Nano Sensors

PhD/ MTech/ BTech
Course No.: EEL7450
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Prof. AJAY AGARWAL
ELECTRICAL ENGINEERING
IIT JODHPUR

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Nanoscale Characterization

Important characterizations for nanomaterials and nanostructures are:

1. Structural Characterization
    1. X-ray diffraction (XRD),
    2. Various electron microscopy (EM) including
        i. scanning electron microscopy (SEM)
        ii. transmission microscopy (TEM), and
        iii. scanning probe microscopy (SPM)
            i. scanning tunneling microscopy (STM) and
            ii. atomic force microscopy (AFM)
    3. Gas adsorption
2. Chemical Characterization
    1. Optical spectroscopy
    2. Electron spectroscopy
    3. Ionic spectrometry

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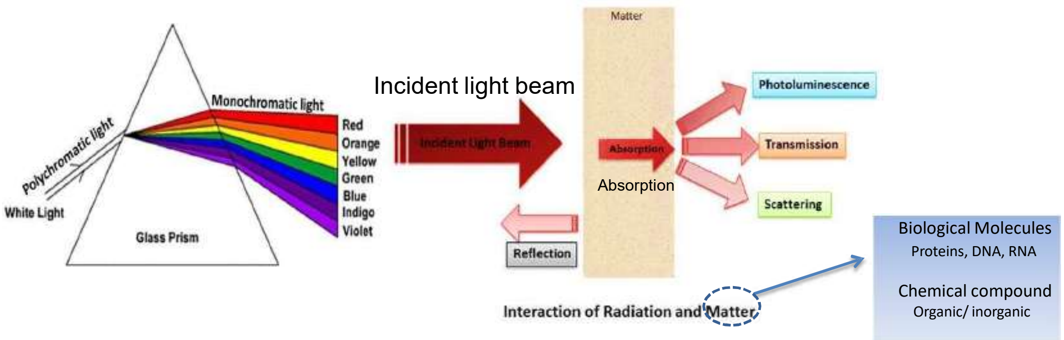
Introduction to Spectroscopy

Spectroscopy/ Spectrometry/ Spectrophotometry

- **Spectroscopy is the branch of science that deals with the study of interaction of electromagnetic radiation with matter [**as a function of wavelength (λ)**]**.



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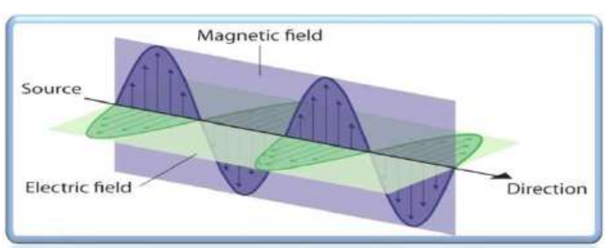
Electromagnetic Radiation

- Electromagnetic radiation consist of discrete packages of energy which are called as photons.
- A photon consists of an oscillating electric field (E) & an oscillating magnetic field (M) which are perpendicular to each other.



- The relationship between frequency & wavelength can be written as: $\nu = c/\lambda$
- Photon energy, $E = h\nu = hc/\lambda$

Where, ν is frequency; c is speed of light; λ is wavelength

E, known as photon energy, h, is known as the Planck constant.

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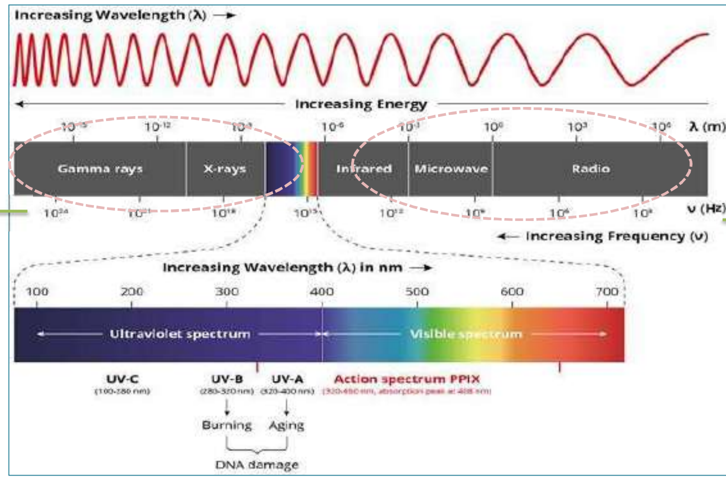
Electromagnetic Radiation

