Chapter 1

INTRODUCTION AND LITERATURE SURVEY

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Nanocomposites, a high performance material exhibit unusual property combinations and unique design possibilities. Polymeric materials containing metal oxide particles constitute a new class of polymer composites materials. The main purpose of the preparation of the nanocomposite is to obtain the synergic effect of the polymer and the inorganic compound. Nanocomposites have a peculiar structure, i.e. a phase separated structure, with a nanoscale interface between the polymer matrix and the inorganic compound (nanophase separated structure). This phase separated structure plays a very important role in the production of a molecular-level synergic effect between the organic and inorganic compounds in nanocomposites. Conducting polymers are combined with metal oxides because of their enhanced physical and electronic properties. Nanocomposite material composed of conducting polymers & oxides have open more field of application such as drug delivery, conductive paints, rechargeable batteries, toners in photocopying, smart windows, etc.
1.1. Introduction

Progress in the field of materials science has taken a new lead since the advent of the nanocluster-based materials or nanocomposites. Nanoclusters are ultrafine particles of nanometer dimensions and whose characteristics are size dependent and are different from those of the atomic and bulk counterparts [1]. Recently nanocomposite materials have become one of the most extensively studied material all over the world as they have shown to possess several technological application such as effective quantum electronic devices, magnetic recording materials sensors etc [2]. Nanocomposites are as multiphase materials, where one of the phases has nanoscale additives and are originating from suitable combinations of two or more such nanoparticles or nanosized objects in some suitable technique, resulting in materials having unique physical properties and wide application potential in diverse areas [1,3]. Novel properties of nanocomposites can be derived from the successful combination of the characteristics of parent constituents into a single material. Materials scientists very often handle such nanocomposites, which are an effective combination of two or more inorganic nanoparticles. They are expected to display unusual properties emerging from the combination of each component [3]. Organic-inorganic composites have attracted considerable attention as they can combine the advantages of both components and may offer special properties through reinforcing or modifying each other [4]. To exploit the full potential of the technological applications with good processability which has ultimately guided scientists toward using conventional polymers as one component of the nanocomposites, resulting in a special class of hybrid materials termed “polymeric nanocomposites”[1]. Significant scientific and technological interest has focused on polymer-inorganic nanocomposites (PINCs) over the last two decades. The use of
inorganic nanoparticles into the polymer matrix can provide high-performance novel materials that find applications in many industrial fields. As a result of the development in nanotechnology, inorganic nanostructured materials have been designed/discovered and fabricated with important cooperative physical phenomena such as superparamagnetism, size-dependent band-gap, ferromagnetism, electron and phonon transport. Yet, they typically suffer from high manufacture expense, and the shaping and further processing of these materials is often difficult and demanding or impossible [5]. These materials are also intimate combinations (up to almost molecular level) of one or more inorganic nanoparticles with a polymer so that unique properties of the former can be taken together with the existing qualities of the latter. Many investigations [6] regarding the development of the incorporation techniques of the nanoparticles into the polymeric matrices have been published. In most of the cases [7] such combinations require blending or mixing of the components, taking the polymer in solution or in melt form.

According to their matrix materials, nanocomposites can be classified as ceramic matrix nanocomposites (CMNC), metal matrix nanocomposites (MMNC), and polymer matrix nanocomposites (PMNC). Organic polymer-based inorganic nanoparticle composites have attracted increasing attention because of their unique properties emerging from the combination of organic and inorganic hybrid materials. Generally, the resultant nanocomposites display enhanced optical, mechanical, magnetic and optoelectronic properties. Therefore, these composites have been widely used in the various fields such as military equipment, safety, protective garments, automotive, aerospace, electronics and optical devices [3]. Moreover nanocomposite material composed of conducting polymers & oxides have open more field of application such as drug
delivery, conductive paints, rechargeable batteries, toners in photocopying, smart windows etc [8, 9].

Synthesis of polymer composites of core shell inorganic particle-polymer has attracted much research attention in recent years because of its properties [10, 11]. In particular, the composites of core shell metal oxide particles-conducting polymer combine the electrical properties of the polymer shell and the magnetic, optical, electrical or catalytic characteristics of the metal oxide core, which could greatly widen their applicability in the fields of catalysis, electronics and optics [12].

Polymers are already widely used in the optoelectronics industry and are playing important roles in various applications. Therefore, the drawbacks of using inorganic nanostructured materials can be overcome by employing a polymer matrix to embed a relatively small content of inorganic nanoparticles. The integration of inorganic nanoparticles into a polymer matrix allows both properties from inorganic nanoparticles and polymer to be combined/enhanced and thus advanced new functions can be generated to the PINCs [13]. The PINCs are one kind of composite materials comprising of nanometer-sized inorganic nanoparticles, typically in the range of 1-100 nm, which are uniformly dispersed in and fixed to a polymer matrix. In this way, the inorganic nanoparticles are acting like ‘additives’ to enhance polymer performance and thus are also termed ‘nano-fillers’ or ‘nano-inclusions’ [14, 15].

Among various PINCs, there is a new class of PINCs comprised of a polymer matrix with ‘transparent nano-fillers’ that is usually fabricated by in-situ polymerization for the formation of nanocomposite and sol-gel methods for the formation of nano-fillers. This class of material is also sometimes called polymer-inorganic ‘hybrid/nanohybrid’ [16, 17].
These nanocomposite materials are especially important due to their bridging role between the world of conducting polymers and that of inorganic materials. Inorganic nanoparticles of different nature and size can be combined with the conducting polymers, giving rise to a host of nanocomposites with interesting physical properties and important application potential. Inorganic materials used for this purpose are generally of two types: nanoparticles and some nanostructured materials or templates. Depending upon the nature of association between the inorganic and organic components, nanocomposites are also classified into two categories: one in which the inorganic particle is embedded in organic matrix and the other where organic polymer is confined into inorganic template. However, in each case the composite formation demands some entrainment or encapsulation (Scheme 1) rather than simple blending or mixing [1].

Scheme 1.1. Formation of Nanocomposite from the Constituents

Inorganic nanoparticles can be introduced into the matrix of a host-conducting polymer either by some suitable chemical route or by an electrochemical incorporation technique. These two synthesis techniques have given birth to materials that are widely different from one another in common physical properties. However, each synthesis route opens a way to a group of materials with complementary behaviour between two components. Chemical origins as well as the special properties of the incorporated materials viz. its
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catalytic property, magnetic susceptibility, colloidal stability, etc. always add
new dimensions to the characteristics of the resulting composites and have
accordingly divided them into different subgroups [1].

Table 1.1. shows relevant categorization of the nanocomposites as
followed here [1].

Table 1.1. Categorization of the nanocomposites

**Conducting Polymer Nanocomposites**

<table>
<thead>
<tr>
<th>Chemical Preparation</th>
<th>Electrochemical Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Nanocomposites with Colloidal stability (SiO₂, SnO₂, BaSO₄ etc are core materials).</td>
<td>1) Nanocomposites with charge storage, optical and electrochromic activities (Incorporation of MnO₂, SnO₂, CB, PB, WO₃, SiO₂ etc).</td>
</tr>
<tr>
<td>2) Nanocomposites with improved physical and mechanical properties (Fe₂O₃, ZrO₂, TiO₂ etc are incorporated materials).</td>
<td>2) Nanocomposites with catalytic activities (incorporation of catalytically active Pd, Pt, Cu etc. microparticles and some bimetallic couples like Pd/Cu etc).</td>
</tr>
<tr>
<td>3) Nanocomposites with magnetic susceptibility (using Fe₃O₄, γ-Fe₂O₃ etc as magnetic particles).</td>
<td>3) Nanocomposites with magnetic susceptibility (γ-Fe₂O₃, magnetic macro anion).</td>
</tr>
<tr>
<td>4) Nanocomposites with dielectric, energy storage, piezoresitive and catalytic activities (with BT, POM, PtO₂, TiO₂, Pt, Pd etc incorporation)</td>
<td></td>
</tr>
<tr>
<td>5) Nanocomposites with surface functionalization (-NH₂/-COOH functional groups on surface and colloidal silica as core).</td>
<td></td>
</tr>
</tbody>
</table>
1.2. Hybrid Materials and Nanocomposites

The term hybrid material is used for many different systems spanning a wide area of different materials, such as crystalline highly ordered coordination polymers, amorphous sol–gel compounds, materials with and without interaction between the inorganic and organic units. The most wide-ranging definition is the following: a hybrid material is a material that includes two moieties blended on the molecular scale. Commonly one of these compounds is inorganic and the other one organic in nature. A more detailed definition distinguishes between the possible interactions connecting the inorganic and organic species. *Class I* hybrid materials are those that show weak interactions between the two phases, such as Van der Waals, hydrogen bonding or weak electrostatic interactions. *Class II* hybrid materials are those that show strong chemical interactions between the components. Because of the gradual change in the strength of chemical interactions it becomes clear that there is a steady transition between weak and strong interactions. For example there are hydrogen bonds that are definitely stronger than for example weak coordinative bonds [18].

