Chapter 3

Smart materials: Natural Conducting Polymers and Nano Phosphors
SMART MATERIALS: NATURAL CONDUCTING POLYMERS AND NANO PHOSPHORS

With the development of science and technology, many new, high quality and cost efficient materials have come into use in various fields of engineering. In the last ten decades, multifunctional materials have been developed with optimisation of various properties [19-21]. A natural material is considered as some physical matter, sourced from living beings or otherwise from the earth. Natural materials can be conventional materials or advanced materials [34]. There can be composite materials with addition of two different compounds materials and recently, ‘smart materials’ have gained importance as they exhibit properties responding to the system or the environment of operation. New generation of nano materials, with multifold efficiency compared to their conventional counterparts can be placed in this category [35].

![Classification of Materials](image)

Fig.3.1 Figure indicates classification of materials.

Describing natural conducting polymers i.e., MP microfibers and quantum nano phosphors, this chapter covers detailed explanation of the specific materials employed, and is divided in the following two sub sections:

**Natural Conducting Polymers: MP microfibers**

**Nano phosphors: CdSe-CdS core shell QDs and rods**
3.1 Natural Conducting Polymers: MP microfibers

3.1.1 Polymers

A polymer is a large molecule comprised of repeating structural units joined by covalent bonds. "Poly" comes from the Greek word for "many" and "mer" comes from the Greek word for "parts" or "units" [34-36]. Polymer has grown as an interdisciplinary area with the objective of miniaturization of electronics to the molecular level and many others. The fine tuning of the physics and chemistry of polymers today, tailors their properties in many ways stimulated by the same objective as the early work on conventional polymers. Only time can tell the extent up to which the scientists are able to exploit their riches.

3.1.2 Classification of polymers

On the basis of the degree or polymerization (n), polymers can be classified as high polymers and oligopolymers [37]. Polymers by means of a far above the ground amount of n are called "high polymers" and by means of nearer to the ground value of n are called “oligopolymers". Since far above the ground polymers have very far above the ground molecular weight (10^4 to 10^6), they are called "macro molecules". Macromolecules consisting of monomers of identical or different chemical structures are called homo-polymers or copolymers, respectively. According to the arrangement of monomeric units, the macromolecules can be classified into linear (one dimensional), branched (two dimensional) or cross linked (three dimensional) structures. Linear copolymers, inside which the units of every kind form fairly long incessant sequence (block), are called "block copolymers". Again, in a branched and cross linked copolymer, the monomers may be in order inside the chain at chance or in usual style. The former is called "statistical" or “irregular” and the latter is called "regular" copolymer. Branched copolymers with one type or monomers in their major chain and one more kind of monomer in their surface chains are called “graft copolymers”. If the main chain or polymer consists of same type or atoms, they are called "homochain polymers" and when it contains different types of atoms, they are known as "heterochain polymers". If the monomers are arranged in the polymer chain in a random fashion, the polymer is called "atactic"; if all the side groups lie on the same side of the chain, it is called “isotactic”, and if they lie in alternating fashion, it is “syndiotactic".
3.1.3 Properties of polymers

Amorphous Properties

Solids, in which there is no long range order of the positions of the atoms, are called amorphous solids. Many polymeric solids are mainly found in amorphous state. Amorphous polymeric solids can exist in two different states, viz., the ‘rubbery’ and the ‘glassy’ states. In the melt, thermal energy is sufficiently high for long segments of each polymer chain to move in random micro Brownian motions [57]. As the melt is cooled, a temperature is reached at which all long range segmental motion ceases the transition.

Thermal Properties

The thermal stability of polymers extremely significant for their appropriateness for service [58]. The effect of high temperature causes most polymers to degrade, i.e., their macro molecules break up into smaller molecules or monomers. In others, beneath long lasting heating, there occurs a random breaking of bonds and the configuration of steady molecules by means of an inferior molecular weight, and from time to time the detachment of near to the ground molecular products because of reactions of side groups without any appreciable change in the initial molecular weight. Such belongings too reason the chaotic irritated flanked with the macro molecules and the configuration or split and cross linked arrangement. The rates of radical polymerization and depolymerisation increase with the temperature. At a certain temperature, these rates may become equal. The higher the heat or polymerization, the lower is the tendency of a polymer to decompose thermally by a depolymerisation mechanism (i.e., with the formation of monomer). At a heat of polymerization below 60 kJ/mol, a polymer mainly degrades to a monomer. The improvement of thermal stability of polymers is associated with the factors of inhibiting these reactions or with the synthesis of more thermo stable polymer structures.