Shorter Wavelengths
High Energy Rays



longer Wavelength
low Energy Rays

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Importance and Principle of Spectroscopy

Spectrometry is the spectroscopic technique often used in physical & analytical chemistry, materials analysis, and biological laboratories for the identification of molecular structure of chemical compounds

- ✓ **Detection of Functional Groups**
- ✓ **Detection of Impurities**
- ✓ **Measurement of the concentration of molecules (or amount of given species).**
- ✓ **Determination of nature of the chemical bonds/ conjugation in the organic compounds**

- *The principle is based on the* ***measurement*** *of intensity spectrum of the radiation when passed through a sample containing atoms / molecules.*
- *Spectrometer is an instrument design to measure the spectrum of a compound.*
- *Spectrum is a graph of intensity of absorbed or emitted radiation by sample verses frequency (ν) or wavelength (λ).*

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Classification of Spectroscopy

Most spectroscopic methods are differentiated as either atomic or molecular based on whether or not they apply to atoms or molecules.

The study of spectroscopy can be carried out under the following two heads:

Atomic Spectroscopy

- Interaction of electromagnetic radiation with **atoms** is called atomic spectroscopy.
- This results in **transitions within the electronic state** (ground state to higher energy states).
- The spectrum obtained is a line spectrum.

Molecular Spectroscopy

- Interaction of electromagnetic radiation with **molecules** is called Molecular spectroscopy.
- This may result in **transitions between rotational, vibrational and electronic energy levels**.
- The spectrum obtained is a complicated spectrum.

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Differences between Atomic and Molecular spectra		
	Atomic spectra	**Molecular spectra**
1	It is produced due to interaction of atoms with Electromagnetic radiation	It is obtained from the interaction of molecules with electromagnetic radiation.
2	Atomic spectra are Line spectra.	Molecular spectra are complicated spectra.
3	It is obtained due to electronic transition in an element	It is produced due to vibrational, rotational and electronic transition in a molecule.

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Interaction of EMR with matter

1. Absorption Spectroscopy:

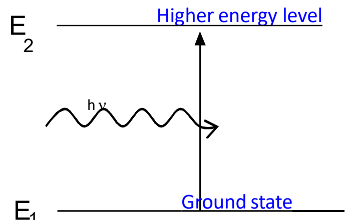
An analytical technique which concerns with the measurement of absorption of electromagnetic radiation.

e.g. UV (190 - 400 nm), Visible (400 - 800 nm) Spectroscopy, IR Spectroscopy (0.76 - 15 μm), Nuclear Magnetic Resonance Spectroscopy (NMR) (Radio frequencies,10 - 1000 cm)

If electromagnetic radiations of certain wavelength range are passed through the substance under analysis, radiations of certain wavelengths are absorbed by the substance.

The wavelength is absorbed by some specific functional group of the compound.

The characterization of the material by study of absorption is called the absorption spectroscopy.



Absorption Spectroscopy

Absorption spectroscopy uses the range of the electromagnetic spectra in which a substance absorbs.

