

❑ Semiconductor Nanocrystals or Quantum dots

- Nanomaterials particles are often classified according to their nature as *inorganic*, *organic*, or *hybrid*.
- **Inorganic Nanomaterials:** *Inorganic nanoparticles* are engineered nanoparticles *made from inorganic sources*. Inorganic nanoparticles cover a broad range of substances: *semiconductor nanocrystals, elemental metals, metal oxides, metal salts, and so on.....*
- Quantum dots (QDs) are a unique type of nanocrystalline semiconductor whose electronic and optical properties are *dependent on the size and shape of the dots*.
- Diameters of these particles can range from about *2-10 nm*, on the order of 10-100 atomic lengths .
- The *small size of the particle* gives a high ratio of *surface-to-volume*, so their properties fall somewhere between that of *individual molecules and bulk semiconductors*.
- Quantum dots can be single elements (*such as silicon, germanium, etc.*) or compounds (Group II–VI (e.g., *CdSe, CdTe, CdS, and ZnSe*), Group III–V (e.g., *InP and InAs*), or Group IV–VI (e.g., *PbSe*), etc.).

❑ Electronic Properties: Band theory of Metal, Semiconductor and Insulator

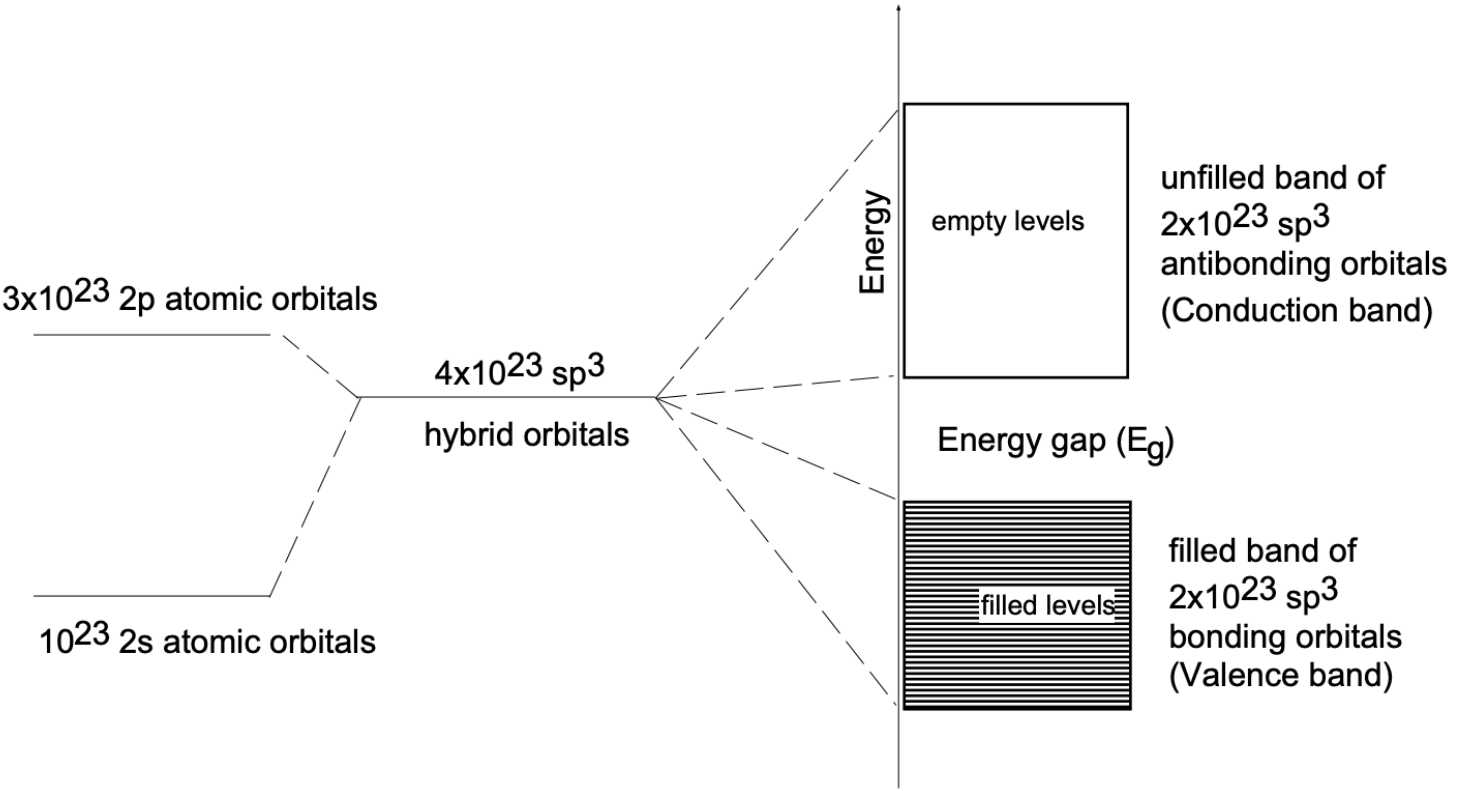
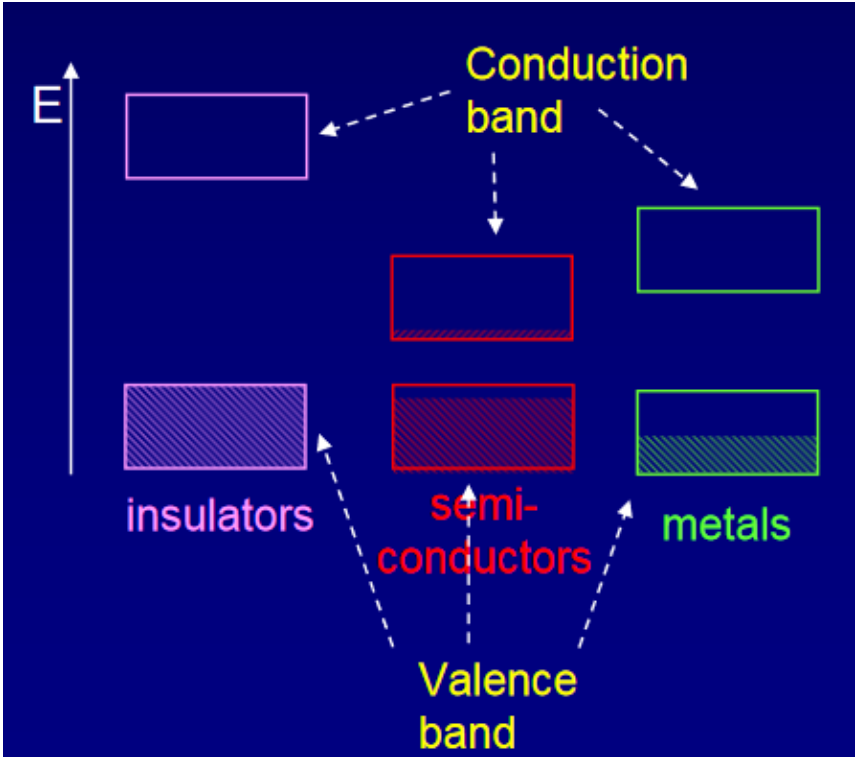
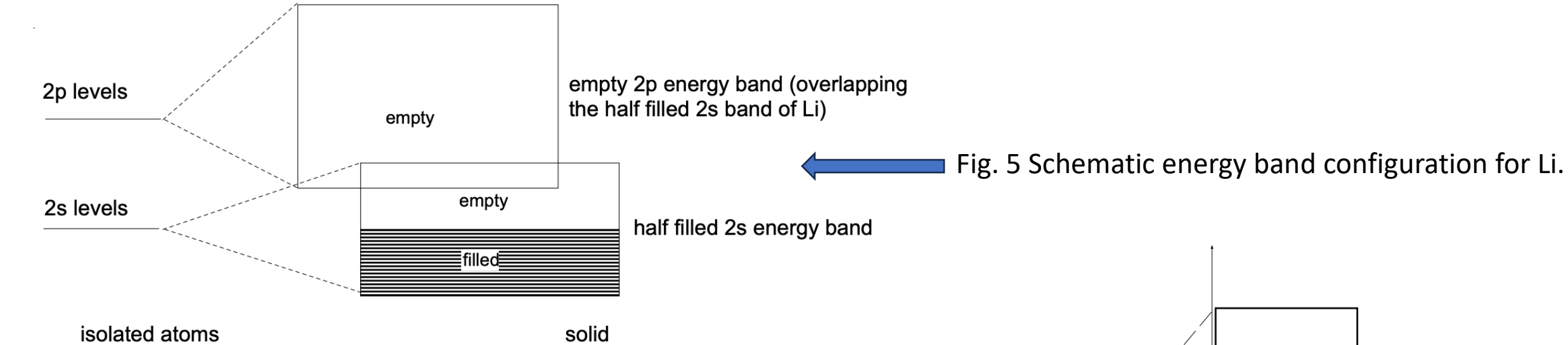
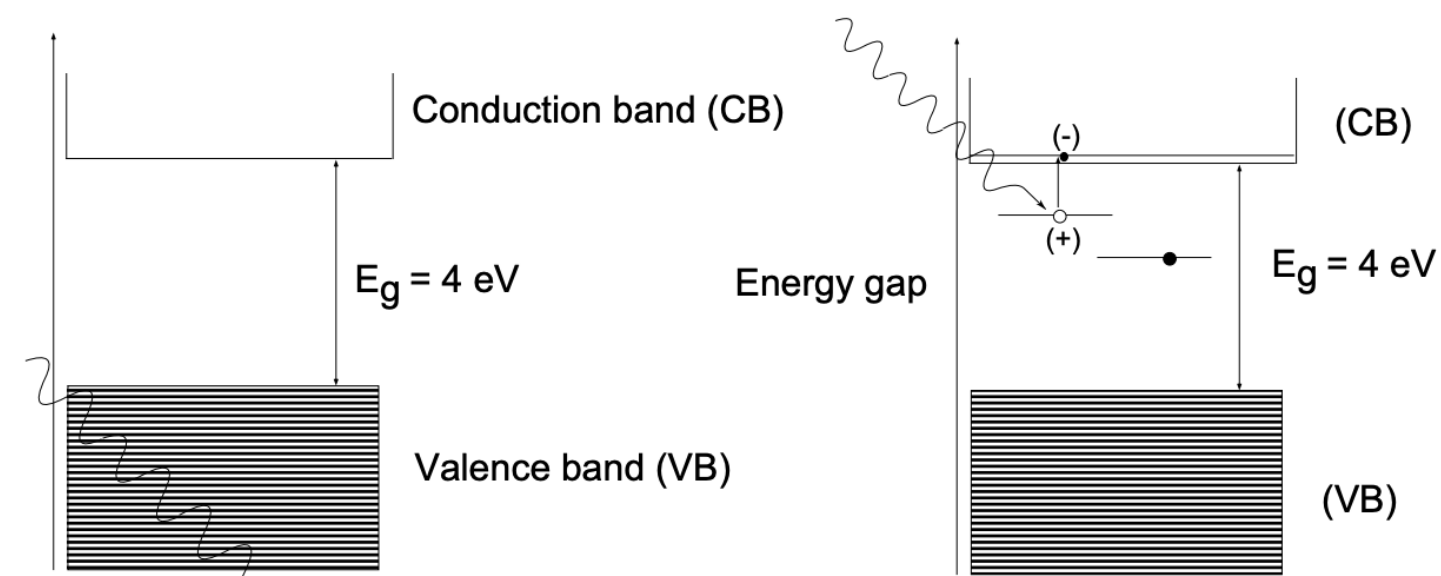


