OPTICAL PROPERTIES OF QUANTUM DOTS

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Abstract

Quantum dots are nanometer-sized particles composed of a heavy metal core, such as cadmium selenium or cadmium telluride with an intermediate unreactive zinc sulfide shell and a customized outer coating of different bioactive molecules tailored to a specific application. The composition and very small size of quantum dots gives them unique and very stable fluorescent optical properties that are readily tunable by changing their physical composition or size. Quantum dots can emit light if excited, the smaller the dot, the higher the energy of the emitted light. This ability to create dots that emit a rainbow of colors suggest that they could be used as biosensors. Unlike the dyes currently being used as biosensors, quantum dots do not degrade as rapidly.

Kye words: quantum dot, band-gap energy, Stokes shift, photoluminisens, life time, quantum yield, photobleaching, autofluoresense

Intoduction

Quantum dots (QDs) are nanoparticles that are restricted in three dimensions to a somewhat spherical shape, typically with a diameter of 2-8 nm. Particles consist of a few handred to a few thausand atoms. Because of theit small size, quantum dots display uniqe optical and electrical properties. These particles behave like atoms and we call them artificial atoms. QDs are characterized by compozition-dependent band gap energy; the band gap energy is dependent on a size of nanoparticle. Special optical properties: wide Stokes shift, high brightness, long time of fluorescence, resistance of photobleaching and tunable wavelenght. These properties of QDs have attracted great interest in biology and medicine in recent years.

The band-gap energy

Small size of semiconductor material of the quantum dot behaves differentlly from other forms of semiconductors. In a bulk semiconductor material the electrons will occupy multiple energy levels. These energy levels are so close that they are considered continuous. The small size of quantum dots lead to what is known as „quantum confinement“. This means that the energy levels that the electrons inhabit become discrete, with a finite separation between them. However, there are some energy levels that the electrons cannot occupy, collectively known as the band-gap (energy barrier) (Figure 1). The band- gap energy is the

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minimal energy required to exite an electron from its orbit to a higher level. As the electron relaxes and returns back to the ground orbit, a photon gets emitted, leading to a visible flourescence. Most electrons occupy energy levels below this band gap in the area known as the valence band, indeed most energy levels in the valence band are occupied. If, however, an external stimulus is applied, an electron may move from the valence band to the conduction band i.e. those energy levels above the band gap. The electron in the conductance band and the hole it has left in the valence band are collectively known as an exciton. Energy is then released in the form of electromagnetic radiation as the electron falls back across the band gap to the valence band. The wavelenghth of these photon emissions depends not on the material from which the dot is made but its size.

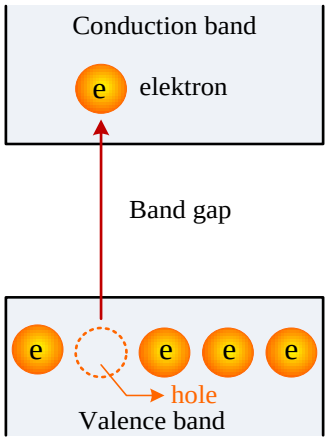


Figure 1. Band-gap energy

The total energy of quantm dot is sum of the band gap energy between occupied level and unoccupied energy level, confinement energies of the hole and the excited electron, and the bound energy of the exciton (Dey S. 2012):

$$E = E_{band\ gap} + E_{confinement} + E_{exciton}$$

The optical properties of quantum dots occur in part due to a quantum confinement. When a photon of sufficient energy strikes a quantum dot, it can excite an electron from the valence band to the conduction band, leaving a positive hole in its place. Generation of an electron-hole pair (exciton) is a common phenomenon in semiconducting materials; however, in a quantum dot, the average exciton size (the exciton Bohr radius[2]) is smaller than the size of the quantum dot, producing a confinement energy as the exciton is squeezed into the material (Melville J.2015). The magnitude of this confinement energy can be aptly modeled as a particle in a box:

$$E_{confinement} = \frac{\hbar^2\pi^2}{2d^2}\left(\frac{1}{m_e}+\frac{1}{m_h}\right) = \frac{\hbar^2\pi^2}{2\mu d^2}$$

m_e is the effective mass of the electron,
m_h is the effective mass of the hole,
μ is the reduced mass of the exciton system,
d is diameter of the confinement (Dey S. 2010).
Decreasing the size of a quantum dot results in a higher degree of confinement, which produces an excitin of higher energy, thereby increasing the bandgap energy.
Energy of exciton is an additional energy associated with the Coulombic attractive between the positive hole and negative electron of the exciton:

