

**SYNTHESIS OF GOLD NANOPARTICLES AND THEIR
INTERACTION WITH POLYPYRROLE**

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the awarded of the degree of

Master of Technology

in

Materials & Metallurgical Engineering

Submitted by

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DECLARATION

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ABSTRACT

Gold Nanoparticles were synthesized by chemical synthesis route. Sodium citrate acted as reducing as well as stabilizing agent in the synthesis of gold nanoparticles. These Au nanoparticles were characterized by UV-Vis. Different chemical and electrochemical methods are generally used in the synthesis of polypyrrole. Despite many interesting applications, the use of polypyrrole is limited because of difficulty in processing it. Several approaches have been explored to improve the ability to process polypyrrole, including the use of emulsion, inverse emulsion, steric stabilizer, and micro emulsion methods. The study involves the synthesis of polypyrrole (PPY) and polypyrrole composite of gold (PPY-Au) by polymerization procedure. Size, shape and morphology of the synthesized particle were analyzed by X-ray diffraction, TEM analytic techniques.

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1.1 BACKGROUND

Nanotechnology includes the study and use of structures between 1 nanometer and 100 nanometers in size. Devices with minimum feature sizes less than 100 nanometers (nm) are considered to be products of nanotechnology. A nanometer is one billionth of a meter (10^{-9} m) and is the unit of length that is generally most appropriate for describing the size of single molecules [1]. Nanotechnology, shortened to "Nanotech", is the study of the control of matter on an atomic and molecular scale. Generally nanotechnology deals with structures of the size 100 nanometers or smaller, and involves developing materials or devices within that size. Nanotechnology is very diverse, ranging from novel extensions of conventional device physics, to completely new approaches based upon molecular self-assembly, to develop new materials with dimensions on the nanoscale, even to speculation on whether we can directly control matter on the atomic scale. The nanoscale marks the nebulous boundary between the classical and quantum mechanical worlds. Scientists have been studying and working with nanoparticles, but the effectiveness of their work has been hampered by their inability to see the structure of nanoparticles.

1.2 IMPLICATIONS OF NANOTECHNOLOGY

The implications of nanotechnology run the gamut of human affairs from the medical, ethical, mental, legal and environmental, to fields such as engineering, biology, chemistry, computing, materials science, military applications, and communications. On tracking the nano evolution, it has been stated that no matter what the market outcomes in the near or long term, nanoscience will never be an industry unto itself but a science of many avenues of application, and possibility that could redefine the direction of several industries [2]. This insight allows one to recognize that nanotechnology is not "a technology" but "a set of technologies," yielding a set of technical breakthroughs that will seep into many different markets. Within such a framework, the world of nanotechnology may be divided into three broad categories: nanostructured materials, nanotools, and nanodevices.

Benefits of nanotechnology include improved manufacturing methods, water purification systems, energy systems, physical enhancement, nanomedicine, better food production methods nutrition and large scale infrastructure auto-fabrication. Products made with nanotechnology may require little labor, land, or maintenance, be highly productive, low in cost, and have modest requirements for materials and energy.

Risks include environmental, health, and safety issues if negative effects of nanoparticles are overlooked before they are released; transitional effects such as displacement of traditional industries as the products of nanotechnology become dominant; military applications such as biological warfare and implants for soldiers; and surveillance through nano-sensors.

1.3 NANOSTRUCTURE MATERIALS

Nanostructure materials are materials with a microstructure the characteristic length scale of which is of the order of a few nanometers (typically 1-100). The microstructure refers to the chemical composition, the arrangement of the atoms (the atomic structure), and the size of a solid in one, two, or three dimensions. Effects controlling the properties of nanostructure materials include size effects (where critical length scales of physical phenomena become comparable with the characteristic size of the building blocks of the microstructure), changes of the dimensionality of the system, changes of the atomic structure, and alloying of components (e.g., elements) that are not miscible in the solid and/or the molten state.

The synthesis, characterization and processing of nanostructure materials are part of an emerging and rapidly growing field. Research and development in this field emphasizes scientific discoveries in the generation of materials with controlled micro structural characteristics, research on their processing into bulk materials with engineered properties and technological functions, and introduction of new device concepts and manufacturing methods.