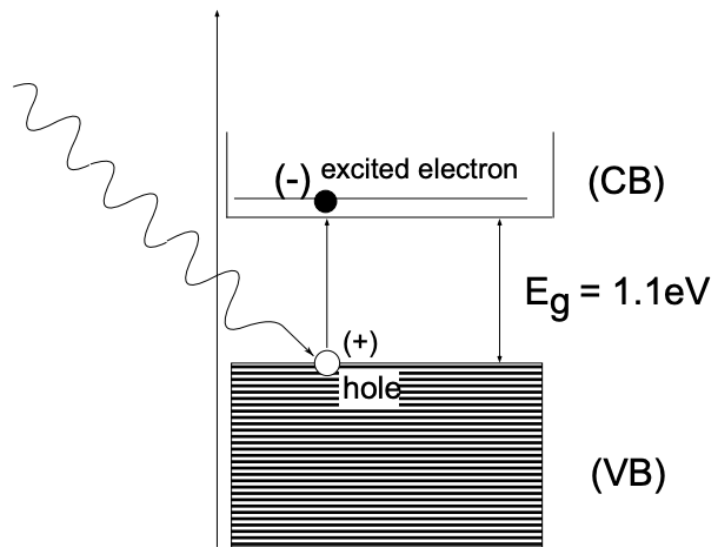
Fig. 6 Band structure of insulators and semiconductors (molecular crystals); the conditions depicted reflect a molar crystal of carbon (diamond).

- Both insulators and semiconductors have the same basic band structure – the primary difference is the width of the forbidden energy gap (E_g) between the valence and the conduction band.
- **Insulators**, generically, are materials with very high resistivity, comprising glasses, polymers, refractories, composites, liquids and gases. In the present context, an insulator is a molecular crystal, such as diamond (C) or sapphire, with **a band gap (E_g) in excess of 4 eV**. Generally, such materials will not conduct electricity since their valence band is filled and the energy required **to transfer electrons from the valence band to the empty conduction band is far in excess of both the thermal energies at room temperature and the energy provided by radiation of the visible spectrum (2eV)**. Therefore, **insulators (in single crystal form) are normally transparent (colorless)**; however, if light is excessively or totally scattered at internal heterogeneities (such as grain boundaries), they may be translucent and even opaque. It should also be recognized that impurities (Cr^{3+} in Al_2O_3) or particular point defects (color centers) may impart a color to the transparent insulator crystals. The color arises because of partial absorption of white light and selective transmission of the other portions of the visible spectrum.
- **Semiconductors**: The conventional **semiconductors, silicon (Si) and germanium (Ge)**, have a band gap (E_g) of 1.1 and 0.7eV respectively and therefore absorb visible radiation; they are opaque (fig. 7). Considering the statistical nature of the thermal energy distribution in the solid matrix (Maxwell-Boltzmann), a significant number of electrons in the valence band will, at room temperature, **acquire sufficient energy to cross the existing energy gap and thus provide for semiconductivity**. The **conductivity will therefore increase with temperature**, contrary to metallic systems, until electron scattering effects, due to increased lattice vibrations (which decrease the mobility of electrons), begin to dominate.



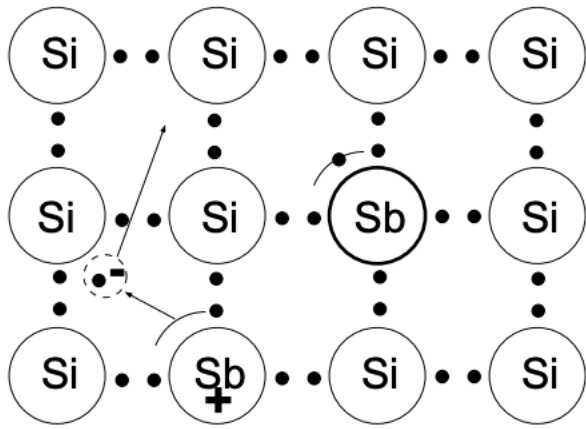
$E_{hv} \text{ (visible)} < E_g$
 Insulators (carbon) (transparent to light)

Impurity and defect levels in the energy gap may give rise to selective absorption of light (colour the object).

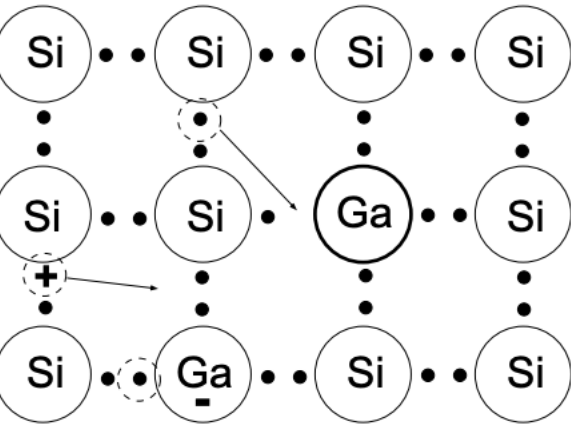


$E_{hv} \text{ (visible)} > E_g$
 Semiconductor (Si) (visible light is absorbed)

Fig. 7 Optical behavior of **insulators** and **semiconductors**



mobile (negative) charge carrier (electron)
from group V dopant element



mobile charge carrier (positive) created by
group III dopant element which has an electron
deficiency of 1 to satisfy bonding requirements in
the Si lattice. It acquires a bonding electron from
the lattice and generates a (positive) hole.

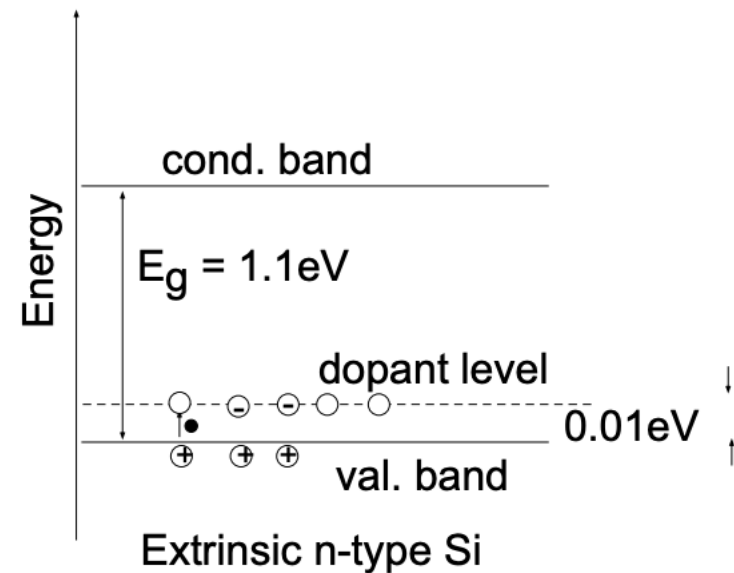
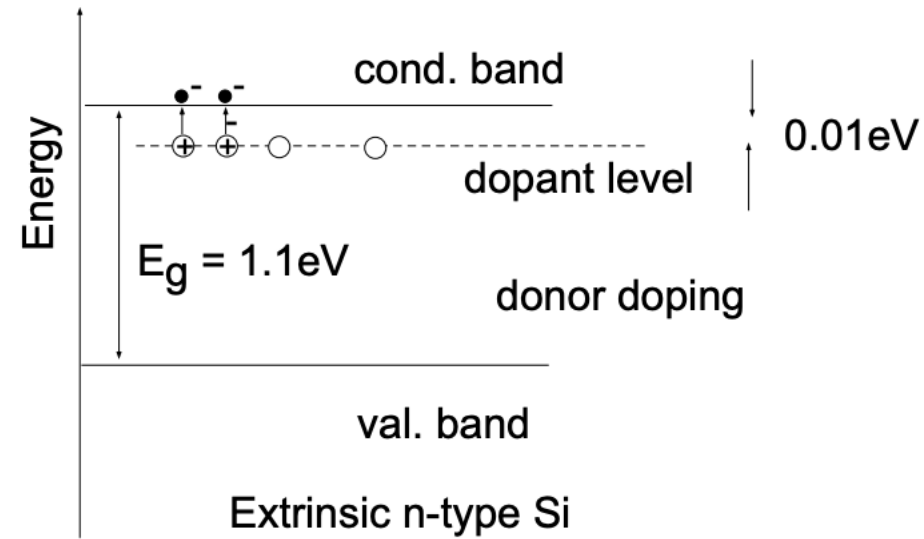


Fig. 8 Extrinsic p- and n-type semiconductors.

