Optical Characterization

- UV–Visible Spectroscopy

- Photoluminescence (PL) Spectroscopy

UV–VISIBLE SPECTROSCOPY FOR NANOMATERIALS

UV–Visible (UV–Vis) spectroscopy is an optical characterization technique that studies the **interaction of ultraviolet and visible light (200–800 nm)** with matter.
In nanomaterials research, UV–Vis is indispensable for probing:

- Optical absorption behavior
- Band gap energy of semiconductors
- Size-dependent effects (quantum confinement)
- Surface plasmon resonance (SPR) in metal nanoparticles
- Concentration and dispersion stability

- UV–Vis spectroscopy is based on electronic transitions. When photons of suitable energy strike a material, electrons are excited from a lower energy level to a higher one.
- Common transitions:σ → σ*n → π*π → π*Valence band → conduction band (in semiconductors)
- Absorption occurs when: $h\nu = E_2 - E_1$

Why UV–Vis Is Important for Nanomaterials

- Nanomaterials show **size-dependent optical properties** due to:

✓ **Quantum confinement effect**

✓ Large surface-to-volume ratio

✓ Altered electronic band structure

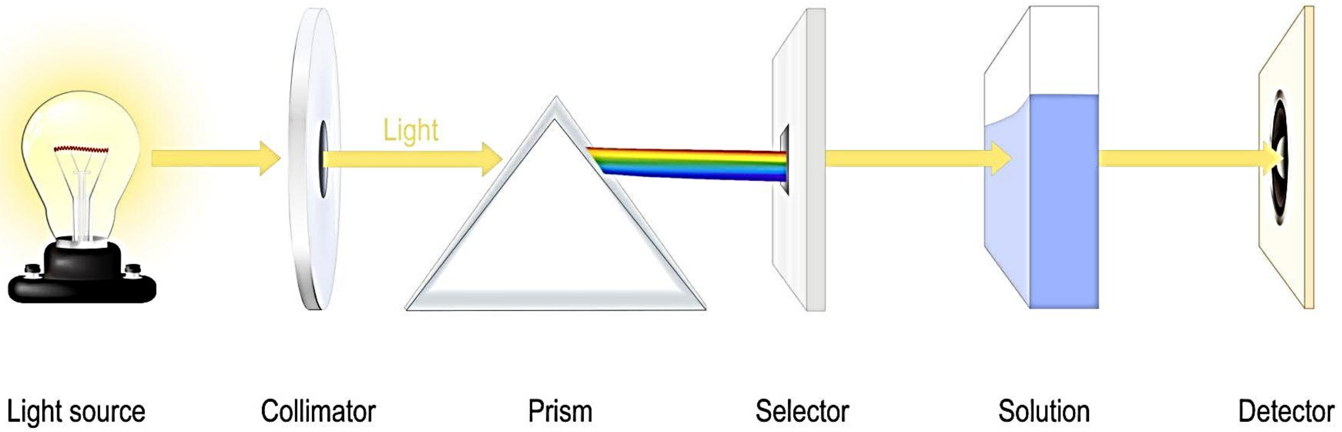
- As particle size decreases:

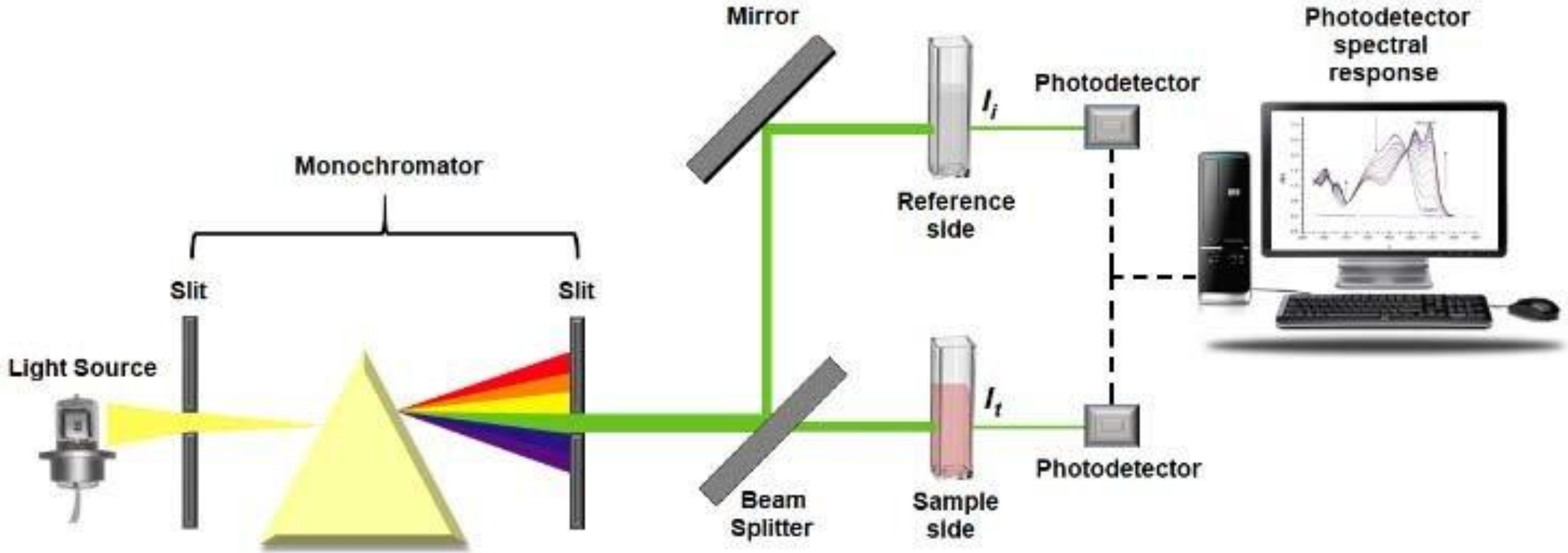
✓ Band gap increases

✓ Absorption edge shifts toward shorter wavelength (blue shift)

- UV–Vis captures these changes clearly.

Spectrophotometer





Radiation Source	Monochromator
The source provides continuous radiation in the **UV and visible regions**.	Selects a **single wavelength** from the broad radiation source.
(a) Deuterium Lamp	**Components of Monochromator**
•Range: **190–350 nm (UV region)**	•Entrance slit
•Produces stable UV radiation	•Collimating mirror
(b) Tungsten–Halogen Lamp	•Diffraction grating or prism
•Range: **350–800 nm (Visible region)**	•Focusing mirror
•Produces intense visible light	•Exit slit
Modern instruments automatically switch between lamps.	**Function:**
Function: Supplies electromagnetic radiation for analysis.	Disperses polychromatic light into individual wavelengths and selects desired wavelength.
	Importance:
	Improves resolution and accuracy.

Beam Splitter (Double-Beam Instruments)

Divides light into:

- **Reference beam**
- **Sample beam**

Both beams pass simultaneously through reference & sample cuvettes.

Advantage:

Compensates for fluctuations in source intensity.

Sample Holder (Cuvette Compartment)

Holds the sample solution.

Cuvette Types

- **Quartz cuvette** → UV & Visible
- **Glass/Plastic cuvette** → Visible only

Typical path length: **1 cm**

Function:

Allows radiation to pass through sample.

Photoluminescence (PL) Spectroscopy

- Photoluminescence (PL) spectroscopy is an **optical characterization technique** that studies the **light emitted by a material after it absorbs photons**.

- For nanomaterials, PL is extremely important because it gives information about:

✓Band gap energy

✓Defect states

✓Recombination processes

✓Charge carrier dynamics

✓Surface states

Basic Principle of PL

- PL is based on three main steps:

❖Excitation: A photon of energy $h\nu$ excites an electron from the valence band to the conduction band.

❖Relaxation: The excited electron loses some energy through non-radiative processes.

❖Emission: The electron recombines with a hole and emits light. $E_{emission}$<$E_{excitation}$.

❖This energy difference is called Stokes shift.