The so-called hybrid organic–inorganic materials [19] are not simply physical mixtures. They can be broadly defined as nanocomposites with organic and inorganic components, intimately mixed. Indeed, hybrids are either homogeneous systems derived from monomers and miscible organic and inorganic components, or heterogeneous systems (nanocomposites) where at least one of the components’ domains has a dimension ranging from some Å to several nanometers [20]. It is obvious that properties of these materials are not only the sum of the individual contributions of both phases, but the role of the inner interfaces could be predominant. The nature of the interface has
been used to divide these materials grossly into two distinct classes [20]. In class I, organic and inorganic components are embedded and only weak bonds (hydrogen, van der Waals or ionic bonds) give the cohesion to the whole structure. In class II materials the two phases are linked together through strong chemical bonds (covalent or ionic bonds) [19]. Maya blue is a beautiful example of a remarkable quite old man-made class I hybrid material whose conception was the fruit of an ancient serendipitous discovery. Maya blue is a hybrid organic–inorganic material with molecules of the natural blue indigo encapsulated within the channels of a clay mineral known as palygorskite. It is a man made material that combines the color of the organic pigment and the resistance of the inorganic host, a synergic material, with properties and performance well beyond those of a simple mixture of its components. Paints are a good link between Mayas and modern applications of hybrids [19].

### Different chemical interactions and their respective Strength [18]

<table>
<thead>
<tr>
<th>Type of Interaction</th>
<th>Strength (kJ/mol)</th>
<th>Range</th>
<th>Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van der Waals</td>
<td>ca.50</td>
<td>Short</td>
<td>Nonselective, Nondirectional</td>
</tr>
<tr>
<td>H-bonding</td>
<td>5-65</td>
<td>Short</td>
<td>Selective, Directional</td>
</tr>
<tr>
<td>Coordination bonding</td>
<td>50-200</td>
<td>Short</td>
<td>Directional</td>
</tr>
<tr>
<td>Ionic</td>
<td>50-250*</td>
<td>Short</td>
<td>Nonselective</td>
</tr>
<tr>
<td>Covalent</td>
<td>350</td>
<td>Short</td>
<td>Predominantly irreversible</td>
</tr>
</tbody>
</table>

* Depending on solvent and ion solution; data are for organic media

In addition to the bonding characteristics, structural properties can also be used to distinguish between various hybrid materials. An organic moiety containing a functional group that allows the attachment to an inorganic network, e.g. a trialkoxysilane group, can act as a network modifying
compound because in the final structure the inorganic network is only modified by the organic group. The situation is different if two or three of such anchor groups modify an organic segment; this leads to materials in which the inorganic group is afterwards an integral part of the hybrid network.

Blends are formed if no strong chemical interactions exist between the inorganic and organic building blocks. One example for such a material is the combination of inorganic clusters or particles with organic polymers lacking a strong (e.g. covalent) interaction between the components (Scheme 1.2a). In this case a material is formed that consists for example of an organic polymer with entrapped discrete inorganic moieties in which, depending on the functionalities of the components, for example weak cross linking occurs by the entrapped inorganic units through physical interactions or the inorganic components are entrapped in a cross linked polymer matrix. If an inorganic and an organic network interpenetrate each other without strong chemical interactions, so called interpenetrating networks (IPNs) are formed (Scheme 1.2b), which is for example the case if a sol–gel material is formed in presence of an organic polymer or vice versa. Both materials described belong to class I hybrids. Class II hybrids are formed when the discrete inorganic building blocks, e.g. clusters, are covalently bonded to the organic polymers (Scheme 1.2c) or inorganic and organic polymers are covalently connected with each other (Scheme 1.2d) [18].
In fact there is no clear borderline between these materials. The term nanocomposite is used if one of the structural units, either the organic or the inorganic, is in a defined size range of 1–100 nm.

There is a gradual transition between hybrid materials and nanocomposites, because large molecular building blocks for hybrid materials, such as large inorganic clusters, can already be of the nanometer length scale. Commonly the term nanocomposites is used if discrete structural units in the respective size regime are used and the term hybrid materials is more often used if the inorganic units are formed in situ by molecular precursors, for example applying sol–gel reactions. Examples of discrete inorganic units for nanocomposites are nanoparticles, nanorods, carbon nanotubes and galleries of clay minerals.
Usually a nanocomposite is formed from these building blocks by their incorporation in organic polymers [18].

1.3. Synthetic Strategies towards Hybrid Materials

In principle two different approaches can be used for the formation of hybrid materials: Either well-defined preformed building blocks are applied that react with each other to form the final hybrid material in which the precursors still at least partially keep their original integrity or one or both structural units are formed from the precursors that are transformed into a novel (network) structure.

1.3.1. Building block approach

Building blocks at least partially keep their molecular integrity throughout the material formation, which means that structural units that are present in these sources for materials formation can also be found in the final material. At the same time typical properties of these building blocks usually survive the matrix formation, which is not the case if material precursors are transferred into novel materials. Representative examples of such well-defined building blocks are modified inorganic clusters or nanoparticles with attached reactive organic groups.

Fig.1.1. Typical well-defined molecular building blocks used in the formation of hybrid materials.
1.3.2. **Insitu formation of the components**

Contrary to the building block approach the *in situ* formation of the hybrid materials is based on the chemical transformation of the precursors used throughout materials’ preparation. Typically this is the case if organic polymers are formed but also if the sol–gel process is applied to produce the inorganic component. In these cases well-defined discrete molecules are transformed to multidimensional structures, which often show totally different properties from the original precursors. The insitu formation method can be any one of the following: (1) Insitu Formation of Inorganic Materials (2) Formation of Organic Polymers in Presence of Preformed Inorganic Materials (3) Hybrid Materials by Simultaneous Formation of Both Components. Here we are interested in Formation of Organic Polymers in Presence of Preformed Inorganic Materials.

1.3.2.1. **Formation of Organic polymers in presence of preformed inorganic materials**

If the organic polymerization occurs in the presence of an inorganic material to form the hybrid material one has to distinguish between several possibilities to overcome the incompatibility of the two species. The inorganic material can either have no surface functionalization but the bare material surface; it can be modified with nonreactive organic groups (e.g. alkyl chains); or it can contain reactive surface groups such as polymerizable functionalities. Depending on these prerequisites the material can be pre-treated, for example a pure inorganic surface can be treated with surfactants or silane coupling agents to make it compatible with the organic monomers, or functional monomers can be added that react with the surface of the inorganic material. If the inorganic component has nonreactive organic
groups attached to its surface and it can be dissolved in a monomer which is subsequently polymerized, the resulting material after the organic polymerization is a blend. In this case the inorganic component interacts only weakly or not at all with the organic polymer; hence, is a class I material formed.