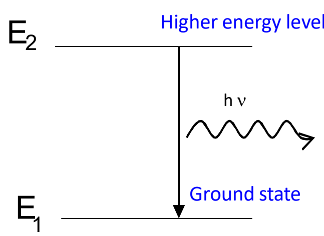
2. Emission Spectroscopy:

*An analytical technique in which **emission** (of a particle or radiation) is dispersed according to some property of the emission & the amount of dispersion is measured.*

e.g. Mass Spectroscopy (MS) and Photoluminescence (PL)

Emission spectroscopy

- If electromagnetic radiation is passed through a substance or thermal energy is given to the substance under analysis, the energy is absorbed by the atom.
- The electrons in the ground state get excited to higher energy metastable states.
- These excited electrons are short lived. So, they emit energy to return to the stable state.
- The study of this is called the emission spectroscopy.
- The spectrum obtained is called the emission spectrum.



Emission Spectroscopy

2. Emission Spectroscopy:

Fluorescence

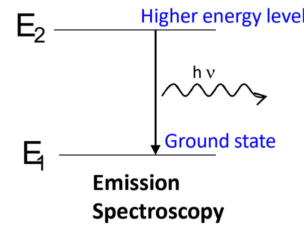
- The electron in the excited level return to it's ground state either directly or in steps with the emission of certain amount of energy.
- When this **emission of light is instantaneous** the phenomenon is known as **fluorescence**

Phosphorescence

- When the electron in the excited level return to it's ground state with the **emission of light after some time lag**, it is known as **phosphorescence**

Photochemical reaction

- When the absorbed energy is stored by the atom or molecule and used in producing some chemical reaction, the resulting chemical reaction is called **photochemical reaction.**



Emission spectroscopy uses the range of electromagnetic spectra in which a substance radiates (emits).
The substance first must **absorb** energy. This energy can be from a **variety of sources**, which determines the name of the **subsequent emission**, like luminescence.

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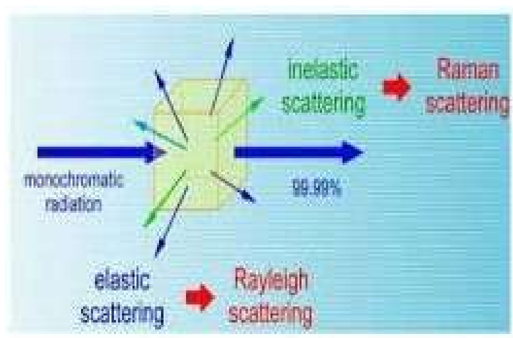
3. Scattering Spectroscopy:

An analytical technique which concerns with the measurement of scattering of electromagnetic radiation.

e.g. Raman Spectroscopy,

- Scattering spectroscopy measures the amount of light that a substance scatters at certain wavelengths, **incident angles**, & polarization angles.
- The scattering process is much faster than the absorption/ emission process.
- One of the ***most useful applications*** of light scattering spectroscopy is → **Raman spectroscopy.**



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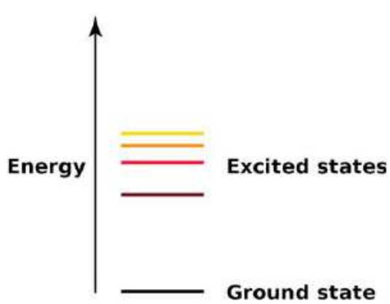
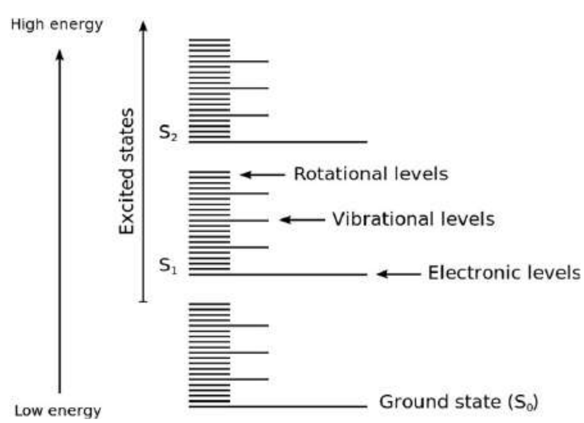
Energy levels of a molecule present in a compound