[2] Exciton Bohr radius is the average distance between the electron in the conduction band and the hole it leaves behind in the valence band

$$E_{exciton} = -\frac{1}{\varepsilon_r^2}\frac{\mu}{m_e}R_y$$

ε_r is the size-dependent dielectric constant of the semiconductor
R_y is the Rydberg energy.

$$E = E_{band\ gap} + \frac{\hbar^2\pi^2}{2\mu d^2} - \frac{1}{\varepsilon_r^2}\frac{\mu}{m_e}R_y$$

Size-Dependent Optical propertis

Quantum dots exhibit size-dependent discrete energy levels. The energy gap increases with decrease in the size of the nanocrystal, thus yielding a size-dependent rainbow of colors. The wavelenghth of the emission photon depends not on the material from which the dot is made but its size. The ability to control the size of quantum dot enables the manufacturer to determine the wavelenght of emission, which in turn determines the color of light the human eye perceives. The smaller the dot, closer its to the blue end of the spectrum and the large the dot, closer to the red. Light wavelengths from ultraviolet to infrared region (400-4 000nm) can be achived with variation of the size and composition of nanoparticles. The optical properties of QDs will change with proximity of quantum dots to each other (Figure 2,3).

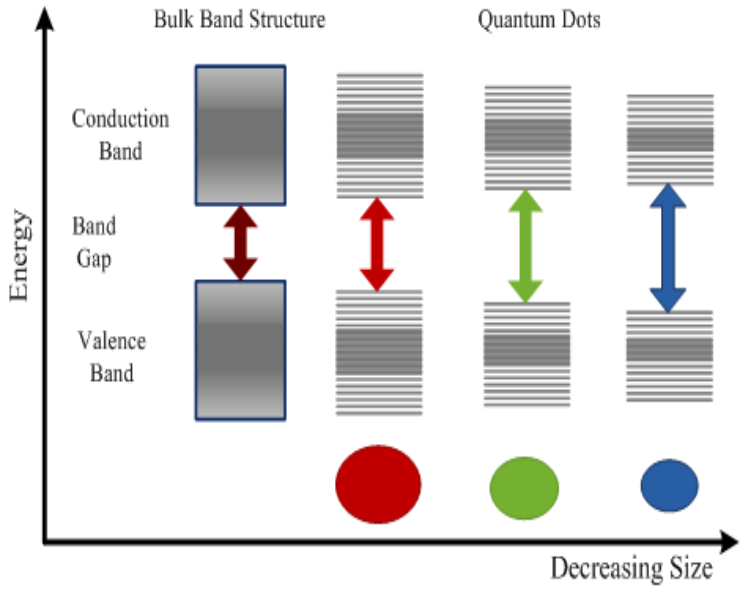


Figure 2. Size-dependent band-gap energy [1, 2]

Stokes shift. One of the most common features of quantum dots is the photoluminescence redshift relative to absorption also called Stokes shift.Named after Irish physicist George G. Stokes, Stokes shift is the difference between quantum dot's peak excitation and the peak emission wavelengths (Figure 4). The energy (wavelength) associated with emission is typically lower (higher) than the excitation light.