- The value of bulk semiconductors for solid state device fabrication lies in the fact that the number and type of conducting electric charge carriers [electrons are n-type (negative), holes are p-type (positive)] can be controlled through incorporation of appropriate dopant elements. Thus the substitutional incorporation of Group V elements (Sb, As, P) provides for shallow donor levels in the band gap at about 0.01eV from the conduction band. The substitutional incorporation of Group III elements (B, Al) generates acceptor levels in the band gap at about 0.01eV from the valence band. The two types of impurities are almost completely ionized at room temperature and give rise to extrinsic n-type and p-type conductivity – the basis for the formation of junction devices such as diodes and transistors (fig. 8).
- Of increasing importance are compound III-V (adamantine) semiconductors, such as GaAs, InSb, InP and GaP (compounds of Group III and Group V elements). Together these compounds provide eight valence electrons and, by sp^3 hybridization, are able to form a diamond-like, covalent crystal structure with semiconductor properties. These compounds (GaAs, for example) exhibit electron mobilities which are higher than those of silicon and, therefore, are of considerable interest for advanced device technology.

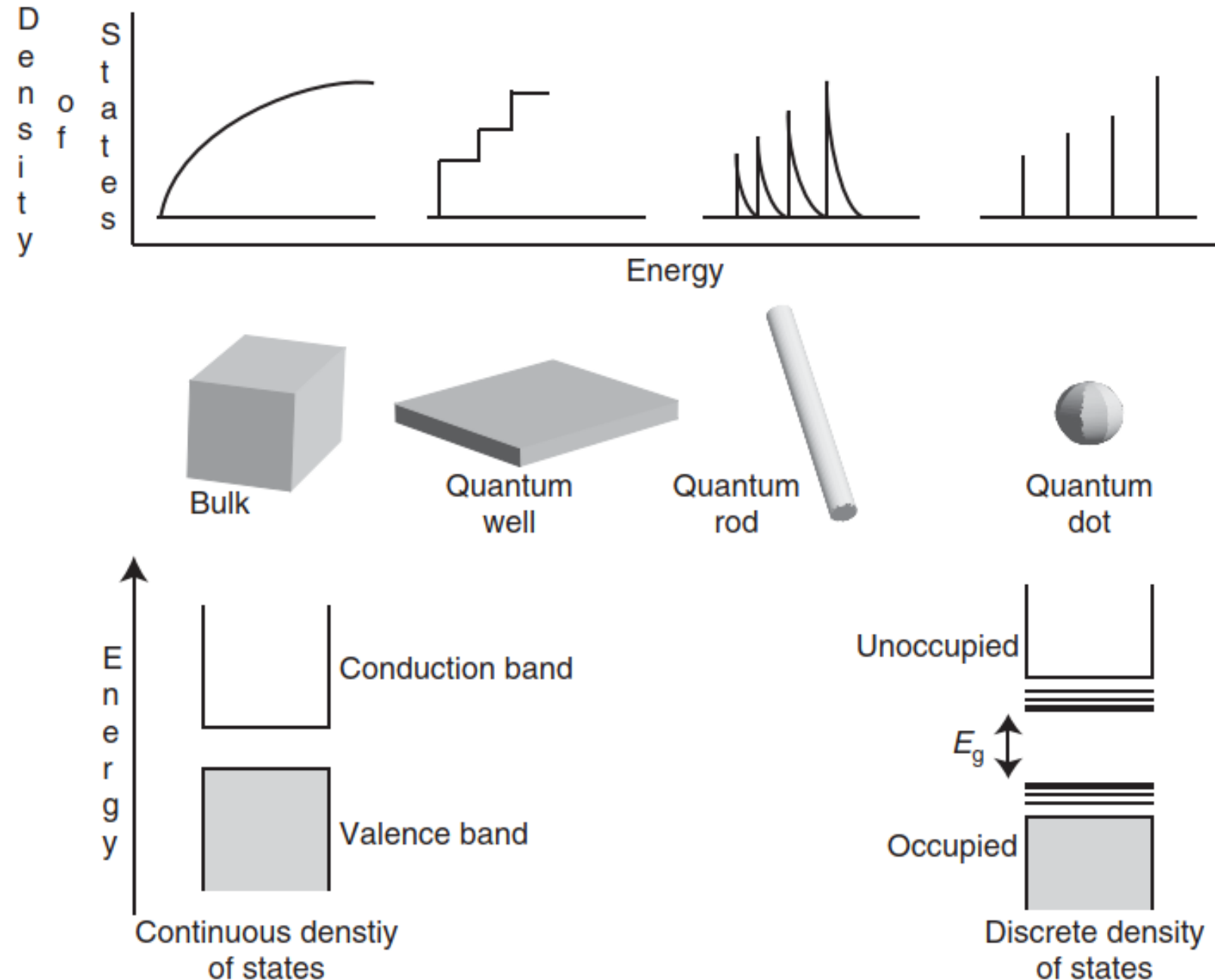
❑ Electronic Properties: Quantum Dots (QDots or QDs)

- These particles are often called **quantum dots (QD)** because quantum effects become important in ***these three-dimensionally confined particles (dots)***.
- *Unlike bulk semiconducting materials, quantum dot's energy states are too sparse to create the continuous valence and conduction bands typical of macroscopic semiconductors.*
- Instead, ***quantum dots of size roughly at 1 to 10 nm (about 10–100 atoms across) or below produce a rarefied electronic structure*** that is more reminiscent of the discrete electronic states found in single atoms. Therefore, sometimes ***quantum dots are called “artificial atoms”***.
- The equations of quantum mechanics can be applied to electrons (and holes) in semiconductors to estimate the size where materials undergo a crossover from molecular orbitals to bands. ***Semiconductor crystals of size less than double the Bohr radius of the excitons experience quantum*** confinement.
- *Unlike bulk semiconducting materials, the band gap (E_g) depends on the size of the QDs. The larger the quantum dot, the smaller its band gap (E_g) finally approaching the bulk value.*
- Unlike a single atom, however, ***this size dependence allows the band gap energy to be modulated by varying the size of the quantum dot, essentially allowing for the synthesis of materials with arbitrary band gap energies.***

❑ Electronic Properties: Quantum Dots (QDots or QDs)

FIGURE 10.1 Diagrams illustrating the fundamental principles of quantum confinement and size-dependent properties of semiconductor quantum dots.

- As the dimensionality decreases, the energy levels become less continuous and more discrete. In zero-dimensional structures such as quantum dots, the energy levels appear as sharp, quantized lines.
- The QD bandgap energy is the function of particle size, which allows continuous tuning of the emission wavelength.



- A **quantum dot** is confined in all three spatial dimensions, but semiconductors with other modes of confinement include **quantum wires** (holes or electrons confined in two spatial dimensions with one degree of freedom), and **quantum wells** (confined in one spatial dimension with two degrees of freedom).

❖ Optical Properties of QDots

❑ Semiconducting nanoparticles have been investigated intensively for their **novel optical properties**.