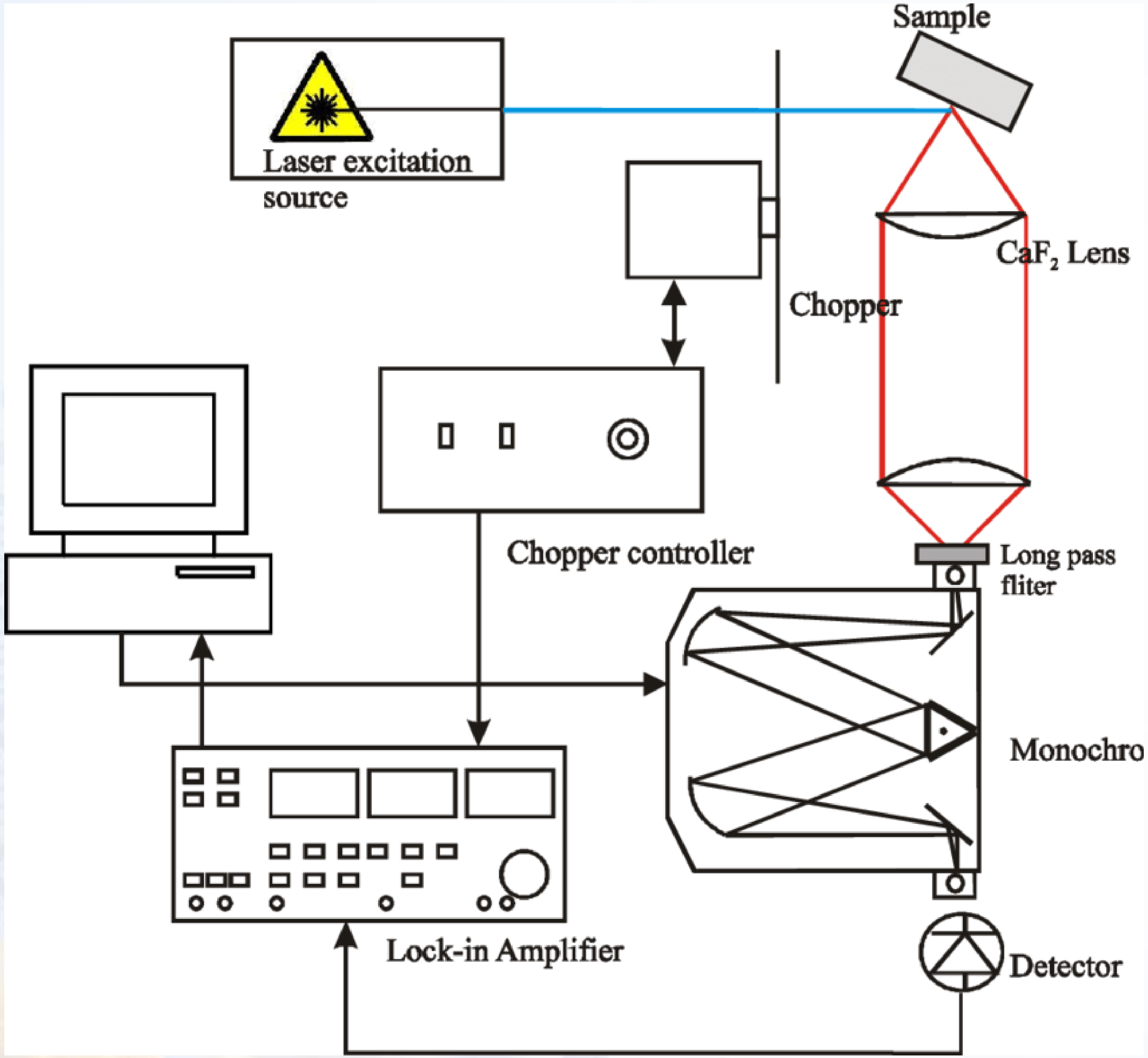
Types of Photoluminescence

(A) Fluorescence

- Fast emission (10^{-9} s)
- Common in semiconductors

(B) Phosphorescence

- Slow emission
- Involves forbidden transitions
- Most semiconductor nanomaterials show fluorescence.



Main Components:

Excitation Source

- Laser or Xenon lamp
- Provides monochromatic light

Monochromator (Excitation Side)

- Selects specific excitation wavelength

Sample Holder

Emission Monochromator

- Separates emitted wavelengths

Detector

- Photomultiplier tube (PMT)

Data System

Why PL Is Important for Nanomaterials

Nanomaterials have:

✓ High surface area

✓ Surface defects

✓ Quantum confinement effects

- PL helps in studying:

✓ Band-to-band recombination

✓ Defect-related emission

✓ Surface trap states

✓ Charge recombination rate

PL in Semiconductor Nanoparticles

(A) Band-Edge Emission

•Sharp peak

•Near band gap energy

(B) Defect Emission

•Broad peak

•Due to oxygen vacancies, surface defects

Example: ZnO nanoparticles

•UV peak → band-edge emission

•Visible peak → defect emission

Quantum Confinement Effect in PL

As particle size decreases:

- Band gap increases
- Emission peak shifts toward shorter wavelength (blue shift)

This confirms nanoscale size.

PL and Photocatalytic Activity

Very important for PG students:

- High PL intensity → high recombination rate
- Low PL intensity → better charge separation

Better charge separation → better photocatalyst.

Thus, lower PL intensity often indicates improved photocatalytic efficiency.

Advantages of PL

✓ Non-destructive

✓ Highly sensitive

✓ Simple sample preparation

✓ Detects defects

Limitations

✕ Only luminescent materials can be studied

✕ Surface contamination affects results

✕ Quantitative analysis limited