Energy Levels of an Atom



Electronic, Vibrational, and Rotational Energy Levels of a Diatomic Molecule

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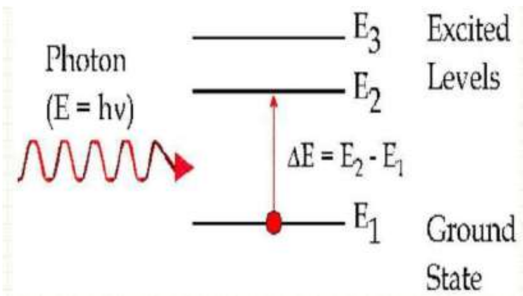
1. Electronic Energy Levels:

- At room temperature the molecules are in the lowest energy levels E_0.
- When the **molecules absorb** ***UV-visible*** light from EMR, one of the **outermost** bond / lone pair electron is **promoted to higher energy** state such as E_1, E_2, …E_n, etc. is called as electronic transition and the difference is as:

$$\Delta E = h\,\nu = E_n - E_0 \qquad \text{where } (n = 1, 2, 3, \ldots \text{ etc})$$

$$\Delta E = 35 \text{ to } 71 \text{ kcal/mole}$$



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2. Vibrational Energy Levels:

- These are less energy level than electronic energy levels.
- The spacing between energy levels are relatively small i.e. 0.01 to 10 kcal/mole.
- e.g. when IR radiation is absorbed, molecules are excited from one vibrational level to another or it vibrates with higher amplitude.

3. Rotational Energy Levels:

- These energy levels are **quantized** & **discrete**.
- The **spacing** between energy levels are **even smaller** than vibrational energy levels.

$$\Delta E_{rotational} < \Delta E_{vibrational} < \Delta E_{electronic}$$

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Classification of Different Spectroscopic Methods

Absorption Spectroscopy

Atomic Spectroscopy

- *Atomic Absorption Spectroscopy*

Molecular Spectroscopy

- *Ultraviolet-visible Spectroscopy*
- *IR Spectroscopy*
- *Nuclear Magnetic Resonance Spectroscopy*

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Emission Spectroscopy

- *Fluorescence/ Photoluminescence Spectroscopy (light)*
- *Mass Spectroscopy (particles)*

Scattering Spectroscopy

- *Raman Spectroscopy*

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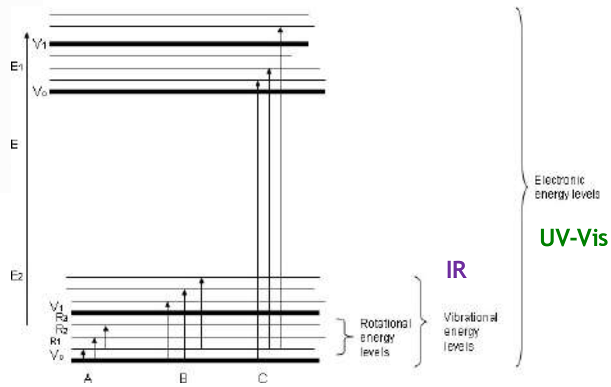
Absorption Spectroscopy

- Electromagnetic radiation is energy and when a substance absorbs electromagnetic radiation, it gains energy. The energy gained by the molecule in this way-
- may break bonds within the molecule (γ ray)
- may raise electrons to higher energy level (UV and visible spectroscopy)
- may bring about increased vibration and rotation of atom (IR spectroscopy)
- may change nucleus or electronic spin (microwave used by NMR)