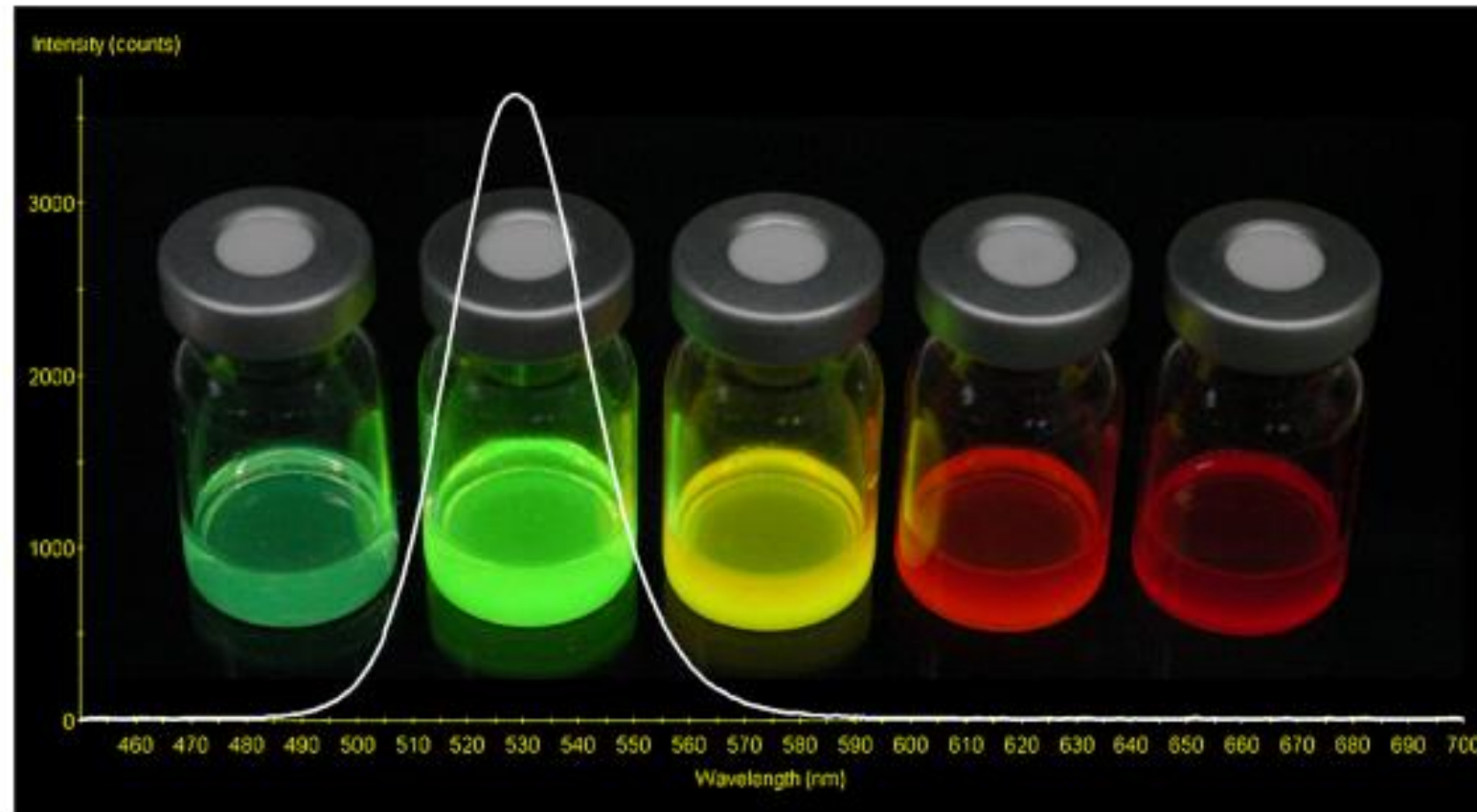


Figure : The electronic and optical properties of quantum dots can be fine-tuned due to their dependent relationship on size.

CdSe qdots" by NASA - mix.msfc.nasa.gov/abstracts.php?p=3906. Licensed under Public Domain via Wikimedia Commons - https://commons.wikimedia.org/wiki/File:CdSe_qdots.jpg

- Semiconducting materials have an intrinsic band gap (E_g) through which electrons can be excited by incident light of appropriate energy (wavelength).
- A semiconductor struck by a photon of light at higher energy than its bandgap will have an electron excited from the valence band to the conduction band (see Figure 2). This process leaves behind a hole, oppositely charged from the electron in the valence band. The hole and electron are attracted by Coulombic forces to create an **exciton**.
- An exciton is an electrically neutral quasiparticle found in semiconductors, insulators, as well as some liquids. The concept of the exciton was first proposed in 1931 by Yakov Frenkel in a discussion on excitation of atoms within the lattice of insulators.

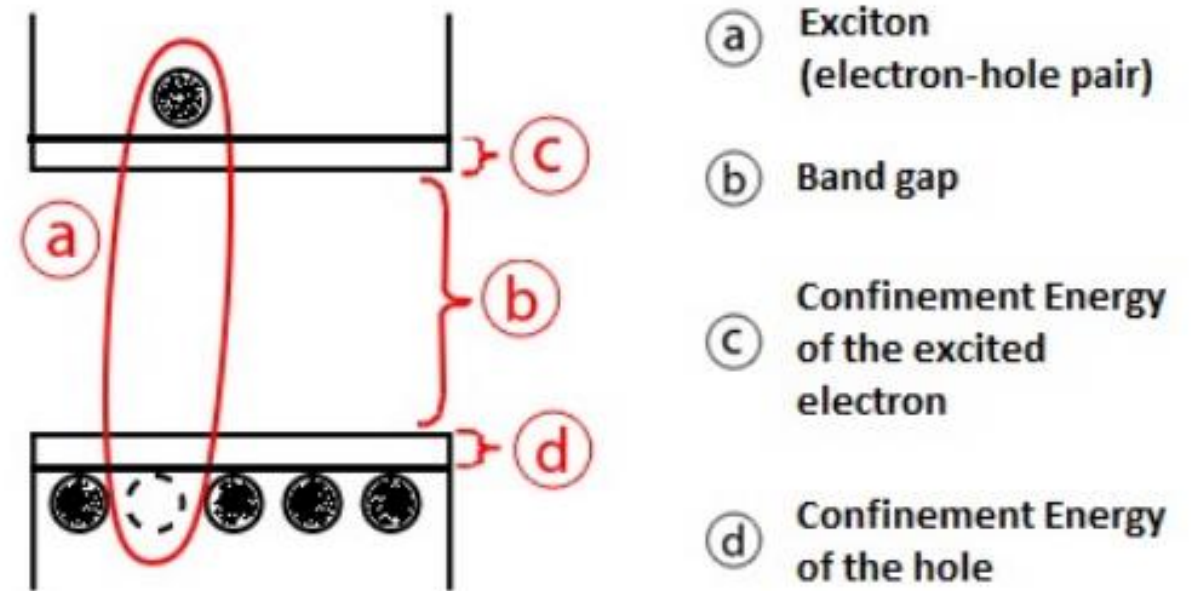


Figure 2: **Creation of the exciton from the electron-hole pair.**

Exciton energy levels" by Jpailee - Own work. Licensed under CC BY-SA 3.0 via Wikimedia Commons -

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- The QDs have **novel optical properties** that are not available from organic dyes and fluorescent proteins.
- **First**, QDs have **very large molar extinction coefficients** in the order of $0.5\text{--}5 \times 10^6 \text{ M}^{-1} \text{ cm}^{-1}$, which makes them **brighter probes** under photon-limited in-vivo conditions (where light intensities are severely attenuated by scattering and absorption).
 - The **second** manifestation of quantum confinement is that the available quantized energy levels inside a QD have **no net linear momentum** and therefore transitions between them do not require any momentum transfer. As a result, **the transition probabilities between any two states are high**. This lack of momentum dependence also explains the **broadband absorption nature of QDs because probabilities are high for most transitions** from the occupied valence band states to unoccupied conduction band states.

Probabilities are also high for intraband transitions, transitions of electrons between states in the LUMO band or of holes in the HOMO band. *These relatively intense intraband transitions are typically in the infrared region of the spectrum and are currently being exploited to make devices such as infrared photodetectors, sensors, and lasers.*

- **Third, longer excited state lifetimes (20–50 ns) and intense fluorescence light emission of QDs.** In theory, the *lifetime-limited emission rates for single QDs are 5–10 times lower than those of single organic dyes because of their longer excited state lifetimes (20–50 ns).* In practice, however, fluorescence imaging usually operates under absorption-limited conditions, in which the *rate of absorption is the main limiting factor of fluorescence emission.* Since the molar extinction coefficients of QDs are about 10–50 times larger than that ($5\text{--}10 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) of organic dyes, **the QD absorption rates will be 10–50 times faster than that of organic dyes at the same excitation photon flux** (number of incident photons per unit area). **Due to this increased rate of light emission, individual QDs have been found to be 10–20 times brighter than organic dyes.** Furthermore, the *longer excited state lifetimes of QDs provide a means for separating the QD fluorescence from background fluorescence* through a technique known as *time-domain imaging*.
- **Fourth, QDs have size- and composition-tunable fluorescence emission** from visible to infrared wavelengths, and *one light source can be used to excite multiple colors of fluorescence emission.* This leads to very large **Stokes spectral shifts** (measured by the distance between the excitation and emission peaks) that **can be used to further improve detection sensitivity.** This factor becomes especially important for in-vivo molecular imaging due to the high *autofluorescence background* often seen in complex biomedical specimens.

Indeed, the Stokes shifts of semiconductor QDs can be as large as 300–400 nm, depending on the wavelength of the excitation light.

Organic dye signals with a small Stokes shift are often buried by strong tissue autofluorescence, whereas ***QD signals with a large Stokes shift*** are clearly recognizable above the background. This “*color contrast*” is only available to QD probes because the signals and the background can be separated by wavelength-resolved or spectral imaging.

➤ **Fluorescence** is generated in quantum dots with an electron is excited from the conduction band to the valence band, and a photon is emitted with a wavelength longer than that absorbed from the recombination of an electron with a hole. The energy difference involved in this process is referred to as the ***Stokes shift***.

➤ The emission wavelength and color depend on the size of the quantum dot.