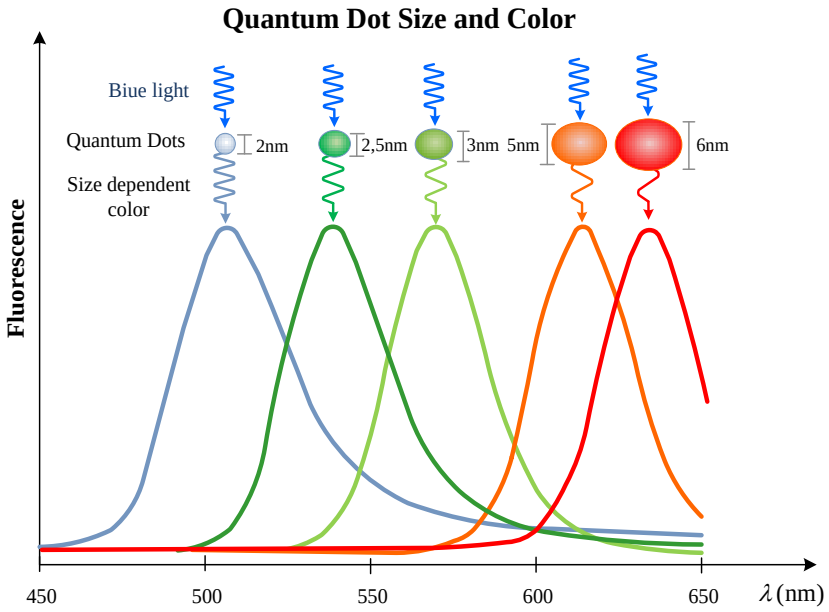


Figure 3. Quantum-dot size relates to emission wavelength.

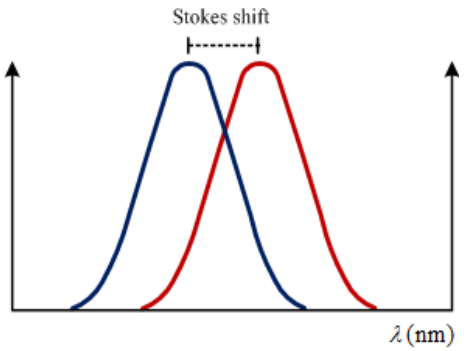


Figure 4. Stokes shift

The redshift of emission peaks with respect to absorption spectra is size dependence. Stokes shift is commonly observed in semiconductor quantum dots and is one of the most important quantities that determine the optical properties of QDs. The large separation between the excitation and emission spectra of the QDs improves the detection sensitivity as the entire emission spectra of QDs can be detected (Figure 5). As the radius of quantum dot increases the redshift decreases and disappears beyond a certain radius. The mechanism of Stokes shift in semiconductor quantum dots is investigated by calculating the energy of the excitonic states. We have taken intoaccount all possible contributions to the total electronic energy in the dot, i.e, dielectric mismatch between dot and surrounding medium, the effects of finite barrier height and electron-hole exchange interaction. The Stokes shift is calculated as a function of radius of dot and compared with experimental data on two different semiconductor based quantum dots. These results provide evidence for exchange splitting of excitonic states, as the mechanism of Stokes shift in quantum dot. Each quantum dot has specific singlet emission peak. With increasing crystal size from 2-3 to 10-12 nm the emission maximum shift from 500 to 800 nm. In addition, QDs have very broad apsorption spectra, and can be excited over the entire visual wavelenght range as well as far into ultraviolet.

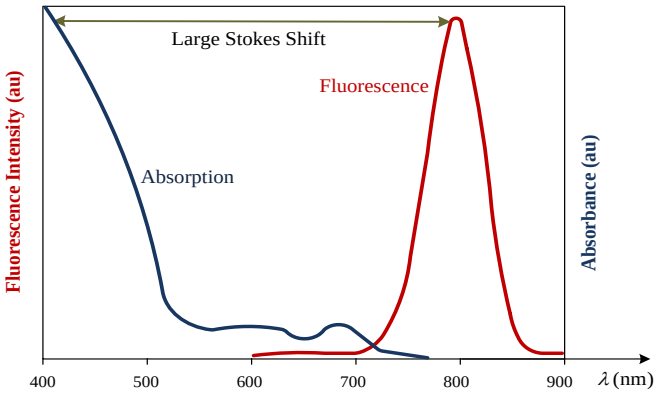


Figure 5. Broad absorption and narrow emission spectrum

Because of thair exceptionally large Stokes shifts (up to 400 nm) QDs can be used for the multicolor detection with a single wavelenth excitation sorce.