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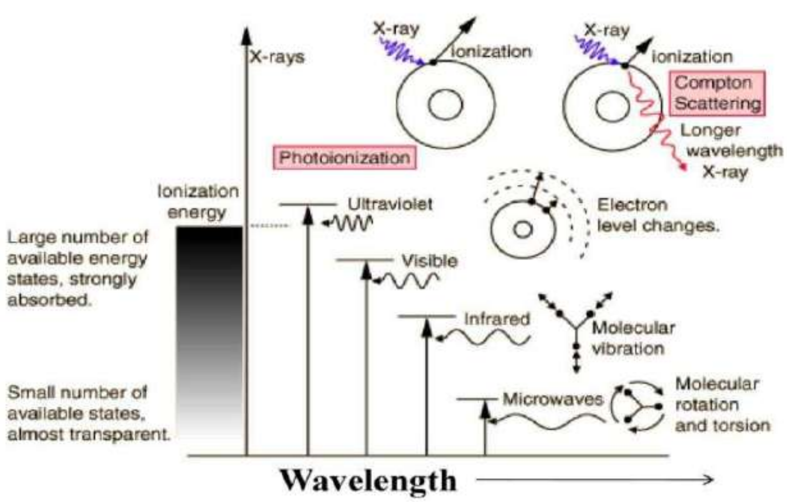
Interaction of radiation with matter



- **If there are no available quantized energy levels matching the quantum energy of the incident radiation, *then the material will be transparent to that radiation***

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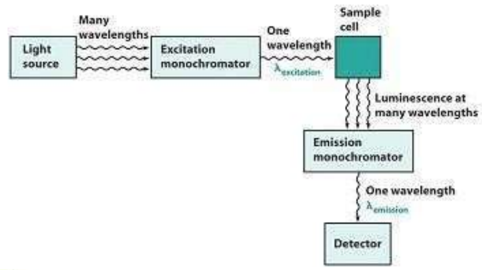
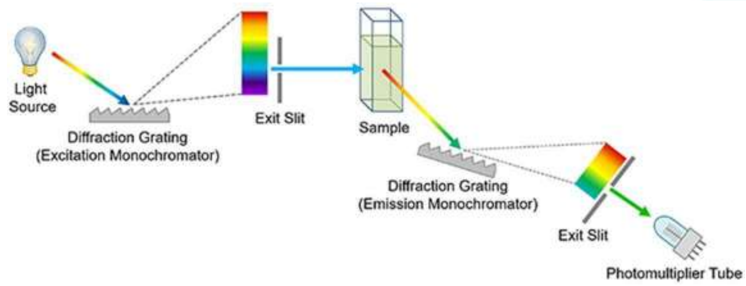
Photoluminescence Spectrophotometer





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Light Sources:

- Excitation sources
  - Xenon lamp ,
  - Quartz halogen,
  - mercury arc lamps
  - Lasers.

Lamp	Wavelengths
Mercury arc lamp	366, 405, 436, 546, 578
Xenon arc lamp	250-1000
Tungsten–halogen lamp	350-1000
Blue diode laser / LED	4xx nm
Helium–cadmium laser	325, 442
Argon ion laser	457, 488, 514
Nd:YAG laser	532
Helium–neon laser	633
Yellow diode laser / LED	5xx nm
Krypton ion laser	568, 647
Red diode laser / LED	6xx nm

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Questions / Discussions

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Excitation and Emission Monochromators:

- Two monochromators are used
  - One for tuning the wavelength of the exciting beam
  - Second one for analysis of the fluorescence emission.
- Due to the emitted light always having a lower energy than the exciting light,
  - the wavelength of the excitation monochromator is set at a lower wavelength than the emission monochromator.

- Monochromators :
  - Interference filters
  - colored glass filters
  - Gratings
  - Prisms.
- Either type of filter is combined with appropriate sharp cutof glass filters to form a single fiter package, which removes
  - undesired transmission of higher orders
  - provides narrow bandwidth, higher peak wavelength transmission, and increased band slope.

Colored glass filters

- used for both excitation and emission wavelength selection,
  - but they are more susceptible to transmitting stray light and unwanted florescence.

