Q-1

The mechanism responsible for the color of semiconductor quantum dots is the **quantum confinement effect**. Here's a breakdown:

1. **Confinement:** Quantum dots are incredibly tiny, often just a few nanometers across. This means their electrons are confined to a very small space. Think of it like a tiny "box" where electrons can only exist at specific, quantized energy levels.
2. **Energy Levels:** In bulk semiconductors, electrons have a continuous range of energy levels, forming a band structure. But in quantum dots, this continuous range breaks down into discrete, quantized energy levels due to the confinement.
3. **Band Gap:** The difference in energy between the highest energy level in the valence band (where electrons normally reside) and the lowest energy level in the conduction band (where electrons can move freely) is called the band gap. The band gap determines which wavelengths of light a material can absorb.
4. **Size Dependence:** In quantum dots, the band gap is directly related to the dot's size. Smaller dots have a larger band gap because the electrons are more confined, requiring higher energy to jump to the conduction band.
5. **Color:** When light interacts with a quantum dot:
   - If the light's energy matches the band gap, the electron absorbs the photon and jumps to a higher energy level.
   - When the excited electron falls back to its ground state, it emits a photon of light.
   - The emitted photon's energy, and therefore its color, is determined by the size of the quantum dot. Smaller dots emit higher energy (bluer) light, while larger dots emit lower energy (redder) light.

In essence, the size of a quantum dot controls its color by dictating its band gap and, consequently, which wavelengths of light it absorbs and emits.

The color of suspensions of silver or gold nanoparticles arises from a phenomenon called localized surface plasmon resonance (LSPR). Here's how it works:

In summary, the color of metal nanoparticles is determined by their ability to absorb and scatter light at specific wavelengths due to the excitation of localized surface plasmons, a collective oscillation of electrons confined to the nanoparticle's surface.

- ### How LSPR Dictates Color:
- **Localized Plasmon Oscillations:** When light hits the surface of a metal nanoparticle, it can excite the free electrons at the interface between the metal and the surrounding medium (such as air or a dielectric). These electrons oscillate collectively and create what is known as localized surface plasmons.

Unlike in continuous metal films, where surface plasmon resonance (SPR) occurs over a large area, LSPR refers to the resonance that is confined within the small volume of a nanoparticle.

- **Size and Shape Dependence:** The frequency at which these localized plasmons resonate depends on the properties of the metal, the dielectric medium, and, importantly, the size and shape of the nanoparticles. For example, gold nanoparticles appear red or purple instead of the typical metallic yellow color of bulk gold. This is due to the LSPR frequency shifting when the particle size decreases to the nanoscale.

○ ## Selective Absorption and Scattering:

- LSPR leads to the selective absorption of certain wavelengths of light. This happens because the localized plasmons absorb light at specific wavelengths that match their resonance frequency, reducing the reflection or transmission of those colors. The remaining wavelengths are either reflected or transmitted, which determines the perceived color of the nanoparticles.

- **Color Change Due to Size Variation:** The color change happens because smaller nanoparticles resonate with shorter wavelengths (e.g., blue and green), leading to absorption in this range and reflection/transmission of longer wavelengths (e.g., red and orange). The color observed in a nanoparticle suspension can shift significantly based on changes in size and shape.

○ ## Influence of the Surrounding Medium:

- The refractive index of the medium surrounding the nanoparticle affects the LSPR condition. A change in the environment can shift the resonance frequency, leading to a change in the color observed. This property is why LSPR is utilized in sensing applications, as detecting changes in color can indicate a change in the surrounding medium.

- In conclusion, LSPR in nanoparticles is a powerful phenomenon that dictates their unique optical properties and the vivid colors seen in suspensions, driven by the interaction of light with the localized electron oscillations at the nanoparticle surface.

Q-2

Factors Influencing Light-Scattering Profiles:

1. **Size of the Nanocrystals**:
   - The figure shows nanospheres of different sizes (e.g., ~40 nm, ~80 nm, ~100 nm) and how they produce varying colors under light-scattering conditions.
   - Smaller nanospheres (~40 nm) appear blue, while larger nanospheres (~100 nm) scatter light in a way that results in different colors like yellow or orange.
   - **Reason**: The size of the nanoparticles affects their surface plasmon resonance (SPR) frequency. Smaller particles resonate with shorter wavelengths (e.g., blue light), while larger particles can resonate with longer wavelengths (e.g., yellow or red light).