If a porous 3-D inorganic network is used as the inorganic component for the formation of the hybrid material a different approach has to be employed depending on the pore size, the surface functionalization of the pores and the stiffness of the inorganic framework. In many cases intercalation of organic components into the cavities is difficult because of diffusion limit. The composites obtained can be viewed as host–guest hybrid materials. There are two possible routes towards this kind of hybrid material; (a) direct threading of preformed polymer through the host channels (soluble and melting polymers) which is usually limited by the size, conformation, and diffusion behaviour of the polymers and (b) the \textit{in situ} polymerization in the pores and channels of the hosts. The latter is the most widely used method for the synthesis of such systems. Of course, diffusion of the monomers in the pores is a function of the pore size; therefore the pores in zeolites with pore sizes of several hundred picometers are much more difficult to use in such reactions than mesoporous materials with pore diameters of several nanometers. Two methods proved to be very valuable for the filling of the porous structures with monomers: one is the soaking of the materials in liquid monomers and the other one is the filling of the pores in the gas phase. A better uptake of the monomers by the inorganic porous materials is achieved if the pores are pre-functionalized with organic groups increasing the absorption of monomers on the concave surface [18].
1.4. Properties and Applications

There is almost no limit to the combinations of inorganic and organic components in the formation of hybrid materials. Therefore materials with novel composition–property relationships can be generated that have not yet been possible. Based on the increased importance of optical data transmission and storage, optical properties of materials play a major role in many high-tech applications. The materials used can reveal passive optical properties, which do not change by environmental excitation, or active optical properties such as photochromic (change of color during light exposure) or electrochromic (change of color if electrical current is applied) materials. Silica is preferred as the inorganic component in such applications because of its low optical loss. Other inorganic components, for example zirconia, can incorporate high refractive index properties, or titania in its rutile phase can be applied for UV absorbers. Functional organic molecules can add third order nonlinear optical (NLO) properties and conjugated polymers, conductive polymers can add interesting electrical properties. The enhancement of mechanical and thermal properties of polymers by the inclusion of inorganic moieties, especially in the form of nanocomposites, offers the possibility for these materials to substitute classical compounds based on metals or on traditional composites in the transportation industry or as fire retardant materials for construction industry [18].

Organic–inorganic hybrid materials do not represent only a creative alternative to design new materials and compounds for academic research, but their improved or unusual features allow the development of innovative industrial applications. Nowadays, most of the hybrid materials that have already entered the market are synthesised and processed by using conventional soft chemistry based routes developed in the eighties. Looking to
the future, there is no doubt that these new generations of hybrid materials, born from the very fruitful activities in this research field, will open a land of promising applications in many areas: optics, electronics, ionics, mechanics, energy, environment, biology, medicine for example as membranes and separation devices, functional smart coatings, fuel and solar cells, catalysts, sensors, etc [19, 20].

1.5. Photocatalysis

From the beginning of the 21st century there has been an increasing demand for the implementation of clean energy technologies rendering little or no environmental footprint. However, until such time that clean, non-carbon based energy becomes a reliable and affordable commodity, environmental pollution abatement for a multitude of everyday industrial and domestic activities remains a crucial responsibility. Amongst the many abatement strategies known, semiconductor mediated photocatalysis has been a subject of vigorous academic research for the past 20 years. Due to the largely insoluble nature of the catalysts during application, the area of semiconductor photocatalysis (SP) invariably constitutes a heterogeneous catalytic system that adheres to the five discrete processes associated with conventional heterogeneous catalysis:

1) Transfer of liquid or gaseous phase reactants to the catalytic surface
2) Adsorption of at least one reactant
3) Reaction in the adsorbed phase
4) Desorption of product(s).
5) Removal of products from the interface region [21].
Photocatalysis is a rapidly developing field of research with a high potential for a wide range of industrial applications, which includes mineralisation of organic pollutants, disinfection of water and air, production of renewable fuels and organic synthesis. A great deal of attention has been devoted in the last years to photocatalytic processes both in the homogeneous phase and in heterogeneous systems. In its broadest sense, photocatalysis concerns the use of light to induce chemical transformations on organic or inorganic substrates that are transparent in the wavelength range employed. Radiation is absorbed by a photocatalyst whose electronically excited states induce electron- or energy-transfer reactions able to trigger the chemical reactions of interest [22-24].

Photocatalysis process, as an environmental application is a relatively novel subject with tremendous potential in the near future. It can be defined as the acceleration of photoreaction in the presence of a catalyst. The initial interest in the heterogeneous photocatalysis was started when Fujishima and Honda discovered in 1972 the photochemical splitting of water into hydrogen and oxygen with TiO$_2$ [25]. From this date extensive work has been carried out to produce hydrogen from water by this novel oxidation reduction reaction using a variety of semiconductors. In heterogeneous photocatalysis two or more phases are used in the photocatalytic reaction. A light source with semiconductor material is used to initiate the photoreaction. The catalysts can carry out substrate oxidations and reductions simultaneously. UV light of long wavelengths can be used, possibly even sunlight [26].

The concept photocatalysis and, of greater importance here, heterogeneous photocatalysis were first introduced in the second decade (1910–1920) of the 20th century. In his introductory remarks into the origins of photocatalysis,
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Teichner affirmed that the study of photocatalytic reactions began in the early part of the 1970s, and that the concept and the term heterogeneous photocatalysis (or photocatalyse hétérogène) was introduced and developed at the Institut de Catalyse and at the Université Claude Bernard in Lyon (France) in 1970 to describe the partial oxidation of alkanes and olefinic hydrocarbons, the photoinduced reactions of CO, SO₂, and NO in the presence of TiO₂, the partial photooxidation of various paraffins to aldehydes and ketones also in the presence of TiO₂, as well as an exhaustive study into the reactivity of various carbon atoms for photooxidation reactions [27,28].

Heterogeneous photocatalysis is an advanced oxidation process which is the subject of a huge amount of studies related to environment recovery, such as air cleaning and water purification, in which organic and inorganic pollutants are totally degraded to innocuous substances over mainly TiO₂ photocatalysts [25, 29].

It also includes a large variety of reactions: mild or total oxidations, dehydrogenation, hydrogen transfer, oxygen-18 and deuterium isotopic exchange, metal deposition, water detoxification, gaseous pollutant removal, bactericidal action etc. In line with the last point, it can be considered as one of the new “Advanced Oxidation Technologies” (AOT) for air and water purification treatments [30].

Attributes of an ideal photocatalyst for heterogeneous photocatalysis

1) Stability and sustained photoactivity
2) Biologically and chemically inert, non toxic
3) Low cost
4) Suitability towards visible or near UV light
5) High conversion efficiency and high quantum yield
6) Can react with wide range of substrate and high adaptability to various environments
7) Good adsorption in solar spectrum [31].

During the last two decades much attention has been paid to the reactions that take place on the illuminated surface of semiconductor metal oxides and sulfides. These compounds, mainly TiO₂, ZnO, CdS, WO₃, etc., are semiconductors, i.e. they have a moderate band-gap between their valence and conduction bands. Under illumination by photons of energy greater than band-gap energies, the valence band electrons can be excited to the conduction band, creating highly reactive electron-hole pairs. After migration to the solid surface, these may undergo electron-transfer processes with adsorbates of suitable redox potentials. In this way, these semiconductor compounds act (if the reaction exhibits a positive free energy gain), or catalytic photoassisted reactions (negative gain).

Among semiconductor photocatalytic materials, TiO₂ becomes a most important one because of its advantages of high photocatalytic activity, strong ultraviolet radiation shielding, good thermal conductivity, good dispersibility, cheap, non-toxic, and no secondary pollution etc.