Metal nanostructure materials have been the subject of much scientific research due to their characteristic properties that are distinctly different from their bulk counterparts, and considerable attention from both fundamental and applied

research has been paid to the synthesis and characterization of these materials. Nanostructure materials may be grouped under nanoparticles (the building blocks), nano-intermediates, and nanocomposites. Particular interest has been focused on the noble metal nanoparticles because they are technologically important in many fields such as catalysis, optics, biological assays, and surface-enhanced Raman scattering (SERS). All the among, metal nanoparticles, significant interest has been in gold nanoparticles over the past few decades, and particularly over the past several years, because of their unique shape-, size, and aggregation (orientation) dependent optical properties. These characteristics have been exploited for a variety of applications, including optical sensing, catalysis, and nanoscale electronics.

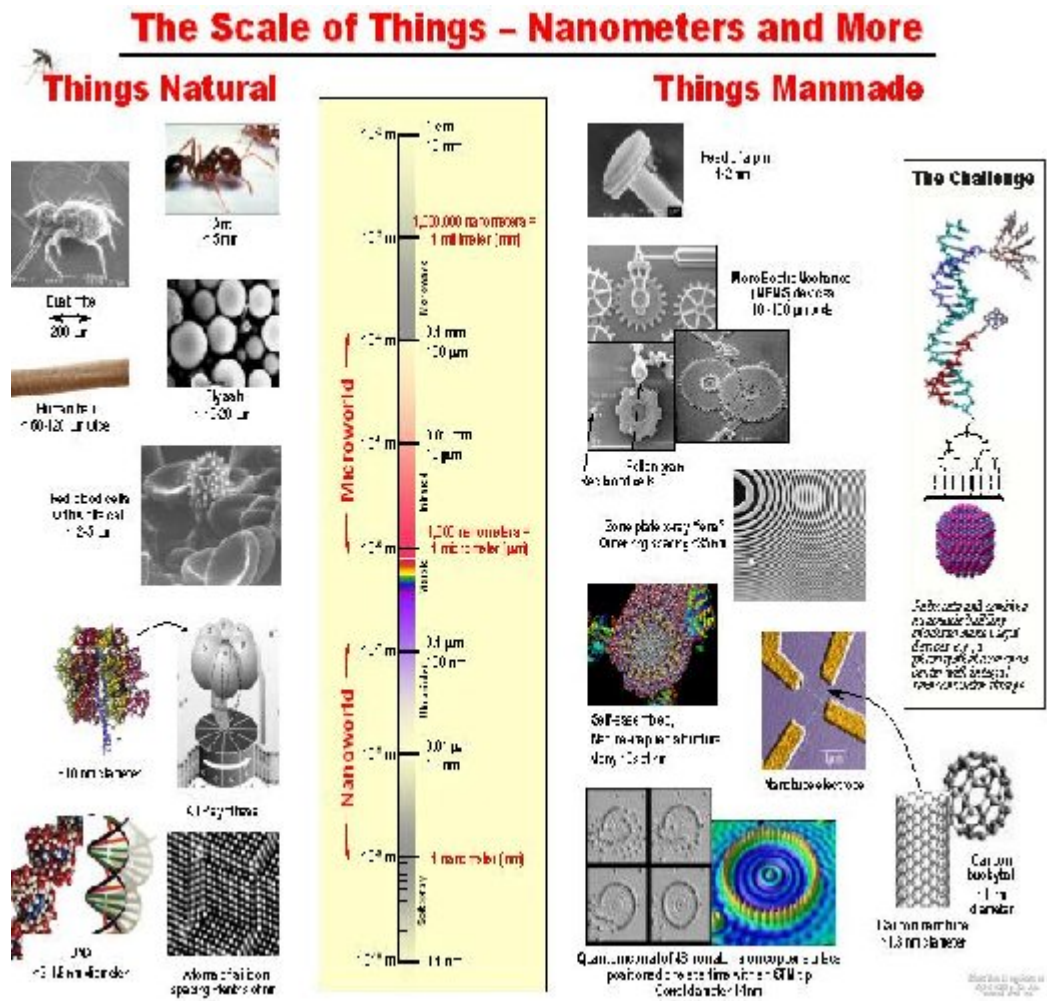


Figure 1.1. Various Scales of Things at Nanometer Range

1.3.1 PROPERTIES OF NANOMATERIAL

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface Plasmon resonance in some metal particles and super-paramagnetism in magnetic materials.

