International Journal of Recent Development in Engineering and Technology
Website: www.ijrdet.com (ISSN 2347-6435(Online) Volume 15, Issue 02, February 2026)

Optical Properties and Characterization of Nanomaterials

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***Abstract*— Nanomaterials are such substances in the world of technology which have brought unprecedented changes in the traditional devices of old methods and for this reason these substances have come to be called the foundation of nanoscience and nanotechnology. To understand the nanomaterials and their properties the characterization should in atomic level. The optical properties of nanomaterials are fundamental and technological aspects that can be investigated initially using low-cost equipment.**

***Keywords*—Nanomaterials, optical properties, UV-vis spectroscopy, absorption spectra, bandgap.**

I. INTRODUCTION

Nanomaterials are materials with at least one dimension in the nanometer range, and they possess unique properties that are distinctly different from their bulk counterparts [1]. The unique properties of nanomaterials such as their size, shape, structure, and surface quality make them highly active and effective. By characterizing the physicochemical properties of nanomaterials, it is possible to better understand the complex relationships between their structure, properties, and applications. Accurate characterization of nanomaterials requires state-of-the-art techniques with sufficient resolution to probe nanoscale dimensions. Over the past few decades, the development of methods for characterizing nanomaterials has progressed in parallel with advances in nanoscience and the synthesis of nanomaterials. Quantum confinement and surface effects are as such phenomenon which influence Optical properties of nanomaterials, including light absorption, emission, scattering, and reflection. Important phenomena include adjustable photoluminescence in semiconductors (quantum dots) and Surface Plasmon Resonance (SPR) in noble metals (like gold and silver), which have uses in bioimaging, sensors, and optoelectronics [2]. The present article deals with optical properties of nanomaterials and their characterization by numerous optical characterization techniques.

II. QUANTUM CONFINEMENT EFFECT ON OPTICAL PROPERTIES OF NANOMATERIALS

When light interacts with small particles and free electrons and holes are created the phenomenon of quantum confinement occurs. The hydrogen-like complex is formed by hole-electron pair is known as an exciton. The radius of the exciton is called “exciton Bohr radius” having range from very few nm to a few nanometers. When carriers' mobility is limited to an area similar to their de-Broglie wavelength, the effects of size quantization become more noticeable. This implies that carriers will exhibit quantum confinement if they are physically trapped in an area on the order of the material's de-Broglie wavelength.

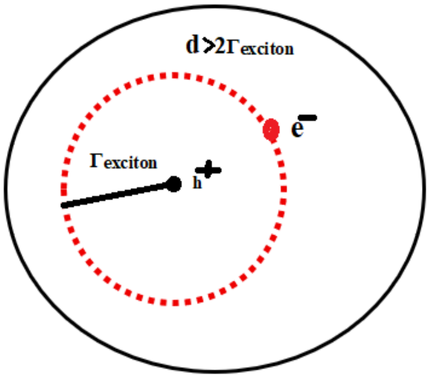

Figure 1: Upon illumination of nanocrystal the created electron-hole pair: the electron moving in circular path around the hole Re-draw figure from Ref. [3].

Figure 1 depicts that an exciton radius smaller than that of diameter of a particle. In the case, the exciton's electron e^- moves in a circular path around the hole h^+ . Besides in figure 2, exciton radius larger than that of diameter of a particle. In this case an electron, which is paired of excitons and excited by a UV quantum, actually, the formation of an exciton is impossible and the path of the electron within the particle is random instead of circular. This phenomenon is generally known as “quantum confinement.”

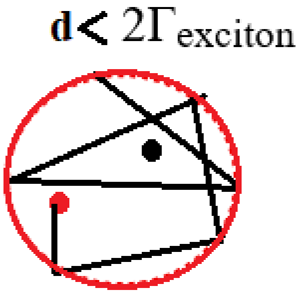

Figure 1: Upon illumination of nanocrystal the created electron-hole pair: the electron moving in random path Re-draw figure from Ref. [3].

This can be considered a free electron in a nanoparticle having the diameter d. However, such a problem can be solved using the Schrodinger wave equation. But here this problem can be described using the basic laws of quantum mechanics. Let us consider a one-dimensional system that representing the particle diameter L like a box, the condition for a standing wave consisting of n half-waves of the wavelength λ is [3]:

$$\frac{n\lambda}{2} = L \, . \qquad (1)$$

By using De Broglie relationship, this leads to

$$p = mv = \frac{h}{\lambda} = \frac{nh}{2L} \qquad (2)$$

where p = momentum, m = mass, v = velocity of the electron, and h is Planck's constant. Now the energy E_n, can be calculated as

$$\mathrm{E}_n = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{n^2h^2}{8mL^2} = k\frac{n^2}{L^2} \qquad (3)$$

Above equation shows that the energy of electron is inversely quadratic to the particle size. This describes the blue shift of the absorption edges with decreasing particle size. The energy difference ΔE between the two quantum levels n and n+1 describes the energy of an emitted photon.

$$\mathrm{E}_{n+1} - \mathrm{E}_n = \Delta\mathrm{E} = \frac{(2n+1)h^2}{8mL^2}$$

leading to

$$\lambda = \frac{8mcL^2}{(2n+1)h} \qquad (4)$$

Equation (4) clearly shows the blue shift with decreasing size *L* of the box, which is equivalent to the particle size D, or the wavelength of the emitted photon increases quadratically with the particle size D.