1.5.1. Photocatalysis by TiO₂

Titanium dioxide (TiO₂) is an n-type semiconductor [32]. Photocatalysis technology with titanium dioxide (TiO₂) photocatalyst has attracted extensive attention because of its low cost, nontoxicity, and structural stability. TiO₂ photocatalyst could be activated only by UV light due to its large energy band gap (ca. 3.2 eV for anatase). On the other hand, TiO₂ has a small surface area
and low adsorbability, which results in low photocatalytic efficiency in much dilute solutions [33-37]. The actual efficiency of titanium dioxide depends not only on its phase composition, but also on the particle size, morphology, and porosity [38]. Anatase form has been found to exhibit higher activity compared to the rutile. Although the mechanism responsible for this is a controversial subject, at present there are four hypotheses seeking explanation for this behaviour are (1) crystal size, surface area, defect population and porosity (2) higher Fermi level (3) indirect band gap and (4) excitation electron mass [40]. Higher photocatalytic activity of anatase is usually attributed to its larger specific surface area. Poor adsorption and low surface area properties lead to great limitations in exploiting the photocatalyst to the best of its photoefficiency. On the other hand, lower photocatalytic activity of the rutile sample is probably related to the lower specific surface area due to calcination at temperatures above 950°C [38]. TiO₂ photocatalysis has shown great promise as an innovative and "green" technology due to its ability to generate electron and holes under UV illumination, which can produce radicals and/or initiate redox reactions to degrade trace level environmental pollutants. Starting in the late 1960s, we had involved in an unfolding story whose main character is the fascinating material titanium dioxide (TiO₂) [41]. In 1972, Fujishima and Honda discovered the phenomenon of photocatalytic splitting of water on a TiO₂ electrode under ultraviolet (UV) light [25, 32, 42]. Since then, enormous efforts have been devoted to the research of TiO₂ material, which has led to many promising applications in areas ranging from photovoltaics and photocatalysis to photo-electrochromics and sensors [43-46]. Even though titanium dioxide is the most widely used photocatalyst, there are several limitations that make its activity far from optimum [26, 47]. Particularly, the wide band gap of TiO₂ restricts photoexcitation of this
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semiconductor to the UV region with onset about 350 nm. Also, the electron–hole recombination of the photoinduced charge separated state represents an energy wastage that is detrimental for the photocatalytic activity. It has been estimated that the amount of solar energy reached on the earth every day is more than that mankind could use for 30 years. In whole energy of incoming solar spectrum, ultraviolet radiation ($\lambda < 400$ nm) accounts to only less that 4%, while the visible light is more than 50%. Hence, effective utilization of the visible light of solar radiation, as in the photosynthesis of plants, is a long “dream” of the photochemical researchers. Visible light activated TiO$_2$ can be prepared by several methods, including metal-ion implantation, reducing of TiO$_2$, sensitizing of TiO$_2$ with dyes, or non-metal doping by incorporation of various dopants into the TiO$_2$ lattice [48,49]. Hence, doping a foreign element into TiO$_2$ has been performed since the early 1980s. For example, studies, which substitute d transition metal ions for Ti sites, have been performed. In 2001, N-doped TiO$_2$ in which a nitrogen atom is substituted for a lattice oxygen site was reported as a visible light sensitive photocatalyst, and has attracted a lot of attention. Since then, various types of TiO$_2$ doped with anions such as sulphur, carbon, etc. have been extensively studied. In the N-doped TiO$_2$, the localized N 2p level in the forbidden band is the origin of the visible light sensitivity. The hole mobility in the localized N 2p level should be very low. Moreover, the oxidation power of holes produced in the N 2p level by visible light is low due to its potential of 2.25 V (vs. SHE). Thus, we concluded that the photo-produced holes in the valence band of TiO$_2$ with high mobility and oxidation power should be utilized to obtain high activity even under visible light.
1.5.2. Characteristics of TiO$_2$ photocatalyst.

1. High oxidizing ability
   As oxidative OH radicals produced by TiO$_2$ photocatalysis have high oxidation potential, TiO$_2$ photocatalyst exhibits high oxidizing ability.

2. Chemical stability
   TiO$_2$ is chemically stable and not dissolved in water; although some other semiconductive photocatalytic compounds are dissolved when irradiated in water. TiO$_2$ is so chemically stable that it is not dissolved in almost all acidic, basic and organic solvent.

3. Safety
   A safe and inert material in general.

1.5.3. Potential Applications

- Wastewater & potable water treatment
- Air toxics abatement
- Disinfection & Self Cleaning Devices
- Hydrogen production (water splitting) [50]

1.5.4. Advantages of TiO$_2$ Photocatalyst

- Photostable, cheap & reusable
- Chemically & biologically inert
- High Activity
- Operate at ambient temperature
- Ideal to treat trace level pollutants

1.5.5. Titanium dioxide

Pure titanium dioxide does not occur in nature but is derived from ilmenite or leucoxene ores. It is also readily mined in one of the purest forms,
rutile beach sand [51]. Titanium Dioxide (TiO\textsubscript{2}) has a wide range of applications. Since its commercial production in the early twentieth century, it is used as a pigment in paints, coatings, sunscreens, ointments and toothpaste. TiO\textsubscript{2} is considered as a “quality–of–life” product with demand affected by gross domestic product in various regions of the world. Titanium dioxide pigments are inorganic chemical products used for imparting whiteness, brightness and opacity to a diverse range of applications and end–use markets. TiO\textsubscript{2} as a pigment derives value from its whitening properties and opacifying ability (commonly referred to as hiding power). As a result of TiO\textsubscript{2}'s high refractive index rating, it can provide more hiding power than any other commercially available white pigment [52].

1.5.5.1. Structure of TiO\textsubscript{2}

Titanium dioxide is a polymorphic compound having three polymorphous structures; anatase, rutile and brookite. Both anatase and rutile are tetragonal, whereas brookite is orthorhombic. Rutile is the preferred polymorph of TiO\textsubscript{2} in such environments because it has the lowest molecular volume of the three polymorphs; it is thus the primary titanium bearing phase in most high pressure metamorphic rocks, chiefly eclogites. Brookite and anatase are typical polymorphs of rutile formed by retrogression of metamorphic rutile.

In all the three modifications, each titanium atom is coordinated to six almost equidistant oxygen atoms and each oxygen atom to three titanium atoms [53]. The octahedra differ however in rutile anatase and brookite with respect to their spacing relative to each other. In the case of anatase TiO\textsubscript{6} octahedron is slightly distorted, with two Ti-O bonds slightly greater than the other four and with some of the O-Ti-O bond angles deviating from 90°. Distortion is greater in anatase compared to rutile. The structure of anatase and
rutile has been described frequently in terms of chains of TiO$_6$ octahedra having common edges. Two or four edges are shared in rutile and anatase respectively. In brookite the interatomic distance and Ti-O-Ti bond angles are similar to those of rutile and anatase. Brookite is formed by joining together the distorted TiO$_6$ octahedra sharing three edges.

![Fig.1.2. Structures of Anatase, Rutile and Brookite](image)

Rutile has a primitive tetragonal unit cell, with unit cell parameters $a=4.584\text{Å}$, $c=2.953\text{Å}$ and $Z=2$. It is having the space group 136 and point group $4/m\ 2/m\ 2/m$. The titanium cations have a co-ordination number of 6 meaning they are surrounded by an octahedron of 6 oxygen atoms. The oxygen anions have a co-ordination number of 3 resulting in a trigonal planar
co-ordination. In rutile there is hexagonal close packing of oxygen atoms, in which half of the octahedral spaces are filled with titanium atoms [54].

Anatase belongs to tetragonal crystal system with unit cell parameters $a = 3.7845 \text{ Å}, c = 9.5143 \text{ Å}; Z = 4$. It is having the point group: 4/m 2/m 2/m and space group I41/amd. In the case of anatase, (cubic close packing of oxygen atoms) half of tetrahedral spaces are filled with titanium atoms.

Brookite belongs to the orthorhombic dipyramidal crystal class 2/m 2/m 2/m (also designated mmm). The space group is Pcab and the unit cell parameters are $a = 5.4558 \text{ Å}, b = 9.1819 \text{ Å}, c = 5.1429 \text{ Å}$ and $Z = 8$. Brookite TiO$_2$ has an orthorhombic unit constructed by an octahedron of oxygen ions arranged about a single titanium ion. Each octahedron shares three edges with adjoining octahedra.