Nanoparticles have a very high surface area to volume ratio. This provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering can take place at lower temperatures, over shorter time scales than for larger particles. This theoretically does not affect the density of the final product,. The large surface area to volume ratio also reduces the incipient melting temperature of nanoparticles.

Moreover nanoparticles have been found to impart some extra properties to various day to day products. Like the presence of titanium dioxide nanoparticles impart what we call as the self-cleaning effect, and the size being nanorange, the particles can't be seen. Nano Zinc Oxide particles have been found to have superior UV blocking properties compared to its bulk substitute. This is why it is often used in the sunscreen lotions. Clay nanoparticles when incorporated into polymer matrices increase re-enforcement, leading to stronger plastics, verified by a higher glass transition temperature and other mechanical property tests. These nanoparticles are hard, and impart their properties to the polymer. Nanoparticles have also been attached to textile fibers in order to create smart and functional clothing as shown by The Textiles Nanotechnology Laboratory at Cornell University.

The change in properties is not always desirable. Ferroelectric materials smaller than 10 nm can switch their magnetization direction using room temperature thermal energy, thus making them useless for memory storage.

1.4 Gold as a chemical compound

Gold is the most malleable and ductile metal; a single gram can be beaten into a sheet of one square meter, or an ounce into 300 square feet. Gold is a good conductor of heat and electricity, and is not affected by air and most reagents. Common oxidation state of gold include +1(gold 1 or aurous compounds) and +3 gold compound or auric compounds). Gold ion in solution is readily reduced and precipitated out as gold metal by any other metal as reducing agent. The added metal is oxidized and dissolved allowing the gold to be displaced from the solution and be recovered as solid precipitate.

1.4.1 The General Characteristics of Gold is given in table 1.1

Table 1.1

PROPERTY	VALUE
Atomic number	79
Atomic mass	196.966569 g.mol ⁻¹
Electro negativity according to Pauling	2.54(pauling scale)
Density	19.3 g.cm ⁻³
Melting point	1064.18 °C
Boiling point	2856 °C
Vanderwaals radius	166 pm
Isotopes	5(mass no. 195-199)
Electronic shell	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹
Energy of first ionization	890 kJ.mol ⁻¹
Energy of second ionization	1980 kJ.mol ⁻¹

Gold reacts with alkaline solution of potassium and sodium cyanide and gold cyanide is an electrolyte used in commercial electroplating of gold onto base metal. Electroforming gold chloride solution are used to make gold colloidal by reduction with citrate or adsorbate ions. Gold chloride and gold oxide are used to make highly

valued cranberry or red coloured glass, which like colloidal gold salt contains evenly sized spherical gold nanoparticles.

1.4.2 GOLD NANOPARTICLES

When the size decreases from bulk to nano the properties of gold nanoparticles changed and it behaves completely different from their conventional size. Gold nanoparticles are being used for an ever-growing number of applications [3].

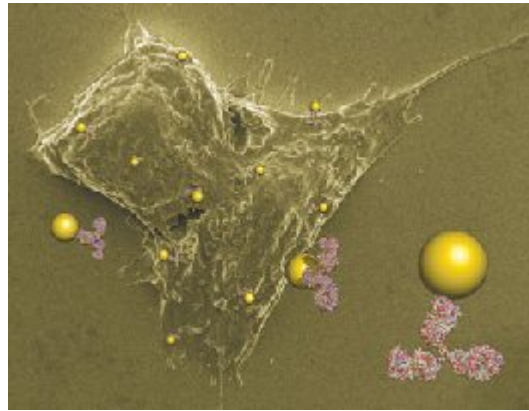


Figure 1.2: Gold particles.