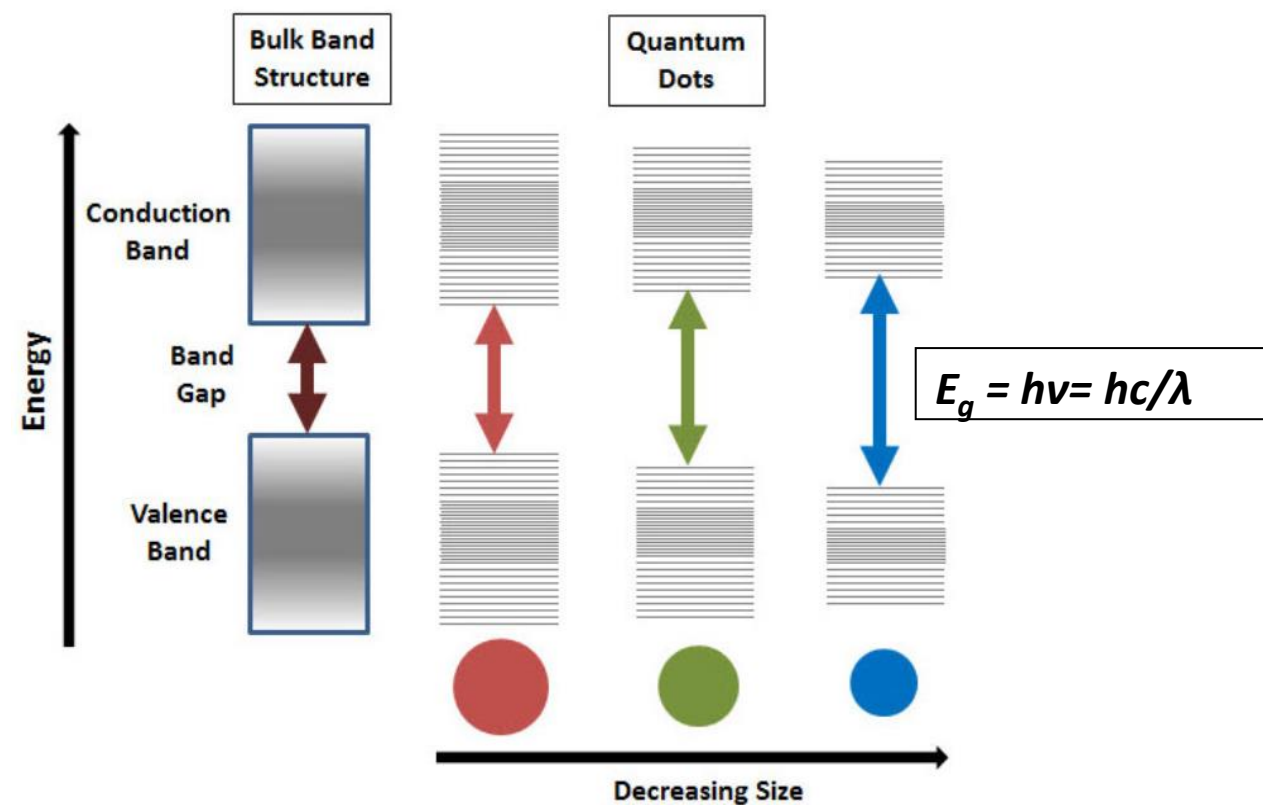
➤ By utilizing the calculated energy along with the deBroglie relationship:

$$E = \frac{hc}{\lambda}$$

➤ Emitted wavelengths range from infrared (IR) to ultraviolet (UV). Since quantum dots of different sizes are able to emit varied wavelengths when excited by a single light source, multiplexing can occur.

➤ Wavelengths of light emitted by a quantum dot depends on its size. As the size decreases, the wavelength emitted also shortens and moves toward the blue end of the visual electromagnetic spectrum. Conversely, increasing the dot size lengthens the wavelengths emitted, moving toward the red end.

Figure 5: The electronic structure of quantum dots varies with the size of the dot.



As we learned earlier that some semiconductor devices can emit light when a voltage is applied. Another way to make semiconductors emit light is to illuminate them with light whose photons have energies larger than the energy of the band gap of the semiconductor. A photon with a certain energy E_p can be absorbed if its energy is exceeding the band gap energy of the QD, i.e., $E_p > E_g$. Hence, larger QDs are allowed to absorb photons with lower energy than smaller QDs. An electron that was elevated from the valence band to the conduction band upon absorption of a photon can relax radiatively to the ground state by emitting another photon, a process called **photoluminescence (fluorescence)**.

- The size-dependence of the emission color comes primarily from a particle-in-a-box effect. The electron and hole that are created when the quantum dot absorbs light are bound together as an exciton by the confines of the "box". Louis Brus used first-order perturbation theory to determine that the bandgap of a semiconductor quantum dot is given approximately by (**Brus Equation**):

$$E_{gap} = E_{gap,bulk} + \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{4R\pi\epsilon\epsilon_0} + \dots$$

where R is the particle radius, μ is the electron-hole reduced mass ($1/\mu = 1/m_e^* + 1/m_h^*$), m_e^* and m_h^* are the electron and hole effective masses, and ϵ is the dielectric constant of the semiconductor.

- In this equation, the first term after the bulk bandgap is the **kinetic energy due to confinement of the exciton**, and the second term represents the **electrostatic attractive energy** between the confined electron and hole.
- **Because the confinement energy is a function of R , it can be widely tuned across the visible spectrum by changing the size of the quantum dot.**