2. **Shape of the Nanocrystals**:
    - The figure includes silver (Ag) nanoprisms (~100 nm) that appear red compared to spherical nanoparticles of similar sizes.
    - **Reason**: The shape of the nanoparticle changes the distribution and oscillation of electrons on its surface, shifting the SPR. Triangular or prismatic shapes have sharper corners, which enhance the electric field at those points and shift the resonance to longer wavelengths, leading to a different color profile.
3. **Material Composition**:
    - The figure shows both gold (Au) and silver (Ag) nanoparticles, and their colors differ even at the same size (e.g., ~100 nm Au spheres vs. ~100 nm Ag spheres).
    - **Reason**: Different metals have distinct dielectric properties and electron densities, which influence their SPR. Gold and silver are common in SPR applications, but they absorb and scatter light differently. Silver typically resonates at shorter wavelengths (e.g., green/blue) compared to gold, which can resonate at longer wavelengths (e.g., red/orange).

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> ➢ *Note that* **very small** *nanoparticles (<~2 nm) do not display this LSPR phenomenon, as their electrons exist in discrete energy levels, and bulk metal has a continuous absorbance in the ultraviolet (UV)/visible/infrared (IR) regions without any resonance.*

> ➢ *By reducing the size of the particles further below the mean free path, critical scale is attained when dimensions become comparable to the Fermi wavelength of metals, λ_F ~1–2 nm. Electrons in these subnanometric-sized particles do not have a continuous DOS, which is necessary to support the plasmon and therefore SPR disappears.*

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$$E_{loc} = \frac{3\varepsilon}{\varepsilon + 2\varepsilon_m} E_0$$

where ε is the complex dielectric constant of the metal and ε_m is the dielectric constant of the surrounding medium ($\varepsilon_m = n_m^2$ where n_m is the refractive index of the (nonabsorbing) medium).

> ➢ *Under the resonance condition*, when $\varepsilon = -2\varepsilon_m$, E_{loc} *is strongly enhanced* with respect to the far field. This *huge increase in the local field around metal nanoparticles* (or metal

Q-6

Plasmonic nanoparticles play a crucial role in **Surface-Enhanced Raman Scattering (SERS) spectroscopy**, a powerful technique for enhancing the Raman signal of molecules. Here's a breakdown of how plasmonic nanoparticles contribute to this enhancement:

1. Localized Surface Plasmon Resonance (LSPR):

- **Fundamental Mechanism**: When plasmonic nanoparticles, such as gold or silver, are illuminated by incident light, their conduction electrons oscillate collectively at a specific frequency known as **localized surface plasmon resonance (LSPR)**. This resonance leads to a substantial increase in the electromagnetic field near the nanoparticle surface.
- **Electromagnetic Enhancement**: The enhancement of the local electromagnetic field is one of the primary mechanisms behind SERS. It results in an exponential increase in the Raman scattering intensity of molecules adsorbed on or near the nanoparticle surface.

2. "Hot Spots" Formation:

- **Nanoparticle Aggregation**: When plasmonic nanoparticles aggregate or form complex structures, "hot spots" are created at junctions or sharp features. These areas exhibit extremely high local electromagnetic fields.
- **Significance of Hot Spots**: Molecules situated within these hot spots experience a massive increase in Raman signal, sometimes by factors as high as 106106 to 10101010 or more. This makes it possible to detect single molecules using SERS.

3. Chemical Enhancement Mechanism:

- **Charge Transfer**: Beyond electromagnetic enhancement, plasmonic nanoparticles can also facilitate a **chemical enhancement** mechanism. This involves the transfer of electrons between the metal surface and the adsorbed molecules, modifying the polarizability of the molecules and enhancing the Raman signal.
- **Surface Chemistry**: The interaction between the molecule and the nanoparticle's surface can alter the electronic states of the molecule, providing an additional boost to the Raman signal.