Gold nanoparticles have been used in nanotechnology and biotechnology due to their optical properties in the visible spectrum and high bioaffinity [4-6]. It is well known that the particle size influences the chemical and physical properties of gold nanoparticles. Many methods synthesis including mechanical, chemical, and physical have been reported [7-10]. In particular, gold nanoparticles obtained using the chemical reduction methods have excellent monodispersity in particle size. However, this method requires a reducing agent to fabricate gold nanoparticles from a solution containing metal ions and an extraction process to separate the residues. It is also unsuitable for mass production due to a low reaction rate.

Gold nanoparticles have many applications in biology, including immunostaining and delivering drugs or DNA into cells [11-13]. Gold nanoparticles can also be used as sensors. Their optical properties can change upon binding to certain molecules, allowing the detection and quantification of analytes. The absorption spectra of gold nanoparticles change drastically when several particles come close to each other. Gold is used for nanoparticle applications because it is unreactive and isn't sensitive to air

or light. But gold does like to form bonds with itself. So to make sure the particles don't clump together, their surfaces have to be covered with a layer of protective molecules. The enhancement factor of surface-enhanced Raman scattering using gold nanoparticles has been experimentally and theoretically estimated to be of the order of 10^6 – 10^{15} . Because of this extraordinary sensitivity, surface-enhanced Raman scattering is expected to be a practical technique for single-molecule detection. Preparation of uniform gold nanoparticles becomes an important issue in applications because physical and chemical properties of particles highly depend on their size and shape. Gold particles at their conventional size (micrometer) are yellow in color but at nanosize it gives red appearance. Particles at nanosize behave completely different as compared with the properties at conventional size. Gold metallic nanoparticles are commonly used in the lab as a tracer, to detect the presence of specific proteins or DNA in a sample.

Gold nanoparticles can experience Surface Plasmon Resonance (SPR) in the visible portion of the spectrum. This means that a certain portion of visible wavelengths will be absorbed, while another portion will be reflected. The portion reflected will lend the material a certain color. Small nanoparticles absorb light in the blue-green portion of the spectrum (~400-500 nm) while red light (~700 nm) is reflected, yielding a deep red color. As particle size increases, the wavelength of surface plasmon resonance related absorption shifts to longer, wavelengths (red shift). This means that red light is now adsorbed, and blue light is reflected, yielding particles with a pale blue or purple color. As particle size continues to increase toward the bulk limit, surface plasmon resonance wavelengths move into the IR portion of the spectrum and most visible wavelengths are reflected. This gives the nanoparticles clear or translucent color. These properties have been used to create biosensors. Individual small gold nanoparticles appear red; however, when particles aggregate together the plasmon resonances can combine. The particle will appear as one large particle rather than two separate ones. Plasmon resonance associated-absorption wavelengths will shift from blue to red, and reflected light will shift from red to blue. Therefore particle color will change from red to blue on aggregation. These nanoparticles could also serve as the basis for new technologies that will render obsolete the energy intensive methods currently used to fabricate computer semiconductors. These materials would therefore be excellent components of nanoelectronics, optics and biology [14].

1.4.3 APPLICATION OF GOLD NANOPARTICLES

- Colloidal gold has been successfully used as a therapy for rheumatoid arthritis [15]. In a related study, the implantation of gold beads near arthritic hip joints in dogs has been found to relieve pain.
- An in vitro experiment has shown that the combination of microwave radiation and colloidal gold can destroy the beta-amyloid fibrils and plaque which are associated with Alzheimer's disease .
- Gold nanoparticles are being investigated as carriers for drugs such as Paclitaxel [16]. The administration of hydrophobic drugs requires encapsulation and it is found that nanosized particles are particularly efficient in evading the reticuloendothelial system.
- In cancer research, colloidal gold can be used to target tumors and provide detection using Surface Enhanced Raman Spectroscopy (SERS). These gold nanoparticles are surrounded with Raman reporters which provide light emission that are over 200 times brighter than quantum dots. It was found that the Raman reporters were stabilized when the nanoparticles were encapsulated with a thiol-modified polyethylene glycol coat. This allows for compatibility and circulation. To specifically target tumor cells, the pegylated gold particles are conjugated with an antibody, against e.g. epidermal growth factor receptor, which is sometimes overexpressed in cells of certain cancer types. Using SERS, these pegylated gold nanoparticles can then detect the location of the tumor [17].
- In Chemistry- catalysis, chemical sensors, nanoreactors, polymer additives, polyreagents, etc.
- In Material science- nanoscale electronics, electrooptics, photography, optical filters and switches electronic inks, thin films, molecular machines, decorative applications, etc.

