Quantum Dots

1 Part 1: Quantum Dot Size and Emission Wavelength - The Particle-in-a-Box Model

1.1 Theoretical Foundation

Quantum dots are semiconductor nanocrystals that exhibit quantum confinement effects when their size approaches the exciton Bohr radius of the material. This confinement fundamentally alters their electronic properties compared to bulk semiconductors. To understand how the size of quantum dots affects their emission wavelength, we can apply the quantum mechanical "particle-in-a-box" model.

In this model, we consider an electron confined to a potential well with infinitely high walls. The confinement of the electron in this potential well leads to the quantization of energy levels, which directly influences the wavelength of emitted light when an electron transitions from a higher energy state to a lower one.

1.2 Mathematical Derivation

For a three-dimensional cubic quantum dot with side length L, the time-independent Schrödinger equation for an electron confined within the dot can be written as:

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{1}$$

Where:

- $\hbar$ is the reduced Planck's constant (1.054×10^{-34} J $\cdot$ s)
- m_e is the effective mass of the electron in the semiconductor material
- ∇^2 is the Laplacian operator ($\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$)
- $\psi(\mathbf{r})$ is the electron wavefunction
- E is the energy eigenvalue

With boundary conditions:

- $\psi(0, y, z) = \psi(L, y, z) = 0$

- $\psi(x, 0, z) = \psi(x, L, z) = 0$
- $\psi(x, y, 0) = \psi(x, y, L) = 0$

The solution to this equation gives us the energy eigenvalues:

$$E_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2m_eL^2}(n_x^2 + n_y^2 + n_z^2) \tag{2}$$

Where n_x, n_y, and n_z are positive integers representing quantum numbers.

For simplicity, if we consider a spherical quantum dot with radius R, the energy levels can be approximated as:

$$E_n \approx \frac{\hbar^2\pi^2n^2}{2m_eR^2} \tag{3}$$

Where n is a positive integer representing the principal quantum number.

Key Insight

Key Insight: Equation (3) reveals the critical inverse square relationship between quantum dot size and energy levels. As the radius R decreases, the energy E_n increases by a factor of $1/R^2$.

1.3 Band Gap and Emission Wavelength

In semiconductor quantum dots, the emission wavelength is primarily determined by the band gap energy (E_g), which is the energy difference between the conduction band minimum and the valence band maximum. When an electron-hole pair (exciton) recombines, a photon with energy approximately equal to the band gap is emitted.

The band gap energy of a quantum dot can be expressed as:

$$E_g(\text{QD}) = E_g(\text{bulk}) + \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0R} \tag{4}$$

Where:

- $E_g(\text{bulk})$ is the band gap energy of the bulk semiconductor material
- m_e and m_h are the effective masses of the electron and hole, respectively
- e is the elementary charge (1.602×10^{-19} C)
- ε is the dielectric constant of the semiconductor
- ε_0 is the vacuum permittivity (8.85×10^{-12} F/m)
- R is the radius of the quantum dot

The second term represents the quantum confinement energy, which increases as the size of the quantum dot decreases. The third term accounts for the Coulomb interaction between the electron and hole.

The wavelength of the emitted light (λ) is related to the band gap energy by:

$$\lambda = \frac{hc}{E_g(\text{QD})} \tag{5}$$

Where:

- h is Planck's constant ($6.626 \times 10^{-34}\,\text{J}\cdot\text{s}$)
- c is the speed of light ($3.00 \times 10^{8}\,\text{m/s}$)

1.4 Size-Dependent Emission: Practical Implications

From the equations above, we can derive a crucial relationship: as the size (R) of the quantum dot decreases, the band gap energy increases, resulting in a blue shift in the emission wavelength. Conversely, larger quantum dots emit light at longer wavelengths (red shift).

Quantum Dot Diameter	**Emission Color**	**Wavelength Range**
2-3 nm	Blue	450-495 nm
3-4 nm	Green	495-570 nm
5-6 nm	Red	620-750 nm

Table 1: Relationship between CdSe quantum dot size and emission properties

Key Insight

Size-Tunable Emission: The relationship $\lambda \propto R^2$ means that by precisely controlling the quantum dot radius during synthesis, manufacturers can tune the emission wavelength across the entire visible spectrum without changing the chemical composition.