III. UV-VIS SPECTROSCOPY

Optical spectroscopy is a primary technique for the characterization of nanomaterials. It is based on absorption, emission, and vibration, and is therefore classified into absorption and emission spectroscopy and vibrational spectroscopy. In the first method through absorption and emission electronic structure of an atom, ion, molecule, or crystal is determined. Providing the energy to electron in ground state it raised to higher energy level i.e. excited states is called absorption then allowing them to relax back to the ground state (is called emission). In vibrational techniques, when photons interact with the species present in the sample, energy is either transferred to or from the sample. This occurs as a result of vibrational excitation or de-excitation.

UV-vis spectroscopy is based on the principle of absorption. In this technique, there is a direct relationship between the path length of light passing through the sample solution and the amount of absorption. This relationship is known as the Beer-Lambert law [4]. According to this law,

$$A = \varepsilon \, l \, c \qquad (5)$$

where A= the absorbance of the sample,

ε = molar absorptivity or molar absorption coefficient,

l= length of the light path in the solution (cm), and

c = concentration of the solution (moles/L).

A. *Principle of a UV-Visible Spectroscopy*

In UV-Vis spectroscopy, a lamp generates light in the visible and UV range. Tungsten or xenon is used to produce this light. This light is then separated into different wavelengths using a diffraction grating. The light of each wavelength is then passed through the sample material and a reference material, and the transmitted light is detected. The difference of light wavelength obtained from sample material and reference material may be plotted on a graph as I versus wavelength.

Absorption may be presented as
transmittance ($T = I/I_0$) or
absorbance ($A = \log I_0/I$).

If no absorption has occurred, T = 1.0 and *A*= 0. Here I_0 is the intensity of the reference beam and I is the intensity of the sample beam.

Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance). The wavelength of maximum absorbance is a characteristic value, designated as λ_{max}. Different compounds may have very different absorption maxima and absorbances.

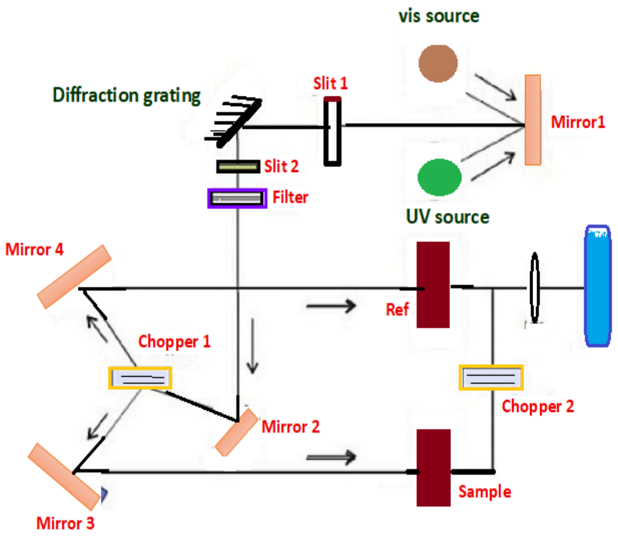

Figure3: Working principle of a UV-Visible Spectroscopy Re-draw figure from Ref. [5].

The relation between A and T is:

$$A = 2 - \log \%T. \tag{6}$$

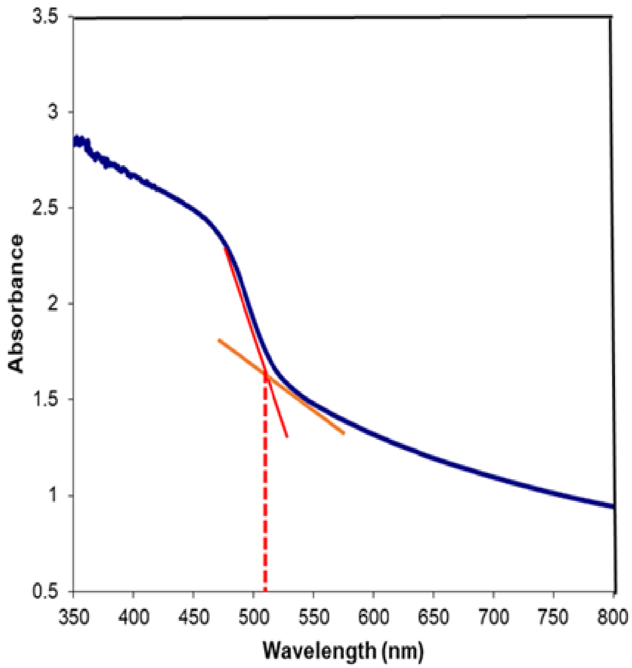

Figure 4: A typical absorption spectra to estimate the band gap of materials

B. Bandgap determination of materials

The relation between absorption coefficient (α) of a thin films and the transmittance (T) value can be expressed as [6]:

$$\alpha = -\ln(T\%)/d \tag{7}$$

Where d = thickness of the film,

A classical relation [7] is used to find out the nature of optical transition.

$$\alpha = \frac{\mathrm{A}\left(h\nu - \mathrm{E}_g\right)^n}{h\nu} \qquad (8)$$

E_g = Band gap energy,
$h\nu$ = photon energy,
A = characteristic parameter and 'n' is constant.

For all allowed direct transition n=1/2 and allowed indirect transition n=2. Thus, a plot between quantity $(\alpha h\upsilon)^2$ against hυ is redraw in excel sheet, if it is linear then the transition is direct allowed. The plot between $(\alpha h\upsilon)^2$ and hυ is known as Tauc plot [8].

The band gap energy E_g is determined by extrapolating the linear portion of the curve to the energy axis at $\alpha = 0$. The value of optical bandgap can also be estimated by a simple technique from the absorption or transmittance spectra. In the technique a projection is draw on the two slops of the spectra at wavelength (or hυ) axis as shown in the figure 4.

These two projections intersect at a certain point, and a perpendicular line is drawn from this intersection point to the energy axis. This point on the energy axis is then used to determine the band gap.

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