1.5 POLYMER

Polymers have emerged as one of the most important materials in the twentieth century. The twenty-first century will undoubtedly see the use of polymers move from primarily passive materials such as coatings and containers to active materials with useful optical, electronic, energy storage and mechanical properties. Indeed, this

development has already begun with the discovery and study of conducting polymers [18].

1.5.1 CONDUCTING POLYMERS

Electronically conducting polymers possess a variety of properties related to their electrochemical behavior and are therefore active materials whose properties can be altered as a function of their electrochemical potential. The importance and potential impact of this new class of material was recognized by the world scientific community when Hideki Shirakawa, Alan J. Heeger and Alan G. MacDiarmid were awarded the Nobel Prize in Chemistry in 2000 for their research in this field [19-20]. Although these materials are known as new materials in terms of their properties, the first work describing the synthesis of a conducting polymer was published in the nineteenth century. At that time ‘aniline black’ was obtained as the product of oxidation of aniline, however, its electronic properties were not established [21].

The conducting polymers may be divided into three categories:

1. Redox polymer.
2. Ion conducting polymer.
3. Inherently conducting polymers.

Ionically conducting polymers (polymer/salt electrolytes) are of great interest because they exhibit ionic conductivity in a flexible but solid membrane. Ionic conductivity is different than the electronic conductivity of metals and conjugated conducting polymers, since current is carried through the movements of ions. They have been critical to the development of devices such as all-solid-state lithium batteries.

In ‘conjugated conducting polymers’, the redox sites are delocalized over a conjugated π system; however, ‘redox polymers’ have localized redox sites. The redox polymers are well known to transport electrons by hopping or self-exchange between donor and acceptor sites. The redox conductivity is comparatively lower than that of conjugated conducting polymers, likely due to slow electron transport to from the redox centre [22].

An organic polymer that possesses the electrical and optical properties of a metal while retaining its mechanical properties and processability, is termed an ‘intrinsically conducting polymer’ (ICP). These properties are intrinsic to the ‘doped’ form of the polymer. The conductivity of ICPs lies above that of insulators and

extends well into the region of common metals; therefore, they are often referred to as ‘synthetic metals.’ The common feature of most ICPs is the presence of alternating single and double bonds along the polymer chain, which enable the delocalization or mobility of charge along the polymer backbone. The conductivity is thus assigned to the delocalization of π -bonded electrons over the polymeric backbone, exhibiting unusual electronic properties, such as low energy optical transitions, low ionization potentials and high electron affinities of the many interesting conducting polymers that have been developed over the past 30 years, those based on polyanilines, polypyrroles, polythiophenes, polyphenylenes and poly(*p*-phenylene vinylene) have attracted the most attention. Figure 1.2 shows the structure of some conjugated polymers in their neutral insulating form. In order to make them electronically conductive, it is necessary to introduce mobile carriers into the conjugated system; this is achieved by oxidation or reduction reactions and the insertion of counterions (called ‘doping’).

During the doping process, an organic polymer, either an insulator or semiconductor having small conductivity, typically in the range of 10^{-10} to 10^{-5} S/cm, is converted to a polymer which is in a ‘metallic’ conducting regime (1 to 10^4 S/cm).