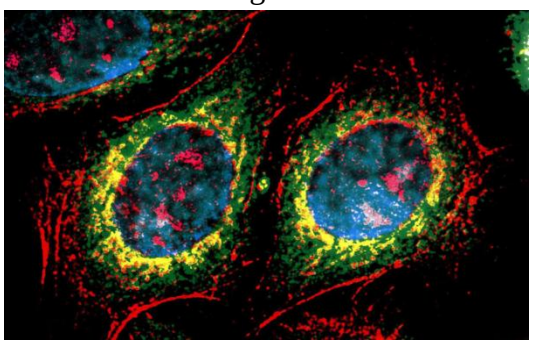


Figure 6. QDs allow simultaneous five-color imaging in fixed human epithelial cells

The mechanism of fluorescence

Fluorescent molecules, also called fluorophores or simply fluors, respond distinctly to light compared to other molecules. A photon of excitation light is absorbed by an electron of a fluorescent particle, which raises the energy level of the electron to an excited state. During this short excitation period, some of the energy is dissipated by molecular collisions or transferred to a proximal molecule, and then the remaining energy is emitted as a photon to relax the electron back to the ground state. Because the emitted photon usually carries less energy and therefore has a longer wavelength than the excitation photon, the emitted fluorescence can be distinguished from the excitation light. The excitation and photon emission from a fluorophore is cyclical, and until the fluorophore is irreversibly damaged (see Photobleaching; below), it can be repeatedly excited. Because fluorophores can therefore emit numerous photons through this cycle of excitation and emission, fluorescent molecules are used for a broad range of research applications.

Fluorescence intensity and lifetime

The lifetime characterizes a delay between the moment in which the QD absorbs a photon from the light sorce and moment of radiative recombination of the exciton (Figure 6).The lifetime of fluorescence is determined by the size of the quantum dot. Larger dots have more closely spaces energy levels in which the electron-hole pair can be trapped. Therefore, electron-hole pairs in larger dots live longer. Long lifetime provides difference of quantum dot fluorescence signal from background fluorescence. For example, QDs have a fluorescence lifetime of 20-30 ns about 10 times longer than the background autofluorescence of proteins. Fluorescence from single CdSe crystal has been observed much longer than from other fluorofores, resulting in high turnover rates and a large number of emitted photone (Figure 7).