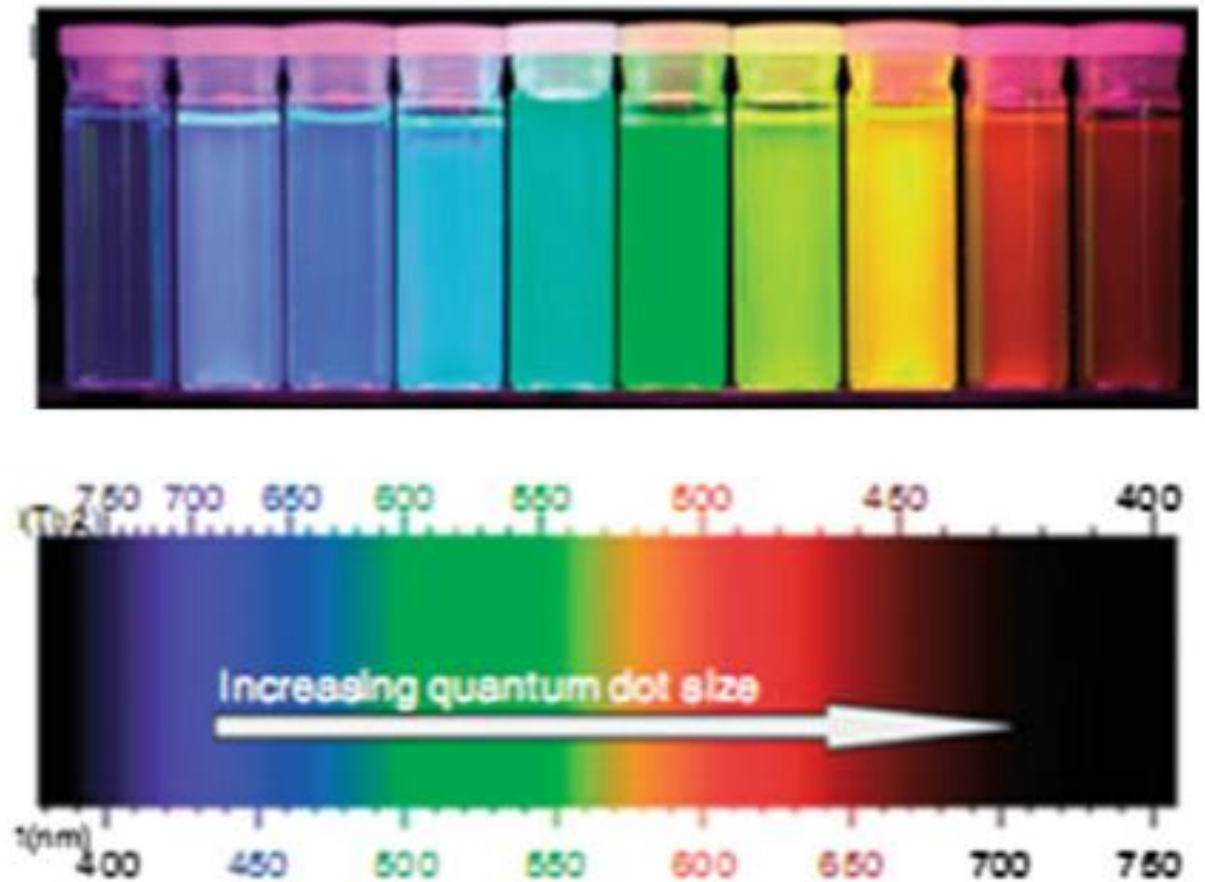
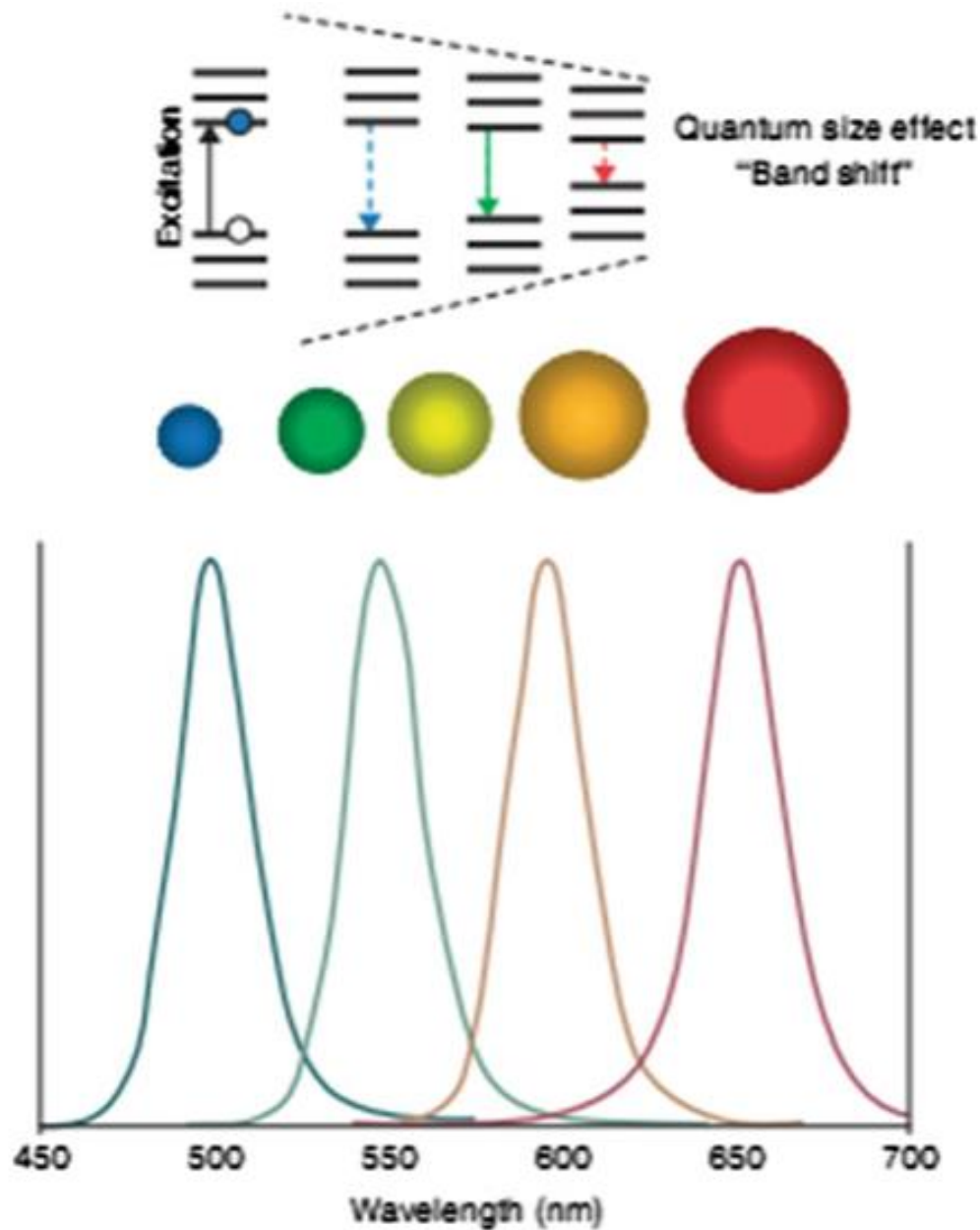
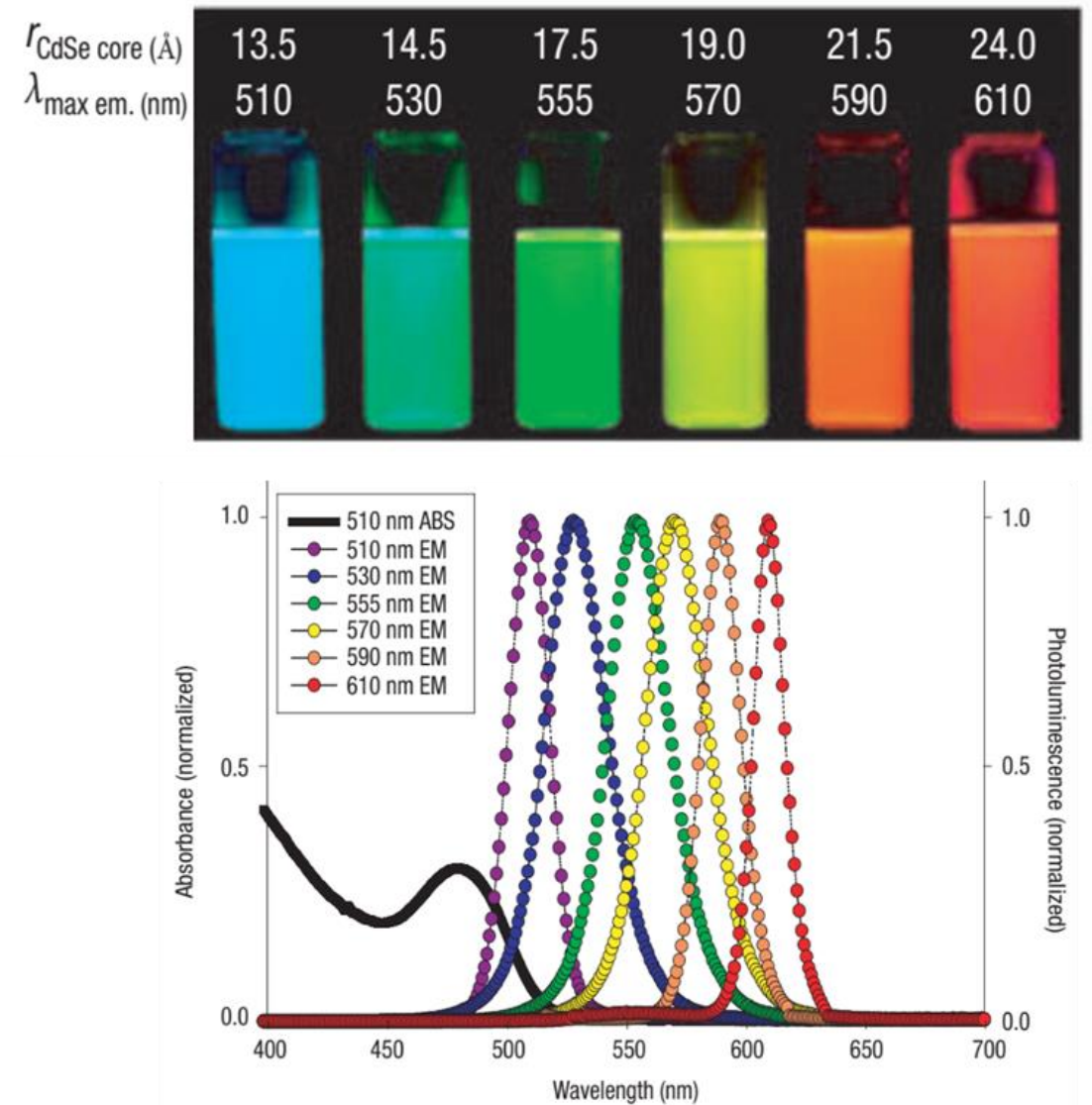


Fig. 5 Size-dependent PL colors of semiconductor QDs. Electronic structure of QDs correlated with the QD radius and resulting 'blue shift' due to quantum confinement as the QD size decreases.

- The wavelengths of interband transitions depend on the size of the dots and it is ***possible to tailor their luminescence simply by changing their size***. A key example of these QD materials is CdSe.
- ***By varying the size of the CdSe nanoparticle it is possible to tune emission over the entire visible spectrum***, making them ideal for *LED and fluorescent display technologies*.

Fig. (Top) Photo demonstrating the size-tunable fluorescence properties and spectral range of the six QD dispersions versus CdSe core size. All samples were excited at 365 nm with a UV source. r = core radius.

(Bottom) Absorption and emission of six different CdSe QD dispersions. The black line shows the absorption of the 510-nmemitting QDs.



- Quantum dots are nearly spherical, luminescent nanosized crystals made of semiconductor materials, of the order of 2–10 nm comprising 200–10 000 atoms.
- Their optical properties are size-dependent. A decrease in the crystal size causes an increase in energy shift between the absorbing and the emitting state.
- Optical excitation across the band gap in a semiconductor depends on the size of the crystal even for larger crystals, as large as those comprising 10 000 atoms. A similar trend can be expected with the quantum dots which are often far too small with a minimum of 200 atoms extending to a maximum of 10 000 atoms.
- The band gaps of such nanocrystals are often tunable to the interest of the user, for instance a CdS crystal can be tuned between 2.5 and 4 eV.

❑ One of the *most spectacular effects of reducing the size of a semiconductor crystal is that the band gap changes substantially with size in the 1–10-nm range. As the particle gets smaller, the band gap gets larger*, an effect observable by the naked eye, as shown in Figure 12.44.

➤ Could you explain the origin of the color change?



Figure 12.44 Cd_3P_2 powders with different particle sizes. The arrow indicates decreasing particle size and a corresponding increase in the band gap energy, resulting in different colors.

- ❑ One of the *most spectacular effects of reducing the size of a semiconductor crystal is that the band gap changes substantially with size in the 1–10-nm range. As the particle gets smaller, the band gap gets larger*, an effect observable by the naked eye, as shown in Figure 12.44.
- On the macro level, the semiconductor cadmium phosphide looks black because its band gap is small ($E_g = 0.5$ eV), and it absorbs all wavelengths of visible light.
- As the crystals are made smaller, *the material progressively changes color until it looks white! It looks white because now no visible light is absorbed*. The band gap is so large that only high-energy ultraviolet light can excite electrons into the conduction band ($E_g = 3.0$ eV).