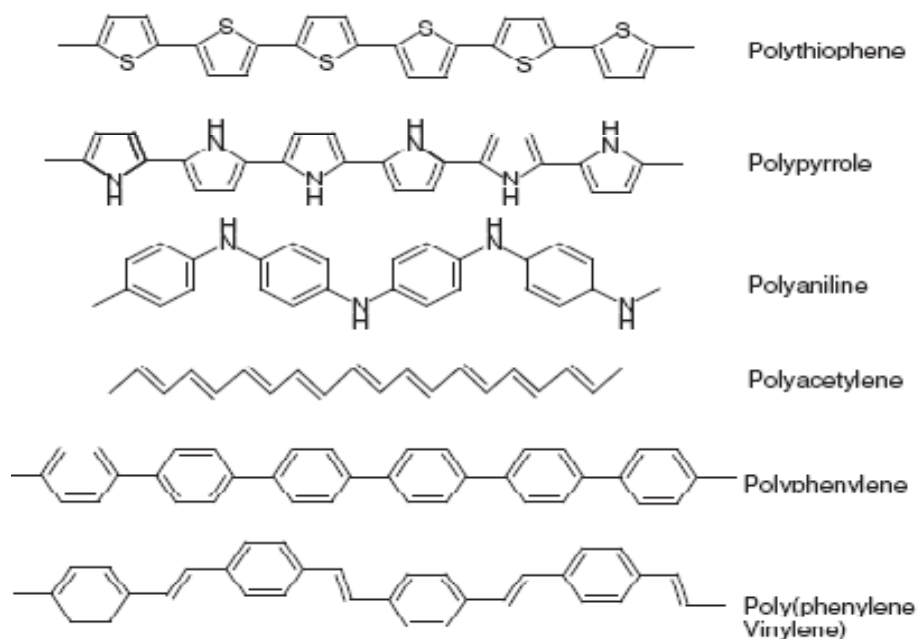


Figure 1.3 Structure of conjugated polymers.

The highest value reported to date has been obtained in iodine-doped polyacetylene ($>10^5$ S/cm) and the predicted theoretical limit is about 2×10^7 , more than an order of magnitude higher than that of copper. Conductivity of other conjugated polymers reaches up to 10^3 S/cm [23].

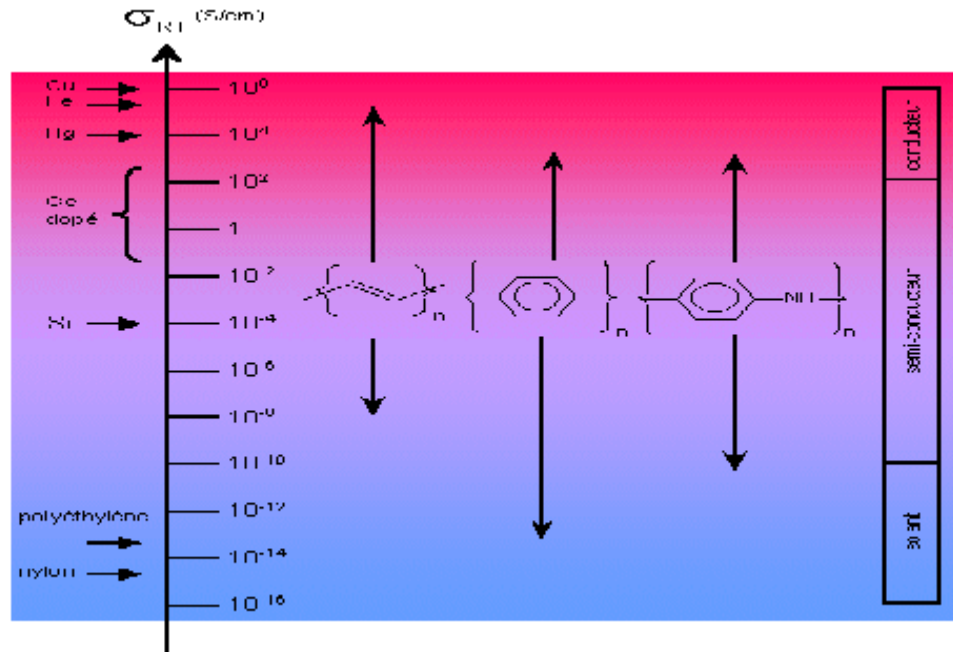


Figure 1.4: Conductivity range of different materials

Conducting polymers are unusual in that they do not conduct electrons *via* the same mechanisms used to describe classical semiconductors and hence their electronic properties cannot be explained well by standard band theory. The electronic conductivity of conducting polymers results from mobile charge carriers introduced into the conjugated π -system through doping. To explain the electronic phenomena in these organic conducting polymers, new concepts including solitons, polarons and bipolarons have been proposed by solid-state physicists. The electronic structures of π -conjugated polymers with degenerate and nondegenerate ground states are different. In π -conjugated polymers with degenerate ground states, solitons are the important and dominant charge storage species. Polyacetylene, $(CH)_x$, is the only known polymer with a degenerate ground state due to its access to two possible configurations as shown in Figure 1.4. The two structures differ from each other by the exchange of the carbon-carbon single and double bonds. While polyacetylene can