Grating monochromators

- Isolate regions of the spectrum
- An advantage of the grating monochromator
  - Provides selectivity of the excitation and emission wavelengths required when working with new fluorophores with absorbance

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Photodetectors:

- Photomultiplier tube (PMT)
- Chargecoupled detector (CCD)

PMT

- commonly used detector in spectroflorometers
- Important features of the PMT for florescence measurements consist of :
  - (1) a wide choice of spectral responses,
  - (2)nanosecond photon response time,
  - (3)sensitivity.
    - Sensitivity is due to the possible gain of 10^6 electrons at the anode of the PMT for each incident photon hitting the photo cathode

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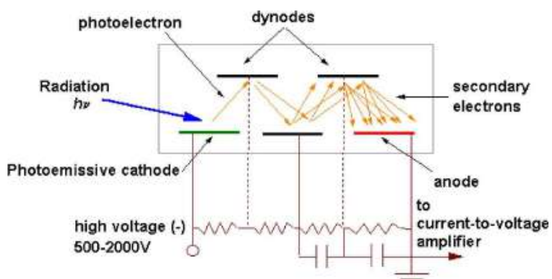
PMT & CCD



Charge-Coupled Detector.

- CCDs are multichannel devices with a dynamic range and a signal-to-noise ratio that are superior to those of PMTs.
- Composed of a large number of photo-detecting shift registers that are read horizontally and vertically.
- Because of their ability to detect very low levels of light
  - they have been used for molecular fluorescence measurement of very low concentrations of fluorescent molecules

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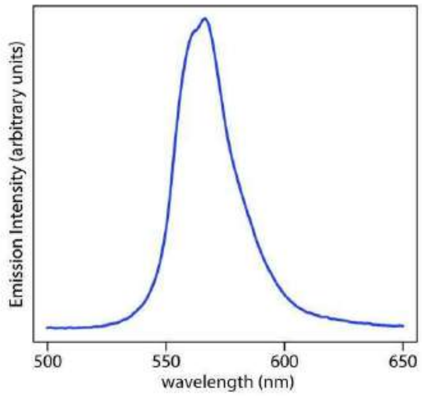
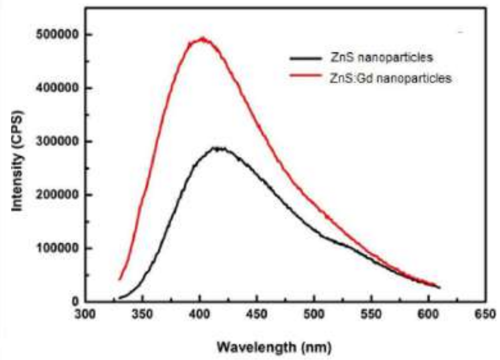
A Typical PL Spectrum:





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Analysis of some Important Parameters

- Peak Intensity (probability of dominant electronic transitions)
- Peak Wavelength
  (Bandgap of material, $E_g = hc/\lambda$)
- Time period (lifetime of excited state)

- **Radiative lifetime, τ_r, is related to k_r**

$$\tau_r = \frac{1}{k_r}$$

k_r Radiative rate constant

- **Quantum yield of fluorescence, Φ_f, is defined as:**

$$\Phi_f = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}}$$

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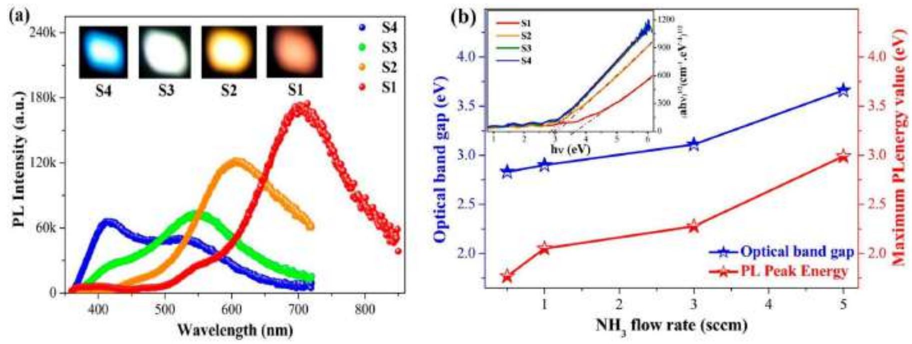
Bandgap, $E_g = hc/\lambda$



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