Mechanical Properties

Strength is the property of a material to resist rupture under the action of mechanical stresses [58]. A material can be ruptured by the effect or an applied external force, in rapid cooling from a melt when appreciable residual (internal) stresses arise in it that may soon cause cracking, or under the action of external forces when a neck appears in the specimen; although in this case the parts of the specimen are joined via the neck, the intactness of the specimen is actually disturbed.
Also strength is an important technical characteristic of a polymer. It can often be measured quite simply by using known, or difficult to understand mechanism or failure, or the laws relating the strength of a polymer to its structure. The strength of a polymer is generally several times lower than the theoretical one, which is due to the presence of defects such as stress concentrations. There is a dispersion of the strength values, and the scale factor affects the strength. Griffith’s theory gives a qualitatively correct explanation of the laws or the strength or solid polymers. The deviation from this theory is greater when the fraction of elastic stress in the specimen being tested to failure is spent on losses associated with the deformation processes.

**Electronic and Electroactive Properties**

Polymers can be considered as organic semiconductors [59], and the concept of energy band theory can be used to characterize their electronic states and properties. The electronic properties are related to the heat capacity and thermal conductivity. For this fact, one should use electronic energy bands and Fermi-Dirac statistics for electrons, where one should use idea of lattice vibration frequencies, and the Bose-Einstein statistics for phonon. All other properties are concerned with the response or the mobile electrons in solids to external electric and magnetic fields.

Again Electroactive Polymers (EAPs) are plastic materials that change shape and size when impressed with some voltage or current. Recent progress in the field of EAP led to the development of materials that exhibit large displacement in response to electrical stimulation. EAP has a good operational similarity to that of biological muscles, and hence this capability or EAP makes it attractive for bio mimetic and robotic applications.

### 3.1.4 Conducting polymers

The conventional polymers such as wood, fiber, plastics, glass, paper, rubber etc, permit an adequate resistance to electrical conduction and these are dielectrics and insulators. After discovery of conducting polymers like polyacetylene in 1970s, the concept of conducting polymers have gained attention from both communities of science and engineering. Natural polymers also gained attention, including naturally found conducting polymer fibers such as Mimosa pudica Linn, a well known touch sensing herb [60], with mild photoluminescence capacity due to the presence of elemental selenium (Se) in the fiber.
3.1.5  Mimosa pudica plant as a natural conducting polymer

Sensitive plant (*Mimosa pudica* Linn.) or *sensory papillae* (kingdom: Plantae, Family: Fabaceae, Genus: Mimosa, Species: *M. pudica*) is a short lived, creeping annual or perennial herb found in America (South and Central), Tanzania, South Asia, South East Asia and many Pacific Islands having near frequent rainfall. *Mimosa pudica* Linn, a seismonastic plant gets its leaves closed and the petiole hanging down, resultant to perceptible acting on stressors for example a wound, wind down, vibration created, touch stimulus-bath hot and cold variations in illuminations etc [60-61].
Through biomimicking of sensing actuation mechanism found in touch-sensitive Mimosa pudica (MP) plants, it may be feasible to design artificial actuators which are sensitive to touch [61-62]. There are previous examples of efficient devices by mimicking the light sensing mechanism in algae eyespots. There are light-sensitive apparels designed as protective devices filtering harmful light rays from the electromagnetic spectrum [63-65]. Manipulation of appearance or mimicking invisibility like that in chameleons has inspired design of wearables for people during wars or similar areas to hide or become invisible [66]. Additionally, designing of nano electronic fabrics is much within our reach when we shall have the scope to incorporate all fancy e-gadgets in our daily apparels [67].
The plant MP shows quick sensing and actuation with its leaf moving muscle, the so called parvenu, which performs touch sensitive hydraulic actuation. Pulvini are swollen parts at the base of MP leaf stalks or petioles, which act as autonomous organ, housing mechano photoreceptors that enable leaves to move in response to external stimuli [68]. This exhibits one of the remarkable weathering phenomena in plant tissues, when they are touched, and exemplifies the fastest plant movements [69]. Careful observation, analysis and mimicry of
of this methodology is found to be promising in the fields of soft robotics [70], bio mimetic based monitoring [71], artificial muscles and development of bio inspired devices.

3.2 Nano phosphors: CdSe-CdS core shell QDs and rods

Nano phosphors have been widely synthesised throughout the last few years due to their significant potential for application in various high performance devices [66-69]. Nanophosphors are usually synthesized through Hydro Chemical Techniques (HEC), such as colloidal, capping, cluster formation, sol-gel, electrochemical etc. Physical techniques extensively used are molecular beam epitaxy, ionised cluster beam, liquid metal ion source, consolidation, sputtering etc., and are much sophisticated. However most commonly used techniques are chemical precipitation with capping agents, reaction in micro emulsions, sol gel reaction and auto combustion etc.