exist in two isomeric forms: cis and trans-polyacetylene, the trans-acetylene form is thermodynamically more stable and the cis–trans isomerization is irreversible [9].

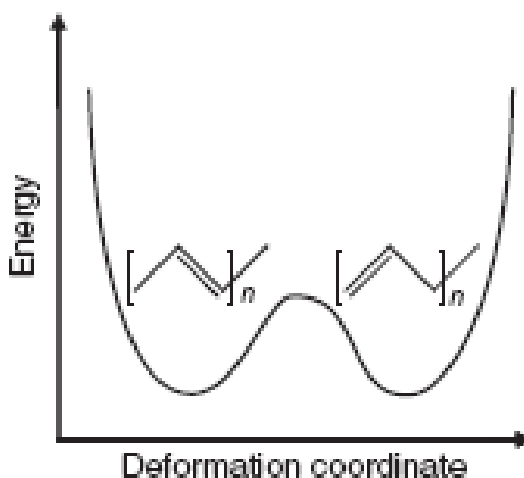


Figure.1.5 Energetically equivalent forms of degenerate polyacetylene.

Oxidative (p-type) doping of polyacetylene involves the chemical or anodic oxidation of the polymer to produce carbonium cations and radicals with simultaneous insertion of an appropriate number of anions between the polymer chains that neutralize the charge as shown in Figure 1.5 [10]. Two radicals can then recombine to give a spinless dication referred to as a positive soliton, which can act as the charge carrier [11]. Each soliton constitutes a boundary which separates domains that differ in the phase of their π -bonds. In solid-state physics a charge associated with a boundary or domain wall is called a soliton, because it has the properties of a solitary wave that can move without deformation and dissipation [12].

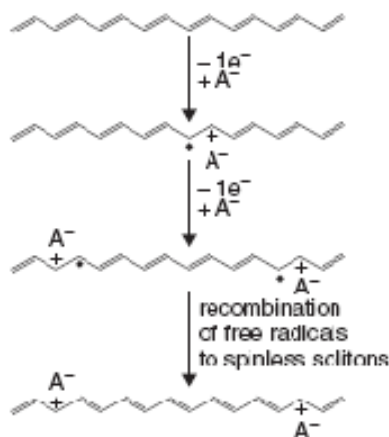


Figure.1.6 p-type doping in polyacetylene.

The π -conjugated systems based on aromatic rings, such as polythiophene, polypyrrole, polyaniline, polyparaphenylene and their derivatives have nondegenerate ground states. In these polymers, the ground-state degeneracy is weakly lifted so that polarons and bipolarons (confined soliton pairs) are the important and dominant charge storage configurations.

1.5.2 POLYPYRROLE

Polypyrrole is a frequently studied conducting polymer due to its application in sensing and catalysis. Polypyrrole is considered among the most promising conductive polymers due to its stability and ease of conversion between conducting and insulating forms. Different chemical and electrochemical methods are generally used in the synthesis of polypyrrole [24]. Despite many interesting applications, the use of polypyrrole is limited because difficulty in processing. Several approaches have been explored to improve the ability to process polypyrrole, including the use of emulsion, inverse emulsion, steric stabilizer, and microemulsion methods. Several reports have also been published on the synthesis of polypyrrole-metal nanocomposites. The sensing and catalytic abilities of the polypyrrole composites are significantly better than those for polymer alone [25]. As most of the important properties of the noble metals depend on their dispersion and surface properties in the surrounding medium, it is important to obtain evenly distributed Au nanoparticles in conducting polymer matrix. In the present study, gold nanoparticles is synthesized by chemical route. Their nano particles are used to synthesize the nanoparticle using polypyrrole as matrix.