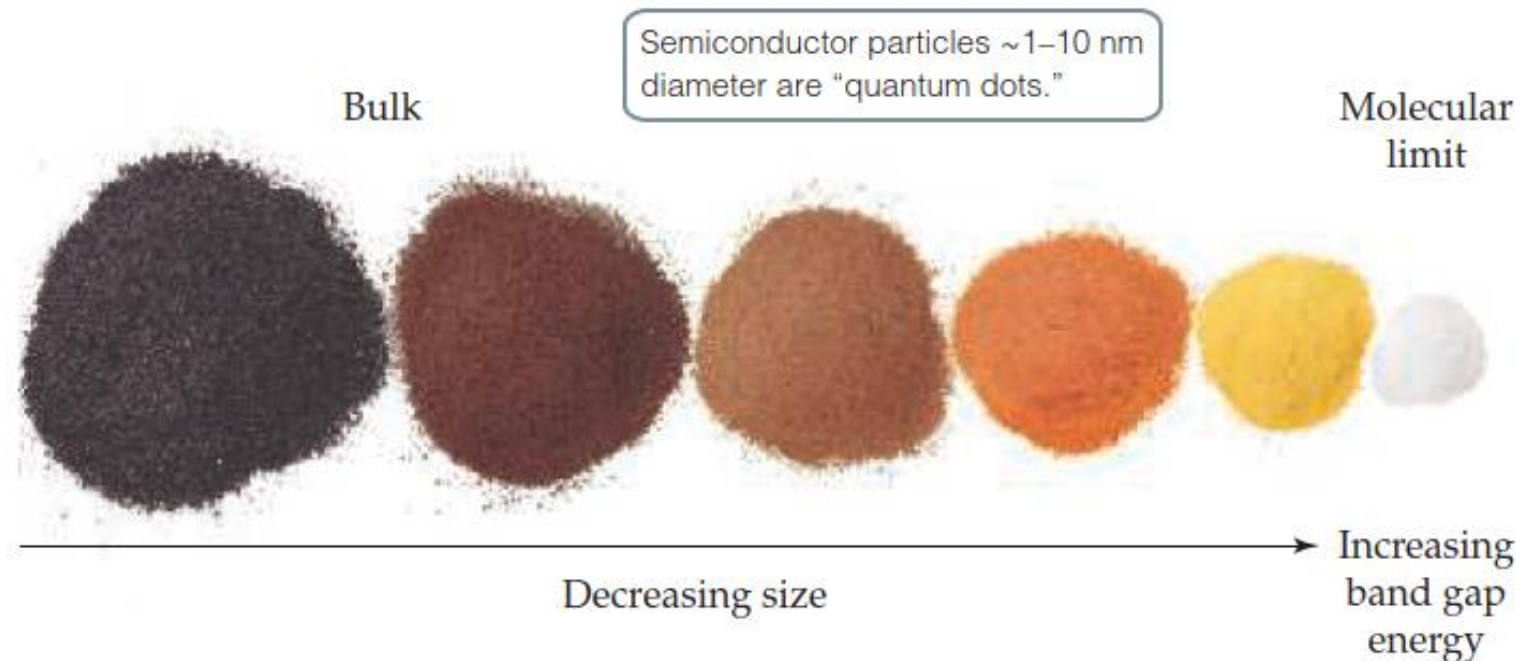


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Applications

❖ Quantum Computing

Quantum dots represent one of the more promising candidates for making solid state quantum computing a reality. By utilizing a small voltage applied to the leads, electron flow through the dot can be controlled. This may allow for precise measurements to be made of properties such as spin. It has been suggested that qubits, or entangled quantum dots, may offer a solution to the quantum computing problem.

❖ Batteries and chargers

Researchers at Vanderbilt University have found that by using quantum dots made of iron pyrite, a modern smartphone can be fully charged within 30 seconds, for dozens of charging cycles. While the technology is still relatively new, it shows great promise for another highly accessible technological use.

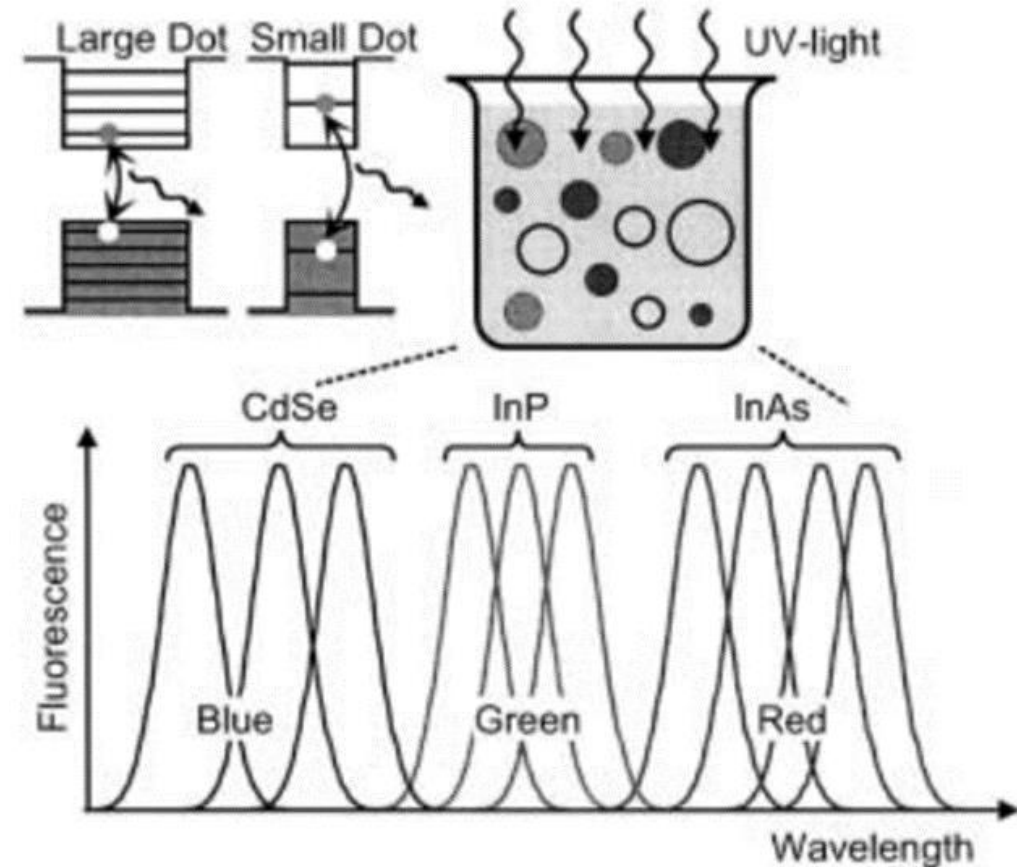
❖ Solar Energy

Incoming sunlight is absorbed by quantum dots, creating excitons which must be quickly separated. Electrons travel to the photoanode by metal oxide nanorods, holes to the photocathode by a conducting polymer. This separation produces a current in the semiconductor. Quantum dots show promising use in producing transparent and semi-transparent windows that are able to act as solar panels.

❖ Use in LED and fluorescent display technologies:

As an example, Fig. 4.1 shows the dependence of the fluorescence wavelength on the **dimensions** and **material composition** of the nanocrystals. The large wavelength differences between the blue, green, and red (BGR) emissions result here from using materials having **different band gaps**: CdSe (blue), InP (green), and InAs (red). The fine-tuning of the fluorescence emission within each color is controlled by the size of the QDs.

Figure 4.1 Nanocrystal quantum dots (NCQD) illuminated by UV-light emit light at a wavelength that depends both on the material composition and the size of the NCQDS. *Large differences in the fluorescence wavelength result from different band gaps of the materials. Within each color (blue, green, and red) the wavelength is defined by the different sizes of the NCQDs.*



❖ Medical Imaging

In addition to the *LED and fluorescent display technologies*, another exciting use of QDs is as chromophores for 'biotags', where dots of different sizes are functionalized to detect different biological analytes.

Researchers have found that using latex beads filled with QD nanocrystals can be used to bind to specific DNA sequences. Probes can be created that combine different sized dots within these beads that emit specific wavelengths and intensities of light. Under UV simulation, these beads serve as markers to identify specific regions within DNA. This process has applications specifically in areas of cancer research.

A further advantage is that **multicolor QD probes** can be used to **image and track multiple molecular targets simultaneously**. It turns out that, although they emit at specific tunable wavelengths, QDs exhibit broadband absorption for energies above the band gap. The intriguing point for bio-applications is that it is possible to excite an array of distinct QD chromophores with a single broadband excitation and to simultaneously detect multiple analytes by their distinct optical emissions. This is a very important feature because tracking a panel of molecular markers at the same time will allow scientists to understand, classify, and differentiate complex human diseases. Most complex human diseases such as cancer and atherosclerosis involve a large number of genes and proteins. These materials have been used to image breast cancer cells and

live nerve cells to track small molecule transport to specific organelles.

Multiple parameter imaging, however, represents a significant challenge for magnetic resonance imaging (MRI), positron emission tomography (PET), computed x-ray tomography (CT), and related imaging modalities. ***On the other hand, fluorescence optical imaging provides both signal intensity and wavelength information, and multiple wavelengths or colors can be resolved and imaged simultaneously (color imaging).*** Therefore, different molecular or cellular targets can be tagged with different colors. *In this regard, QD probes are particularly attractive because their broad absorption profiles allow simultaneous excitation of multiple colors, and their emission wavelengths can be continuously tuned by varying the particle size and chemical composition.*

For organ and vascular imaging , in which micrometer-sized particles could be used, optically encoded beads (polymer beads embedded with multicolor QDs at controlled ratios) could allow multiplexed molecular profiling in vivo at high sensitivities.