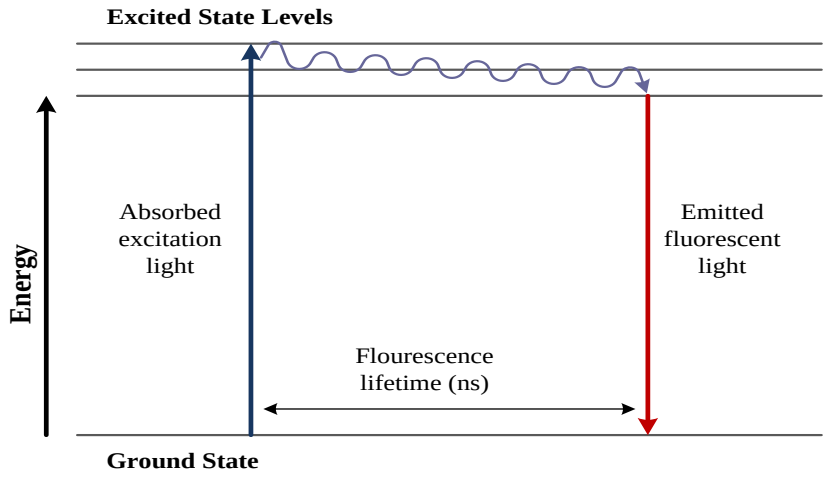


Figure 7. Fluorescence lifetime

Brightness and photostability. Minimizing overlap between total excitation and emission bands enhances the clarity and brightness of the fluorescing quantum dot by avoiding re-absorption of emitted light into nearby quantum dots - characteristics that display manufacturers and end-users find highly desirable (Figure 5). Broad absorption spectra make it possible to excite all quantum dots simultaneously with a single light source and minimize sample autofluorescence by choosing an appopriate excitation wavelenght. QDs have very large molar excitation coefficient in the order of 0.5-5· $10^6 M^{-1}$, about 10-50 times larger than that of organic dyes. QDs are able to absorb 10-50 times more photons than organic dyes at the same excitation photon flux, leading to a significant improvement in the probe brightness (Xing Y, R.Jianghong, 2008).Owing to their inorganic nature, QDs have minimal interaction with the surrounding environment which contributes to their photostability.

Quantum yield. Quantum yield is defined as the ratio of the number of photons emitted to the number of photons absorbed. Quantum dots are relatively efficient with regards to conversion of the excitation light into emission where the quantum yield is generally over 50%. For example, CdSe/ZnS quantum dots have quantum yields ranging from 40% to 80%.The fluorescence quantum yield gives the efficiency of the fluorescence process.

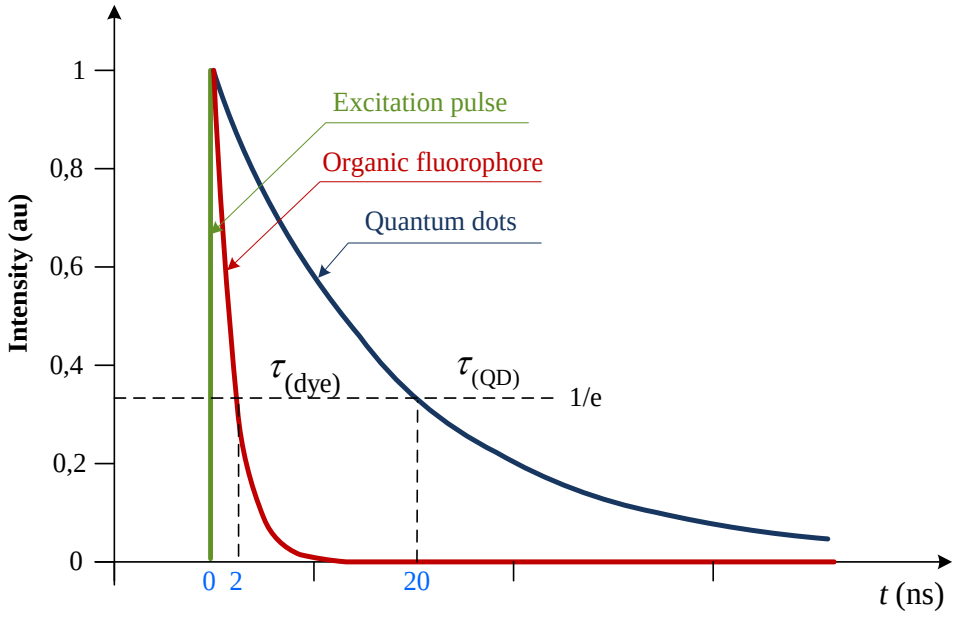


Figure 8. Fluorescence lifetime quantum dots and organic fluorophore

Photobleaching. Photobleaching (fading) is the photochemical alteration of a dye or a fluorophore molecule such that it permanently is unable to fluoresce. This is caused by cleaving of covalent bonds or non-specific reactions between the fluorophore and surrounding molecules. CdSe/ZnS quantum dot: 10^8 photons; τ > 1000 seconds (τ −lifetime) before destruction.Typical organic dye: 10^5-10^6 photons; 1-10 second lifetime.

Biomedical Application of Quantum Dots

In 1998, the potential of these nanoparticles for applications involving biological labeling was first reported (Alivisatos, 2004).The fact that several QDs can be excited by the same wavelength of light opens up several multiplexing potentials, including high-throughput screening of biological samples (Smith M, 2006). One additional feature of QDs is that they can emit in the infrared and near-infrared regions. Size tunable absorption and emission property of QDs is an extremely valuable property for biological imaging as they can be tuned all the way from the UV to the near-infrared of the spectrum.