Q-7
60+(k×6)

P=12 (for caged fullerenes)
60+(k*6)=20+2H (according to property)
40+k*6=2H
20+k*3=H

F=P+H
E=(5P+6H)/2
V=(5P+6H)/3

V+F-E=2
5/3P+2H+P+H-5/2P-3H=5/3P-5/2P=(5/3+1-5/2)*12*=5*4+12-5*6=20+12-30=2

Chat gpt solution

To show that the series of spherical fullerenes with 60+(k×6)60+(k×6) atoms (where k=0,2,3,4,…k=0,2,3,4,…) satisfies Euler's theorem, we can analyze the structure in terms of graph theory and polyhedral properties.

1. Euler's Theorem:

Euler's theorem for polyhedra states that for any convex polyhedron:

V−E+F=2,V−E+F=2,

where:

- VV is the number of vertices,
- EE is the number of edges,
- FF is the number of faces.

2. Properties of Fullerenes:

Fullerenes are carbon molecules that form closed spherical structures where:

- Each carbon atom is a vertex (VV).
- Each carbon-carbon bond is an edge (EE).
- The faces are composed of pentagons and hexagons (FF).

For spherical fullerenes:

- The number of vertices VV is equal to the number of carbon atoms, i.e., V=60+(k×6)V=60+(k×6).
- Each vertex is connected to three others, meaning that the polyhedron is trivalent (each vertex has a degree of 3).

3. Counting Edges (EE):

In a trivalent polyhedron, the total number of edges EE can be determined from the relationship:

2E=3V.2E=3V.

Solving for EE:

E=3V2.E=23V.

4. Counting Faces (FF):

Fullerenes consist of 12 pentagonal faces and a number of hexagonal faces (HH) that varies depending on kk:

$$F = 12 + H. \quad F = 12 + H.$$

5. Relationship Between Faces and Vertices:

To find HH, we need to consider the total number of vertices and faces:

- The total number of vertices VV is $60 + (k \times 6)$ $60 + (k \times 6)$, which means the molecule contains kk additional sets of 6 vertices beyond the initial 60.
- For fullerenes, each added set of 6 atoms forms a hexagon.

Given that each face (pentagon or hexagon) shares edges with adjacent faces, we can count the edges by considering:

$$2E = 5 \times 12 + 6H. \quad 2E = 5 \times 12 + 6H.$$

6. Proof Using Euler's Theorem:

Substitute $V = 60 + (k \times 6)$ $V = 60 + (k \times 6)$ and $E = \frac{3V}{2}$ $E = \frac{3}{2}V$ into Euler's theorem:

$$V - E + F = 2. \quad V - E + F = 2.$$

Plug in $E = \frac{3V}{2}$ $E = \frac{3}{2}V$ and $F = 12 + H$ $F = 12 + H$:

$$V - \frac{3V}{2} + (12 + H) = 2. \quad V - \frac{3}{2}V + (12 + H) = 2.$$

Simplify the expression:

$$\frac{2V - 3V}{2} + 12 + H = 2. \quad \frac{2V - 3V}{2} + 12 + H = 2. \quad \frac{-V + 12 + H = 2.}{} \quad \frac{-V}{2} + 12 + H = 2.$$

Solve for HH:

$$H = \frac{V}{2} - 10. \quad H = \frac{V}{2} - 10.$$

Substitute $V = 60 + (k \times 6)$ $V = 60 + (k \times 6)$:

$$H = \frac{60 + (k \times 6)}{2} - 10. \quad H = \frac{60 + (k \times 6)}{2} - 10.$$

Simplify HH:

$$H = 30 + 3k - 10 = 20 + 3k. \quad H = 30 + 3k - 10 = 20 + 3k.$$

Conclusion:

For spherical fullerenes with 60+(k×6)60+(k×6) atoms:

- VV is satisfied by the vertices of the structure.
- E=3V2E=23V and F=12+(20+3k)F=12+(20+3k) ensure Euler's theorem V−E+F=2V−E+F=2 holds true.

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Therefore, the diameter d of the nanotube can then be calculated as:

$$d = \frac{|\vec{C}|}{\pi} = \frac{\sqrt{3}}{\pi} R_{CC} \sqrt{m^2 + n^2 + mn} = \frac{a_g}{\pi} \sqrt{m^2 + n^2 + mn}$$