![Fig.1.3. Unit cells of (A) rutile, (B) anatase and (C) brookite. Grey and red spheres represent oxygen and titanium, respectively](image)

**1.5.6. Mechanism of Photocatalysis**

Photocatalytic processes involve the initial absorption of photons by a molecule or the substrate to produce highly reactive electronica...
The efficiency of the photoinduced chemistry is controlled by the system's light absorption characteristics. In a compound semiconductor consisting of different atoms, the valence band and conduction band formation processes are complicated, but the principles involved are the same [55]. Unlike metals which have a continuum of electronic states, semiconductors possess a void energy region where no energy levels are available to promote recombination of an electron and hole produced by photoactivation in the solid. The void region which extends from the top of the filled valence band to the bottom of the vacant conduction band is called the band gap. The initial process for heterogeneous photocatalysis of organic and inorganic compounds by semiconductors is the generation of electron-hole pairs in the semiconductor particles [56]. The valence band of titanium oxide is comprised of the 2p orbital of oxygen (O), while the conduction band is made up of the 3d orbital of titanium (Ti). Photocatalytic mechanism is initiated by the absorption of the photon of energy $h\nu$ which is equal to or greater than the band gap of TiO$_2$ (~3.3 eV for the anatase phase) producing an electron-hole pair on the surface of TiO$_2$. An electron is promoted to the conduction band (CB) while a positive hole is formed in the valence band (VB). Excited-state electrons and holes can recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. After reaction with water, these holes can produce hydroxyl radicals with high redox potential [57].
1.6. Hybridization with Conducting Polymers-A Fine way to tune the Photocatalytic Activity in the Visible Region

Polymers that conduct electric currents without the addition of conductive (inorganic) substances are known as "intrinsically conductive polymers" (ICP). Conducting polymers is a prospective class of new materials that combine solubility, processability, and flexibility of plastics with electrical and optical properties of metals and semiconductors. The discovery of conducting polymers opened up many new possibilities for devices combining unique optical, electrical, and mechanical properties [58]. Conductive polymers or, more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity [59]. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not thermoplastics, i.e., they are not thermo formable. But, like insulating polymers,
they are organic materials. They can offer high electrical conductivity but do not show similar mechanical properties to other commercially available polymers [60]. Intrinsically conducting polymers, also known as “synthetic metals”, are polymers with a highly conjugated polymeric chain [61-63]. For the discovery of conducting polymers, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa were awarded the Nobel Prize in Chemistry in 2000. Typical conducting polymers include polyacetylene (PA), polyaniline (PANI), polypyrrole (PPy), polythiophene (Pth), poly (para-phenylene) (PPP), poly (phenylenevinylene) (PPV), polyfuran (PF), etc [64].

![Chemical structures of conducting polymers](image)

**Fig.1.5.** The chemical structures and their abbreviations of several kinds of conducting polymers.

Conducting polymers are generally wide band gap semiconducting materials, which can be chemically doped, with resulting electronic properties ranging from insulating to near metallic [65]. Environmental, energy sources and materials sciences are the three key projects of 21\textsuperscript{th} century. One of them is the photocatalysis using oxide semiconductor, which is closely associated with those topics. Since 1977, conducting polymers (CPs) have drawn considerable interest because of their unusual electrical, optical and photoelectrical properties and
their numerous applications in various fields. Recently, the preparation for the nanocomposites of CPs with inorganic nanoparticles has attracted many researchers’ attention, aiming to obtain the materials with synergetic or complementary behaviours between the CPs and the inorganic nanoparticles. Because of their semiconductor energy level structure, broad absorption spectra and very high stability under irradiation of solar light, CPs can be used to photosensitize semiconductor oxides and to obtain the novel photocatalysts response to the visible light [66]. Conjugated polymers (CP’s) with extend π-conjugated electron systems such as polyaniline, polythiophene, polypyrrole, and their derivatives, etc have shown great promises due to their high absorption coefficients in the visible part of the spectrum, high mobility of charge carriers, and good stability [67]. The properties of delocalized conjugated structures in electron-transfer processes have been widely studied to show that they could effectively active a rapid photo-induced charge separation and a relatively low charge recombination. Furthermore, many CPs in their doped or undoped states are efficient electron donor and good holes transporter upon visible light excitation [68].

1.6.1. Polyaniline

Among conducting polymers, polyaniline has been a significant interest due to its high conductivity, good redox reversibility, and swift change in film colour with potential and high stability in air. Polyaniline is one of the most important conducting polymers because of excellent electrical properties, number of intrinsic redox states, possible processability, good environmental stability, successful combination of chemical & physical properties, as well as its numerous applications in practice. Polyaniline (PANI) is the first polymer of this kind to achieve world-wide commercial availability.
Polyaniline (PANI) exists in a variety of forms that differ in chemical and physical properties [69-72]. The most common green protonated emeraldine has conductivity on a semiconductor level of the order of 100 S cm\(^{-1}\), many orders of magnitude higher than that of common polymers (<10\(^{-9}\) S cm\(^{-1}\)) but lower than that of typical metals (>10^4 S cm\(^{-1}\)). Protonated PANI, (e.g., PANI hydrochloride) converts to a non-conducting blue emeraldine base when treated with ammonium hydroxide [73].

Polymerized from the inexpensive aniline monomer, polyaniline can be found in one of three idealized oxidation states:

- **Leucoemeraldine** – white/clear & colourless \((C_6H_4NH)_n\)
- **Emeraldine** – green for the emeraldine salt, blue for the emeraldine base \((\{C_6H_4NH\}_2[C_6H_4N]_2\}_{n})\)
- **(Per)nigraniline** – blue/violet \((C_6H_4N)_n\)

In Fig. 1.6, \(x\) equals half the degree of polymerization (DP). Leucoemeraldine with \(n = 1, m = 0\) is the fully reduced state. Pernigraniline is the fully oxidized state \((n = 0, m = 1)\) with imine links instead of amine links. Studies have shown that most forms of polyaniline are one of the three states or physical mixtures of these components. The emeraldine \((n = m = 0.5)\) form of polyaniline, often referred to as emeraldine base (EB), is neutral, if doped (protonated) it is called emeraldine salt (ES), with the imine nitrogens protonated by an acid.
Fig. 1.7. Different forms of polyaniline: LB: leucoemeraldine base; LS: leucoemeraldine salt, (radical cation); ES, emeraldine salt (bipolaronic form); EB, emeraldine base; PB, pernigraniline base [74].

Polyaniline can be used for batteries [75] electrochromic devices, [76] photoelectrochemical conversion of light to electricity, [77,78] light-emitting diode [80] and immobilization of enzymes [81,82].

1.6.2. Polypyrrole

Polypyrrole (PPy) is a chemical compound formed from a number of connected pyrrole ring structures. Polypyrroles are conducting polymers of the rigid-rod polymer host family, all basically derivatives of polyacetylene. Polypyrrole was the first polyacetylene-derivative to show high conductivity. Polypyrroles are also called pyrrole blacks or polypyrrole blacks. Polypyrroles also exist naturally, especially as part of a mixed copolymer with polyacetylene and polyaniline in some melanins. Polypyrrole is a conducting polymer that has
attractive characteristics for the use as a radar absorbing material [83]. Polypyrrole (PPy) is a p-type semiconducting polymer that has proven to be relatively highly conductive, easy to synthesize, and environmentally stable. PPy can be prepared by chemical [84-86], electrochemical [85-87], plasma [88, 89] and vapor phase [90, 91] polymerization. In applications like coating dielectric materials (in this case optical plastic) the most suitable process is the in situ chemical polymerization, because it provides relatively high conductivity as well as suitable thickness and uniformity of the film. The main drawbacks of other methods are poor conductivity (plasma); need for conductive substrate, finite size of substrate, porosity, and uneven thickness of films (electrochemical); problematic adhesion of oxidant solution with substrate (vapour phase) [92].