➤ **In addition**, QDs are several thousand times **more stable** against **photobleaching** than dye molecules and are thus well suited for continuous tracking studies over a long period of time.

- ✓ **Optical tunability, multicolor light emission, and better photostability position QDs as the preferred fluorescent probes for dynamic live cell imaging tools and in vivo animal models.**
- ✓ They have unparalleled **sensitivity and spatial resolution**, compared to the organic fluorophores currently available.
- **QDs with organic capping perform even better; these** QDs usually have a core crystal with an inorganic capping with an outer organic group which helps during QD conjugation for functionalization. For instance, a ZnS capped CdS QD is 20 times brighter than rhodamine (a popular organic dye) and at the same time 100 times more stable to photobleaching.
- ✓ QDs can be used for the *study of live cell single-molecule dynamics, monitoring of intracellular protein–protein interactions, disease detection in deeper tissues, detection of cancer/tumor cells based on selective binding of bioconjugated QDs to known cancer biomarkers*, and much more.

Fig. 3.3 shows green QDs conjugated to streptavidin, emitting green fluorescence. The image shows F-actins of fixed fibroblasts.

FIGURE 3.3: Immunocytochemical stain of F-actin in fixed fibroblast cells using green quantum dots.

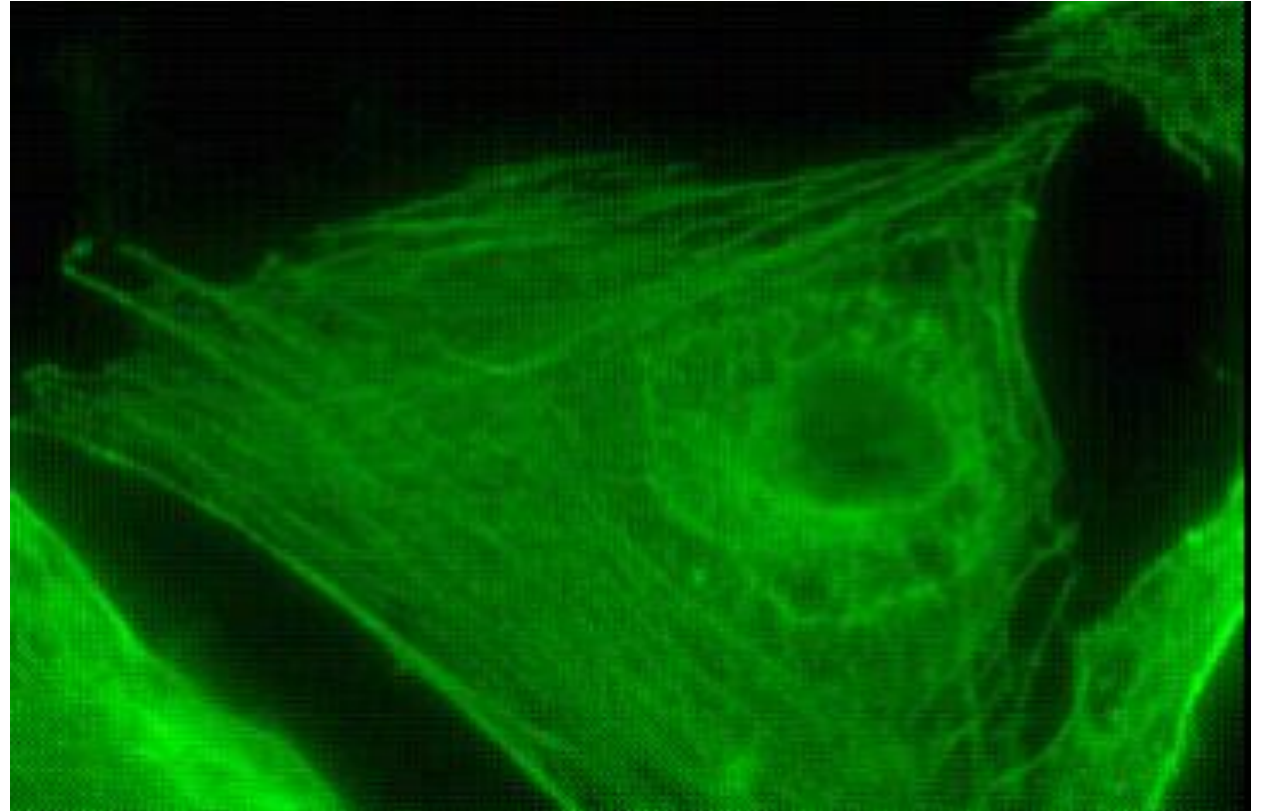


Fig. 3.4 shows the image of cellular uptake of QD-cationic peptide conjugates. The red-fluorescent (CdSe)ZnS QDs were incubated with a monolayer of living human cancer cells. The QDs were previously conjugated with TAT peptides. The image further suggests, from the aggregation of QDs in internal cellular structures, that they are present in endocytotic vesicles.

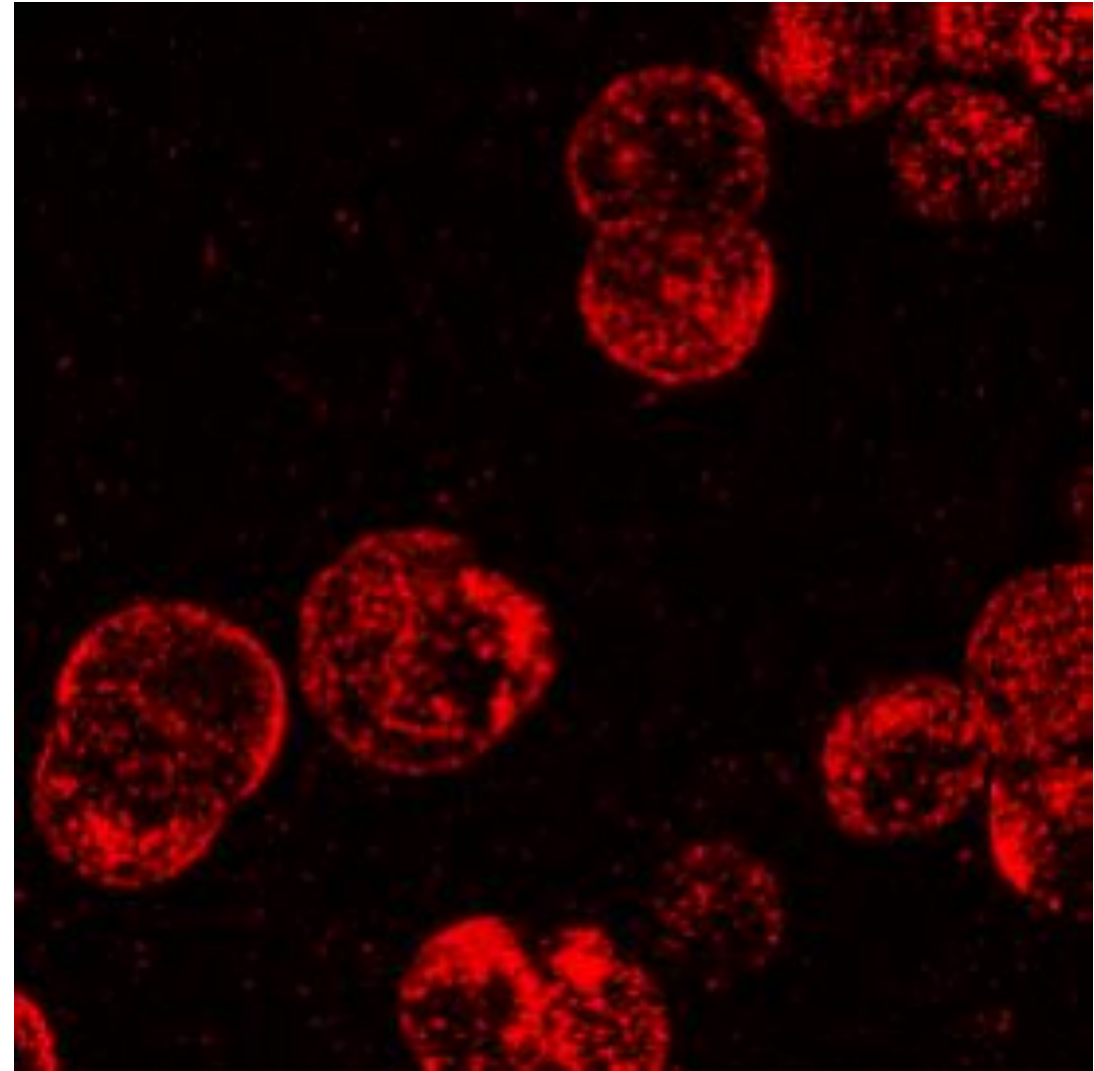


FIGURE 3.4: Cellular uptake of QD-cationic peptide conjugates. Monolayers of living human cancer cells were incubated with red fluorescent (CdSe)ZnS QDs conjugated to TAT peptides. The aggregation of QDs in internal cellular structures is indicative of their presence in endocytotic vesicles

FIGURE 3.8: Versatile applications of QDs in biomedical and biotechnology.