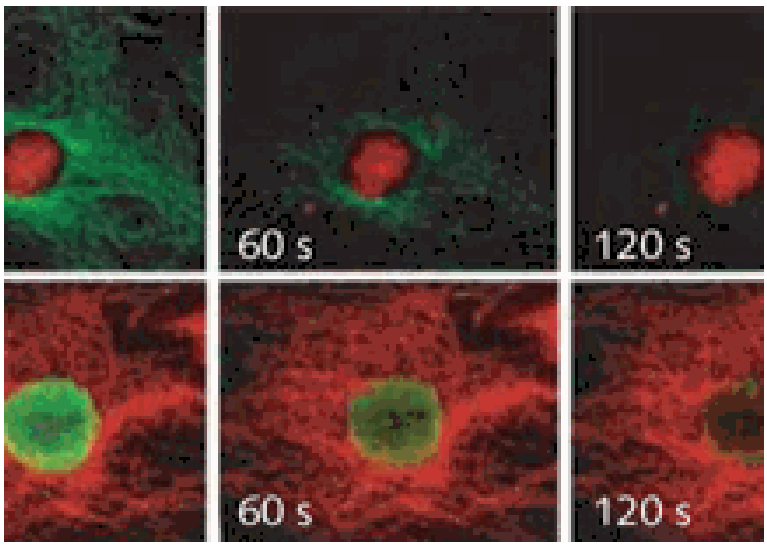


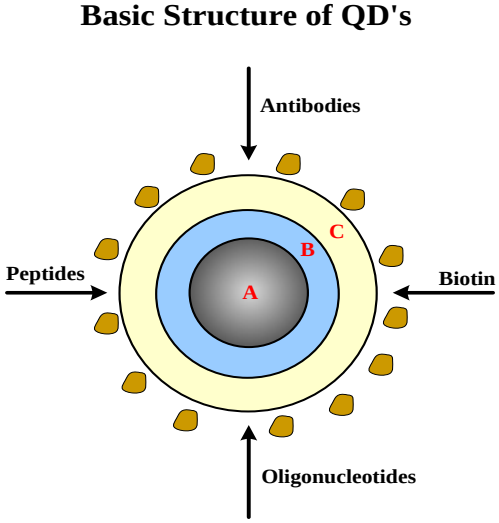
Figure 9. Photobleaching of quantum dot (red 605)

Organic dye molecule (Aleksa Fluor 488 green)

Smaller dots emit in the blue range and larger dots in the red and NIR region. QDs have a broad excitation and narrow, discrete emission spectra. The peak emission wavelength of the QD is slightly longer than the first exciton peak or absorption onset and their peak emission wavelength is independent of the wavelength of excitation light. This means that variable-sized QDs can be excited by a single wavelength of light, as long as this wavelength is shorter than the absorption onset. This property finds application in multiplexed imaging where a number of different-sized QDs with discrete emission peaks and hence different colours can be excited by a single wavelength of light. The use of NIR photons is promising for biomedical imaging in living tissue due to longer attenuation distances and lack of autofluorescence in the IR region. In living tissues, intrinsic chromophores like hemoglobin and water are the major absorbers of visible and infrared light. Near infrared (NIR) light ranging from 700 to 1 300 nm can penetrate into deeper tissues (ca. 0.5 mm to cm) because of the low absorbance and scattering in the tissues. The NIR region is called as “the optical window” for *in vivo* imaging at a whole body level. For *in vivo* fluorescence imaging, NIR fluorophores can be used as optical contrast agents. So far, traditional fluorescent dyes such as Cy7, oxazine 750, and indocyanine green (ICG) have been used as NIR-fluorescent probes for *in vivo* imaging. However, traditional NIR-dyes have several disadvantages for use as fluorescent probes: low solubility in aqueous

solution, low quantum yield, and low photostability. For example, ICG, the most widely used NIR-dye only provides a quantum yield of 1.2% in blood. In addition, the photostability of ICG is very poor and the fluorescence of ICG in aqueous solution diminishes within several days under room light.

