Solvents

Cd(OH): source of Cd. This precursor is safer (less toxic) than $Cd(CH_3)_2$ compound often used in the archival literature [6].

Oleic acid: acts as a surfactant. [2,6], stabilizing the dispersion

Trioctylphosphine: $(CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2)_3P$ A coordinating solvent for Se that stabilizes the nanoparticles against flocculation during synthesis. After synthesis TOP coats the nanoparticles, providing electronic insulation and passivating the nanoparticle surface [3,5].

elemental Se: source of Se

Squalene (shark oil): a viscous, noncoordinating, high boiling point solvent [2].

Oleylamine: acts as a surfactant [5].

Solution Preparation and Reaction

First Solution: The reaction medium

A mixture of 5 ml of squalene, 8 ml of oleylamine 8 ml and 3.5 ml of TOP is prepared in a 3-neck round bottom flask. After sealing the flask, the solution is degassed with nitrogen while heating to 360^0C.

Second solution: Cadmium containing solution

150 mg of Cd(OH) – 1 mmol—are dissolved in 2 millimoles (0.64 ml) of Oleic acid and 3.4 ml of trioctylphosphine (TOP). Dispersion is heated to 100C and degassed for 1h.

Third solution: Se containing solution

This solution has been pre-prepared in a glove box by Johnatan Steckel in the group of Prof. Moungi Bawendi. It was prepared by dissolving 11.8 mg of elemental Se in 100 ml of TOP.

Once the first reaction reaches 360^0C, add 6 ml of the third solution are added to the second solution, then this mixture is rapidly injected to the entire mixture into the 1st solution reaction flask. The reaction vessel is then quickly removed from its heat source and allowed to cool at room temperature.

REFERENCES

1. M. Nirmal and L. Brus, "Luminescence photophysics in semiconductor nanocrystals", *Acc. Chem. Res*. **32**, 407-414 (1999).

2. W.W. Yu and X. Peng, "Formation of high-quality CdS and other II-VI semiconductor nanocrystals in noncoordinating solvents: tunable reactivity of monomers*", Angew. Chem. Int. Ed*. **41**, 2368-2371 (2002).

3. D.J. Norris and M.G. Bawendi, "Measurement and assignment of the size-dependent optical spectrum in CdSe quantum dots", *Phys. Rev. B* **53**, 16338-16346 (1996).

4. M. Bruchez et al., "Semiconductor nanocrystals as fluorescent biological labels", *Science* **281**, 2013-2016 (1998).

5. C.B. Murray, C.R. Kagan and M.G. Bawendi, "Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies", *Annu. Rev. Mat. Sci*. **30**, 545-610 (2000).

6. L. Qu, Z.A. Peng and X. Peng, "Alternative routes to high quality CdSe nanocrystals", *Nanoletters* **1**, 333-337 (2001).

7. D.J. Norris, A.L. Efros, M. Rosen and M.G. Bawendi, "Size dependence of exciton fine structure in CdSe quantum dots", *Phys. Rev. B* **53**, 16347-16354 (1996).

8. Y.-M. Chiang, D.P. Birnie, and W.D. Kingery, *Physical Ceramics: Principles for Ceramic Science and Engineering*, John Wiley & Sons: New York, 1997, pp.80-91.