Fig. 1.8. Chemical structures of polypyrrole in neutral aromatic and quinoid forms and in oxidised polaron and bipolaron forms.
Applications

Applications of PPy were essentially extended during last years and include now such different fields of science and technology as corrosion protection of metals, development of individual electronic devices e.g. diodes, metallization, electromagnetic interference shielding, biosensors, tissue engineering scaffolds, neural probes, drug-delivery devices, and bio-actuators [93-95].

(1) It has been studied as a material for artificial muscles--a technology that would offer numerous advantages over traditional motor actuating elements [96]. (2) Used to coat silica and reverse phase silica to yield a material capable of anion exchange and exhibiting hydrophobic interactions [97]. (3) Used in the microwave fabrication of multiwalled carbon nanotubes, a new method that allows to obtain CNTs in a matter of seconds [98]. (4) polypyrrole (PPy) was synthesized by vapour phase polymerization (VPP) and electropolymerization (EP) and these PPys were employed as counter electrodes in dye-sensitized solar cells [99].

1.6.3. Polythiophene

Polythiophenes and other conjugated polymers have attracted attentions because of their electronic and photonic properties [100-102]. The π-conjugated electronic structure of these polymers facilitates the delocalization of the charge carriers upon doping and imparts high charge mobility. This delocalized electronic structure also leads to characteristic strong absorptions and emissions, in most cases in the UV-Vis. region. Since the original unsubstituted conjugated polymers are not solution- or melt processable, flexible side chains are attached to improve processibility. In addition to solubility and fusibility, the
attachment of various substituents can modify other physical properties of conjugated polymers, and lead phenomena which are not observed in the original unsubstituted polymers [103].

Polythiophenes consist of a chain of alternating double- and single-bonds like polyacetylene, however, each first and forth carbon atoms are connected by a sulfur atom forming a thionyl ring. Therefore the bond between the second and the third carbon atom get more single bond character than the other C-C bonds and consequently also the bonds connecting the thionyl rings are more of single-bond character. Due to this weaker mesomerization than in polyacetylene the band-gaps of polythiophenes are shifted to the blue and UV. Beside of their structure defining function the sulfur atoms will have also a direct influence on the electronic and optical properties of a polythiophene. Nevertheless the conjugation of the C-atoms will dominate the spectroscopic properties of the polythiophenes.

![Fig.1.9. Structure of Polythiophene](image)

Polythiophenes (Pth’s) result from the polymerization of thiophenes, a sulfur heterocycle, that can become conducting when electrons are added or removed from the conjugated $\pi$-orbitals via doping.
Delocalised electrons along the conjugated backbone of polythiophene result in an extended \( \pi \)-system which is filled with valence electrons. Adding or removing electrons from the \( \pi \)-system (doping) produces a charged unit called a bipolaron unit. Polythiophene is insoluble in organic solvents [104-106].

Therefore, recently, conjugated polymers act as stable photo-sensitizer combined with wide band gap inorganic semiconductors (e.g., TiO\(_2\), CdS, and CdSe) was an emerging area of research for optical, electronic, and photoelectric conversion applications [107-109]. And various composites with different combinations of the two components composition have been reported in the literature. In a conjugated polymer/TiO\(_2\) system, polymer, bound to TiO\(_2\), can actively harvest the visible light matching the semiconductor energy levels, and then inject electrons into the conduction band (CB) of TiO\(_2\). Polyaniline (PANI), can generate \( \pi-\pi^* \) transition under visible light, delivering the excited electrons into the conduction band of TiO\(_2\), and then the electrons transferred to an adsorbed electron acceptor to yield oxygenous radicals to degrade pollutants.
The photocatalytic activity of conducting polymers modified TiO₂ under visible light irradiation resulted from the visible light absorption of conducting polymers and effective charge separation of photogenerated carriers owing to the heterojunction built between TiO₂ and the conducting polymers. Zhang et al. and Li et al. prepared PANI modified TiO₂ and other inorganic semiconductors photocatalyst via chemisorptions and insitu polymerization method, respectively [110-114]. The resulting composite photocatalyst exhibited significantly higher photocatalytic activity than that of neat semiconductors on degradation of dye or aqueous solution of phenol under visible light irradiation. Wang and Min [115] have pointed out that PANI/TiO₂ photocatalyst plays an efficient role for the degradation of the dye methylene blue over that of free TiO₂. This behaviour is owing to the ability of PANI to sensitize TiO₂ by absorbing both ultraviolet and visible light (190–800 nm), whereas the pure TiO₂ only absorbs ultraviolet light (λ < 380 nm). Li and co-workers reported that [116] on using PANI/TiO₂ composite sample prepared via self assembling and graft polymerization for degradation of methyl orange under sunlight, the composite exhibits superior photocatalytic activity for the degradation of dye over the neat TiO₂. Min et al. reported Polyaniline (PANI) sensitized nanocrystalline TiO₂ composite photocatalyst (PANI/TiO₂) with high activity and easy separation was facilely prepared by insitu chemical oxidation of aniline from the surfaces of TiO₂ nanoparticles. PANI was able to sensitize TiO₂ efficiently and the composite photocatalyst could be activated by absorbing both the ultraviolet and visible light (λ = 190–800 nm), whereas pure TiO₂ absorbed ultraviolet light only (λ=400 nm). Photocatalytic experiments showed that under natural light irradiation, methylene blue could be degraded more efficiently on the PANI/TiO₂ than on the pure TiO₂, due to the charge transfer from PANI to TiO₂ and efficient separation of e⁻ - h⁺ pairs.
Chapter 1

on the interface of PANI and TiO₂ in the excited state [115]. Wang et al.
reported a series of polypyrrole–TiO₂ (PPy–TiO₂) nanocomposites with
different PPy: TiO₂ ratios were prepared by ‘insitu’ deposition oxidative
polymerization of polypyrrole, and their photocatalytic activities were
evaluated by photocatalytic degradation of aqueous solution of methyl orange
(MeO) under sunlight. According to them the PPy–TiO₂ nanocomposites
showed higher photocatalytic activity than neat TiO₂ nanoparticles on the
degradation of MeO under sunlight irradiation due to the sensitizing effect of
PPy [117]. Shoubin Xu et al reported the visible light photocatalytic degradation
of methyl orange (MeO) using TiO₂/Polythiophene composites [118]. Dan Yi et al
in 2010 also reported the degradation of methyl orange under visible light
using the TiO₂/Polythiophene (Pth) composites. According to them, the
introduction of Pth into the composites provides an apparently additive effect
on their adsorption capacities. A strong adsorption of MeO on the composite
particles results from the electrostatic attraction of the positively charged
composite particle surfaces with the MeO molecules. Under UV light
irradiation, Pth/TiO₂ composites with a certain content of Pth exhibit higher
photocatalytic activities than TiO₂ because of the high electron mobility of
Pth with its p-conjugated structure. Under visible light irradiation, Pth
adsorbed on the surface of TiO₂ acts as a sensitizer and charge transport
t layer; Pth/TiO₂ composites absorb visible light and photocatalytically
degrade MeO [119]. Yi Dan and Yunfeng Zhu also showed that the Poly
(3-hexylthiophene) (P3HT) sensitized TiO₂ shows fairly good activity
towards the degradation of methyl orange under both UV and visible light
irradiation [120]. In 2011, according to Qing Lin Liu et al the composites of
poly (N-isopropyl acrylamide-co-acrylic acid)/ titanium dioxide (TiO₂)
prepared via UV-initiated free radical polymerization shows comparatively
better photocatalytic activity under UV irradiation at various under various pHs and temperatures [121].

Yi Dan et al in 2008 synthesized Polythiophene/titanium dioxide (Pth/TiO₂) composites by the insitu chemical oxidative polymerization method. They showed that the prepared composites exhibited good photocatalytic activity under UV light illumination. The Pth/TiO₂ composites showed good adsorption properties and were more efficient in removing dye from solution than pure Pth and pure TiO₂. The maximum adsorption capacity of the Pth/TiO₂ composites was achieved when the mass percentage of Pth based on total composites was 40 % [122]. According to Liang et al the mechanism of polythiophene sensitized TiO₂ is shown below [123].