Cadmium selenide quantum dot. The classic and most commonly used quantum dots is cadmium selenide. Among various semiconductor materials, CdSe has been most extensively studied because its size-dependent photoluminescence is tunable across the visible spectrum. CdSe quantum dots consisit of a CdSe core and a shell layer (Figure 10). The shell is typically a high band-gap material made of ZnS or CdS (Alivisatos, 2005). Core/shell structures are better for biological applications than the core-only structures. Fluorescence properties are determined by the core materials and the shell layer removes surface defects and prevents nonradiative decey leading to a significant improvement in the particle stability and fluorescence quantum yields. CdSe/ZnS are ideal candidates for light-emission applications due to their high quantum efficiency, narrow-band, and particle-size-tunable photoluminescence. CdSe QDs find a wide range of applications in optoelectronic devices, photo catalysis, solar energy conversion and biological imaging and labeling.The luminescent lifetime of CdSe QDs is longer that of cell autofluorescence (~ 1ns) which permits measurement of marker spectra and location without high backgrounds through the use of time-gated fluorescent spectroscopy and/or microscopy. In addition, the photostability of CdSe is much better than that of conventional organic dyes, allowing data acquisition over long times with continuous excitation (Dubertret, B.2002). Compared with conventional organic dyes, QDs have longer lifetime allowing acquisition of low background photoluminiscent images by using time-gated fluorescent microscopy. After synthesis, the core/shell QDs (CdSe/ZnS, for example) must be covered with an organic layer or incorporated within the organic shell to make them water-soluble and biocompatible (Weal M et al.,2010). In order to utilize quantum dots in a biological environment they need to be made hydrophilic. Core/shell structures do not exhibit aqueous solubility as they are generaly synthesized in organic solution and are surface –stabilized with hydrofobic organic ligands. Thus, they are necessarily made water soluble by surface modifying them with various bifunctional surface ligands or caps to promote aqueous solubility and enhancing biocomptibility (Figure 10).



A - QD CdSe inorganic core
B - QD ZnS inorganic shell
C- organic biocompatible coating
Figure 10. Biocompatible core/shell quantum dot

QDs are adapted to the desired biological application by conjugation to biological molecules without disturbing the function of these molecules. Biomolecules include antibodies, peptides, oligonucleotides etc. Biocompatible quantum dots represent a powerful tool for the direct readout of information down to single molecule level. For example, by conjugating an antibody to the QD, targeting to specific cells or tissues can be affected *in vivo* or in fluorescent antibody immunoassays. Quantum dots have shown great potential to provide spatial, temporal and structural information for biological systems: *in vivo* cell labeling, *in vitro* cell labeling, detection of tumor marker, *in situ* tissue diagnostic, noninvasive toumor imaging, tracking of local cancer grown and its distant dissemination, detection and therapy of variors disease, identyfaing of variors types of biomarker, more effective and early diagnosis of cancer, imaging of live tissue etc.

Future Perspectives

Quantum dots are promising tools for early and accurate detection of tumor cells, multiplexed tissue and intracellular imaging. QD tehnology can prove to be a simple, rapid and successful platform for the early and sensitive prognosis of cancer biomarkers with great precision and accuracy, and hence anti-cancer therapies in future.

Conclusion

The specific optical property of QDs arises from the so-colled „quantum confinement“ efect of the semiconductor materials. This refers to the size- dependence of the semiconductor band gap-energy. For nanocristals smaller than the so-called Bohr excitation radius, energy levels are quatized.This dependence of light emission on the particle size allows the development of new fluorescence emitters with precisely tuned emission wavelenghts. Owning specific optical properties quantum dots are found applications in biological, medicine, electronic, solar cells etc. The unique optical properties of QDs and their surface properties that allow biocompatibility and heteroconjugation make QDs highly promising fluorescent labels for biological applications.The use of QDs emitting in the NIR region will provide greater sensitivity and the longer lifetime of their excited states as compared to organic fluorophores and proteins will lead to for improved bioimaging.

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