3.2.1 Semiconductor nanocrystals

Semiconductors in nanocrystalline form show noticeably improved electrical, optical and structural properties as compared with their bulk forms. Some materials are found to be suitable as phosphors due to their significant dimension dependent relative luminescence characteristics when they are doped with suitable impurities in a quantum confined arrangement. The contamination or impurity agents transfer the leading recombination route from the surface states to contamination states. If the contamination induced change can be restricted as in the case of the rare earth elements, the radiative competence of the contamination induced emission increases considerably. Improved quantum property was additionally established with semiconductor nanoparticles of ZnS, PbS, ZnSe and CdSe [66-70].

3.2.2 Core-shell QDs

A group of materials recognised as ‘core-shell semiconducting nano crystals’ exhibit properties in between the two extremities of small individual molecules and semiconducting nanocrystals. In initial stages, on discovery of nanoparticles, single particles were preferred, because of their increased efficiency and versatility over conventional materials. Further, by combining heterogeneous elements, composites were preferred over single nanoparticles, for newer and improved properties and demands for specific applications. During early 1990s,
concentric, multilayer semiconductor nanoparticles were synthesized and those gained popularity, as it improved the properties of semiconducting materials. Such materials were named as ‘core/shell’ nanostructures. With increasing demand for application and with availability of more advanced characterisation techniques, different core/shell nanostructures were developed. The core/shell semiconductor nanocrystals were first investigated in the 1980s, and led to lot many research and publications in 1990s. Multicomponent nanostructures and their synthesis have developed rapidly over recent years.

The type II–VI, IV–VI, and III–V semiconductors, are in general preferred for core/shell configurations. There is sizable number of examples such as CdS/ZnS, CdSe/ZnS, CdSe/CdS etc., to name a few [70-71]. With improved properties, core/shell structures are found to be economically efficient also. In this form, precious and rare materials are coated over cheap and materials in abundance, so as to reduce the usage of the pure materials and thereby reducing cost. Depending on material properties, core/shell structures can be classified based on combination of organic & inorganic materials, for both core and shell.

![Schematic diagram of core/shell structures](image)

Fig.3.5 Schematic diagram of core/shell structures

Quantum dots are fluorescent semiconducting nanocrystals, and have a radius comparable to the Bohr exciton radius of that particular material. Quantum dots are most advanced class of materials, extensively researched and are preferred for many applications mentioned elsewhere, in this thesis.

Electron hole pairs are created in semiconductors due to transition of electrons from valence to conduction band, simultaneously creating a hole in the valence band. Because of
charge separation, electrons and holes remain bound through a weak coulomb force, and this force creates an exciton. Excitons have material specific separation distance, and, the average distance is known as ‘Bohr exciton radius’. When size of the particles decrease and approach nanometer size, and become comparable to Bohr exciton radius, the energy levels become discrete resulting in a large band gap in the semiconductors. This increase in band gap, leads to a blue shift in optical transitions, not observed in bulk materials. The luminescent consequences of quantum dots result from the above [75-76].

Fig.3.6  Schematic diagram of band structure of semiconductors

Quantum confinement in QDs appear, when the QDs are encapsulated in suitable organic surfactants. Quantum dots have a high population of atoms in their surface (surface to volume ratio of atoms are high). The organic surfactants create trap states on the surface of QDs resulting in reduced fluorescence yield. Hence by growing an inorganic layer over the QD cores, a core/shell QD structure is created to arrest the decreasing fluorescence quantum yield, resulting in enhance photoluminescence properties compared to only QDs [13,78]. CdSe/CdS and ZnSe/CdSe core/shell QDs (CSQD) synthesized have reported 85% and 80–90% quantum yield, respectively [79-82].
3.2.3 Types of Core/shell QDs

Depending on the conduction band and valence band positions in semiconductors (distance between them), and the resulting band gap, CSQDs can be classified as the following three categories:

![Diagram of types of core/shell QDs](image)

Fig.3.7 Schematic diagram of type I, reverse type I and type II core/shell structures

In a type I structure, the core can have a smaller band gap than the shell. In reverse type I structure, just the reverse happens, i.e., core has a larger band gap than the shell. However, in type II structure, conduction and valence band of the core is located within the band gap of the shell. As shown below, in Fig 3.8, the electron and hole of an exciton at the CdSe (bandgap: 1.74 eV) /CdS (bandgap: 2.42 eV) border reside in energy states inside the CdSe core.

![Energy band diagram of CdSe/CdS core/shell structure](image)

Fig.3.8 Schematic diagram of energy band diagram of CdSe/CdS core/shell structure.
As mentioned earlier in this chapter, depending on the materials employed, there can be four types of core/shell structures: a) organic/organic, b) inorganic/inorganic, c) organic/inorganic, d) inorganic/organic. In the present work, we have considered the following three types of core/shell quantum dots.

A) CdSe/CdS core shell QDs
B) CdSe/CdS seeded rod
C) CdSe/CdS dot-in-rod

Details about each of these QDs have been described in chapter four.