Fig.1.11. Mechanism of photocatalysis by polythiophene sensitized TiO₂

1.7. Mechanism of the photocatalysis under UV and Visible light irradiation

The Pth/TiO₂ composites induce the generation of electron-hole pairs under UV light irradiation, which yields radical and hole oxidants. It is well
known that TiO$_2$ particles are not excited by visible light. The surface hybridization of the Pth/TiO$_2$ composite particles will induce visible light photon absorption. The conduction band (CB) position of TiO$_2$ is lower than that of the LUMO of PTh in the Pth/TiO$_2$ composite particles. The Pth layer absorbs visible light, which induces excited-state electrons and these photoexcited electrons are readily injected into the CB of TiO$_2$ and subsequently transferred to the photocatalyst's surface [124]. These electrons react with water and oxygen to generate hydroxyl radicals and superoxide radicals [125], which are able to oxidize the pollutants. From these results, it is clear that the hole and the radical oxidants compete although only one of these is the main element.

Fig. 1.12. Schematic diagram illustrating the photocatalysis process of the PTh/TiO$_2$ composites under UV light (a) and visible light (b).

1.8. Measurement of Thermal diffusivity of a sample using Thermal lens technique

The evaluation of thermal properties of new materials is quite important. For several of their engineering applications in microscopic or macroscopic structures for instance, we need to know how they are able to dissipate heat. The same is true for those systems suitable for the recover or storage of energy.
Photothermal spectroscopy belongs to a class of highly sensitive techniques, which can be used to measure optical absorption and thermal characteristics of a sample. The basis of photothermal spectroscopy is photo-induced changes in the thermal state of the sample due to optical absorption by molecules and the subsequent nonradiative relaxation processes that result in heating of the sample, which in turn modifies its thermal state. Photothermal signals will not be affected by scattered or reflected light unlike conventional optical signal detection. Hence photothermal spectroscopy measures optical absorption more precisely in scattering solutions, solids and at interfaces. The large signal to noise ratio of thermo-optic techniques makes it an effective tool to study the surface and absorption properties of materials, particularly for solids.

The first photothermal spectroscopic method to be applied for sensitive chemical analysis was photothermal lens spectroscopy. The thermal lens effect was discovered when Gordon, et al. (1964) observed transient power and beam divergence changes in the output of a helium-neon laser after placing "transparent" samples in the laser cavity. It is a photothermal effect and results when energy from a laser beam passing through a sample is absorbed, causing heating of the sample along the beam path. The lens is created through the temperature dependence of the sample refractive index. The lens usually has a negative focal length since most materials expand upon heating and the refractive index is proportional to the density. This negative lens causes beam divergence and the signal is detected as a time dependent decrease in power at the center of the beam.

Thermal Lens Spectroscopy (TLS) is a powerful and well-established tool for material characterization. TLS can be applied to the measurement of
analyte concentrations [127,128], characterization of trace elements in gases [129], measurement of absolute absorption coefficients [130], and spectrometry for liquid chromatography [131,132]. In particular, TLS has been established as an accurate technique to evaluate quantum yield, diffusivity and thermal conductivity of liquid and transparent solid media [133].

Thermal lens spectrometry is based on the measurement of the temperature rise that is produced in an illuminated sample by nonradiative relaxation of the energy absorbed from a laser. It is one of the most sensitive techniques for trace determination.

Light energy absorbed and not lost by subsequent emission results in sample heating, [134] and this heating result in a temperature change. The thermally perturbed sample can act as a lens. Light transmitted through an aperture placed beyond the photothermal lens will vary the strength of the lens. Photothermal methods based on measurement of the strength of this lens are called photothermal lensing spectroscopy. The procedure for the thermal lens technique is as follows. An excitation light beam passes through the sample that contains the analyte, the light is tuned to an absorption line of this, and the energy is absorbed by the analyte. The molecules are excited into vibrational, rotational, or electronic states; the excited molecules lose the energy in the form of heat through nonradiative relaxation processes, the heat generated equals the excitation energy. The heating of the sample causes a change of the refractive index, detecting this fact by convergence or divergence through to the sample.
Particularly in high power lasers, the heating of the gain medium (e.g. a Laser crystal) often causes a significant thermal lens through the following mechanisms: The gain medium is hotter on the beam axis, compared with the outer regions, typically causing some transverse gradient of the refractive index (thermo optic effect, quantified with the coefficient dn/dT). Further index change can be caused by thermally induced mechanical stress (photoelastic effect, quantified with photoelastic coefficients $\rho_{ij}$ and the thermal expansion coefficient $a$). Mechanical stress can also lead to bulging of the end faces of the gain medium, so that these also cause lensing. This effect can be important for short laser crystals. Depending on the situation, these effects can have different relative strength and even sign. In many cases, the first mentioned effect (temperature dependence of the refractive index) is most important [136].
Another interesting aspect of thermal lens is that the heating and subsequent lens formation is not instantaneous. It takes a finite time to develop, depending on the laser power and the thermal properties of the sample. In solution, the thermal properties of the solvent (heat capacity and thermal conductivity) determine the time for blooming to occur (typically milliseconds). To best observe the "grow-in" of the thermal lens effect, laser light is focused with a lens at a precise position in the sample. The pump laser is turned off and on with a rotating chopper. By correct choice of components, lens formation will occur during the "on" cycle of the pump laser through the chopper, and it will dissipate by cooling during the "off" cycle, so that the effect can be observed repetitively. During the formation of the lens, the probe beam is deflected and it comes back when the lens is destroyed. The variation of the intensity of the probe beam during lens formation is something like shown in Fig. 1.14.

![Fig. 1.14. Trace of probe beam intensity variation during thermal lens formation](image)

Fig. 1.14. Trace of probe beam intensity variation during thermal lens formation
1.9. Nonlinearity Studies Using Z-scan Techniques: Optical limiting Applications

Nonlinear optics is a study that deals mainly with various new optical effects and novel phenomena arising from the interactions of intense coherent optical radiation with matter. Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light. Typically, only laser light is sufficiently intense to modify the optical properties of a material system. The beginning of the field of nonlinear optics is often taken to be the discovery of second-harmonic generation by Franken et al. (1961), shortly after the demonstration of the first working laser by Maiman in 1960. Nonlinear optical phenomena are “nonlinear” in the sense that they occur when the response of a material system to an applied optical field depends in a nonlinear manner on the strength of the optical field. In order to describe more precisely what we mean by an optical nonlinearity, let us consider how the dipole moment per unit volume, or polarization $\tilde{P}(t)$, of a material system depends on the strength $\tilde{E}(t)$ of an applied optical field. In the case of conventional (i.e., linear) optics, the induced polarization depends linearly on the electric field strength in a manner that can often be described by the relationship

$$\tilde{P}(t) = \varepsilon_0 \chi^{(1)} \tilde{E}(t)$$

Where the constant of proportionality $\chi^{(1)}$ is known as the linear susceptibility and $\varepsilon_0$ is the permittivity of free space. In nonlinear optics, the optical response can often be described by generalizing the above Eq. by expressing the polarization $\tilde{P}(t)$ as a power series in the field strength $\tilde{E}(t)$ as

$$\tilde{P}(t) = \varepsilon_0 [\chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \chi^{(3)} \tilde{E}^3(t) + \cdots] = \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \tilde{P}^{(3)}(t) + \cdots$$
The quantities $\chi^{(2)}$ and $\chi^{(3)}$ are known as the second and third-order nonlinear optical susceptibilities, respectively. We shall refer to $\tilde{P}^{(2)}(t) = \epsilon_0 \chi^{(2)} \tilde{E}^2(t)$ as the second-order nonlinear polarization and to $\tilde{P}^{(3)}(t) = \epsilon_0 \chi^{(3)} \tilde{E}^3(t)$ as the third-order nonlinear polarization.

### 1.9.1. Z-Scan Measurements

Reliable methods for determining the nonlinear optical properties of materials (i.e. nonlinear absorption and nonlinear refraction) have been developed for wide ranging applications such as optical limiting, multiphoton polymerization as well as optical switching. Of these methods, the “Z-scan”, introduced in 1985 by Sheik Bahae et al [137,138] and later developed by Eric Van Stryland remains the standard technique. This is a simple and sensitive single beam technique to measure the sign and magnitude of both real and imaginary part of third order nonlinear susceptibility, $\chi^{(3)}$. The Z-scan technique is performed by translating a sample through the beam waist of a focused beam and then measuring the power transmitted through the sample. Z-scan has many possible configurations (e.g. “E Z-Scan”, “White Light Z-scan”, “Excite-Probe Z-scan”). The two measurable quantities connected with the Z-scan are nonlinear absorption (NLA) and nonlinear refraction (NLR) [139]. These parameters are associated with the imaginary and real part of the third order nonlinear susceptibility, and provide important information about the properties of the material. The Z-scan method is an easy and relatively simple way for measuring nonlinear absorption coefficients as well as nonlinear refractive indices for a wide variety of optically interesting materials.
In the original single beam configuration, the transmittance of the sample is measured, as the sample is moved, along the propagation direction of a focused Gaussian laser beam. A laser beam propagating through a nonlinear medium will experience both amplitude and phase variations. If transmitted light is measured through an aperture placed in the far field with respect to focal region, the technique is called closed aperture Z-scan experiment [137,138]. In this case, the transmitted light is sensitive to both nonlinear absorption and nonlinear refraction. In a closed aperture Z-scan experiment, phase distortion suffered by the beam while propagating through the nonlinear medium is converted into corresponding amplitude variations. On the other hand, if transmitted light is measured without an aperture (in this case the entire light is collected), the mode of measurement is referred to as open aperture Z-scan [138]. In this case, the throughput is sensitive only to the nonlinear absorption. Closed and open aperture Z-scan graphs are always normalized to linear transmittance i.e. transmittance at large values of $|z|$. 

Fig. 1.15. Z scan experimental set-up
In the Z-scan set-up, the transmittance of the sample is measured, using a large area photodetector, as the sample is moved along the propagation direction \((z)\) of a focused Gaussian laser beam. The measurement is done using a 532 nm Gaussian laser beam of a frequency doubled Nd: YAG laser. A portion of the laser beam is sampled out to monitor the input energy. Laser energy is measured and averaged using a commercial energy meter and a ratio meter respectively. From open aperture Z-scan experimental data, nonlinear absorption coefficient is calculated using two-photon absorption (TPA) model. It is obtained by fitting the experimental data to the normalized transmittance equation.

1.9.2. Optical limiting Application

There are three basic requirements for a material to be good optical limiter viz. (1) An excited state absorption cross-section that exceeds the ground state absorption cross-section, (2) fast response and (3) high damage threshold. Magnitude of effective nonlinear absorption coefficient is an indication of the usefulness of a sample to act as good optical limiter. Samples with higher value of effective nonlinear absorption coefficient are obviously better optical limiters.

1.10. Lasing

Lasers (light amplification by stimulated emission of radiation) are radiation sources for coherent, quasi-monochromatic and sharply bundled radiation in the visible region and in the adjacent regions of the electromagnetic spectrum (far infrared, infrared, ultraviolet and X-rays). Lasers are employed in all areas of science and technology. The most important applications use laser light having a wavelength in the range from 300 to 1800 nm.

In principle, all lasers consist of three components: an active medium or laser medium (for example a gas, a solid, for example a crystal or diode, or a
liquid), which substantially determines the optical properties of the laser; a pump source (for example a flash lamp, a pump laser or an electrically operated gas discharge), which-supplies energy-to the active medium, and finally a feedback medium or laser resonator, which provides the feedback and thus induced emission of the radiation. In the present application, the terms laser medium and active medium are used synonymously. The term “amplifying medium” here is taken to mean the system comprising active medium and feedback medium.

Lasers are usually classified according to the active medium used, for example as gas, dye, solid-state or semiconductor lasers.

Dye lasers are of particular interest in many areas of industry since lasers of this type are distinguished by a large continuous tuning range of the wavelength of the emitted laser radiation. In addition, high outputs can be achieved with narrow line widths. The pumping mechanisms, i.e. the processes for exciting the activatable particles of the active medium, are very flexible. The dye is usually excited by so-called optical pumping, with the energy source used being, for example, a flash lamp or a pump laser. Typical pump lasers are nitrogen, argon ion and frequency-doubled Nd: YAG (neodymium/yttrium aluminum garnet) lasers. Dye lasers are operated either continuously or in pulsed mode with pulse energies of up to 1J and pulse durations in the femto second region.

Laser action in random structures where light is multiply scattered and amplified becomes a subject of intense theoretical and experimental studies because of its important potential applications [140]. Following the pioneering theoretical work by Letokhov in the late 1960s [141], experiments by
Markushe et al. on powdered Na$_3$La$_{1-x}$Nd$_x$ (MoO$_4$)$_4$ [142] and Lawandy et al. on solutions containing an organic dye Rhodamine 640, and TiO$_2$ particles [143] demonstrated scattering-assisted optical gain upon laser pumping.

A dye laser is a laser which uses an organic dye as the lasing medium, usually as a liquid solution. Compared to gases and most solid state lasing media, a dye can usually be used for a much wider range of wavelengths. The wide bandwidth makes them particularly suitable for tunable lasers and pulsed lasers. Moreover, the dye can be replaced by another type in order to generate different wavelengths with the same laser, although this usually requires replacing other optical components in the laser as well [144].

The first broadly tunable laser was the organic dye laser discovered in 1966 by Sorokin [145] and Lankard and Schafer et al.[146]. Dye doped polymer gain media for tunable lasers were introduced shortly afterward by Soffer and McFarland [147] and Peterson and Snavely [148].

1.11. Scope of the present work

The current area of research interest includes the synthesis, characterization and applications of hybrid nanocomposites of TiO$_2$ with conducting polymers. Nanocomposite material composed of conducting polymers & oxides have open more field of application such as drug delivery, conductive paints, rechargeable batteries, toners in photocopying, smart windows, etc. The composites of core shell metal oxide particles-conducting polymer combine the electrical properties of the polymer shell and the magnetic, optical, electrical or catalytic characteristics of the metal oxide core, which could greatly widen their applicability in the fields of catalysis, electronics and optics. The hybrid nanocomposites are prepared via hydrothermal technique.
and characterized using various physico chemical techniques. The application studies include photocatalysis, thermal diffusivity measurements, nonlinear optics and lasing studies.

1.12. Objectives of the Present work

- Prepare mesoporous TiO$_2$ and TiO$_2$-conducting polymer (Polyaniline, Polypyrrole and Polythiophene) hybrid nanocomposites via hydrothermal technique.
- Prepare different compositions of the conducting polymer-TiO$_2$ hybrid nanocomposites.
- Physico chemical characterization of the prepared nanocomposites via XRD, UV-Vis, DRS, Raman spectra, FT-IR Spectra, SEM-EDX, TG-DTG analysis, XPS, TEM and conductivity measurements.
- The prepared nanocomposites were used in the field of photocatalysis, thermal diffusivity measurement, nonlinear optics and lasing.
- The photocatalytic efficiency of the prepared systems was evaluated by monitoring the degradation dyes, phenol, 4-nitrophenol, the endocrine disruptor Bisphenol-A, and the antibiotic Sulfamethoxazole.
- The Antibacterial activity of the composites were analysed using the typhoid causing bacteria Salmonella typhi.
- The thermal diffusivity measurements were carried out using thermal lens technique.
- Non-linear Optical properties ($3^{rd}$ order non linearity) were studied using Z-scan technique.
- Study the Light amplification in dye doped nanocomposites: The polyaniline-TiO$_2$ hybrid nanocomposites were used as a potential dye laser gain medium.
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