CHAPTER 2 LITERATURE REVIEW

Sarathy et al. [26] synthesized thin films from a homogeneous solution of Au nanoparticles and polyoctylthiophene was phase-transferred using tetra-*n*-octyl ammonium bromide from the aqueous medium to the non-polar medium, toluene. This was followed by the reduction of the complexed Au ions in toluene NaBH₄ solution, accompanied by vigorous stirring.

Lin et al. [27] developed a unique reverse micelle method to prepare gold-coated iron (Fe-Au) nanoparticles. The absorption band of the Fe-Au colloid shifts to a longer wavelength and broadens relative to that of the pure gold colloid. The nanoparticles were 10 nm.

Salam et al. [28] demonstrated a simple one-step process for the synthesis of water-dispersed spherical gold nanoparticles using the multifunctional molecule oleyl amine (OLA) that electrostatically complexes with aqueous chloroaurate ions, reduces them, and subsequently caps the nanoparticles thus formed. Fang and Zhang [29] examined electrically conductive behavior of Au nanoparticles in chloroform and toluene solvents. Gold Nanoparticles were synthesized by chemical reduction of auric acid with NaBH₄

Liu et al. [30] prepared gold nanoparticles by the reaction of HAuCl₄ and sodium diphenylamine sulfonate in the presence/absence of polyvinylpyrrolidone (PVP) at room temperature. The nanoparticles were characterized by Transmission electron microscopy (TEM), UV-Vis absorption spectrum. Variation of size and morphology of gold nanoparticles depending on amount of sodium diphenylamine sulfonate, PVP and Auric acid was studied.

Liang et al. [31] synthesized monodispersed AuNPs by using chemical reduction of chloroauric acid by sodium citrate. Gold nanoparticles with high salt resistance and high stability, which are essential for the preparation of DNA-AuNPs conjugates for biodetection, were obtained. Indeed, DNA-gold nanoparticles conjugates prepared from the two-step approach showed much improved stability

toward salt-induced aggregation, as well as much longer storage time. Lu et al [32] used Gold (I) halides, including AuCl and AuBr, as precursors in the synthesis of Au nanoparticles. The synthesis was accomplished by dissolving AuI halides in chloroform in the presence of alkylamines, followed by decomposition at 60 °C. The relative low stability of the AuI halides and their derivatives eliminated the need for a reducing agent, which is usually required for Au³⁺ based precursors to generate Au nanoparticles. The average size of the Au nanoparticles was 12 nm in diameter.

Ahirwal et al. [33] studied electrochemistry of horseradish peroxidase (HRP) coupled to gold nanoparticles (AuNP) using electrochemical techniques, which provide some insight in the application of biosensors. Glutathione and lipoic acid capped gold nanoparticles were prepared by borohydride reduction, which were directly used for covalently attaching the HRP and the resulting AuNP-HRP bioconjugate was immobilized onto the gold electrode by direct adsorption.

Chen *et al.* [34] studied that the Polypyrrole is an important conducting polymer with high electrical conductivity and appreciable environmental stability. Conducting polymers are important materials emerging with lot of applications in various fields. Research in the field of such polymers aims mainly at some suitable modifications of existing polymers so that their applicability can be improved. Some of these modifications involve preparing hybrid materials in which organic materials and inorganic oxides or salts of different metals, viz. SnO₂, CeO₂, V₂O₅, TiO₂, fly ash composites; Fe₃O₄, ZrO₂, etc combine in some special fashion with the conducting polymers to give rise to the composites. In almost all the cases some specific nature of association between the two components has been observed.

In 1992 Lee *et al.* [35] studied that A.C. electrical property of conjugated polymers and theoretical high-frequency behavior of multi layer films. The survey of literature reveals that the detailed conductivity studies on PPy/Y₂O₃ composites are scarce. The syntheses, characterization of PPy/Y₂O₃ composites are for different weight percentages of Y₂O₃ in PPY composites. The characterization of the composites has been done by IR, XRD, SEM and DSC analysis techniques.

Unfortunately, practical application of conducting polymers such as polypyrrole, polythiophene and polyaniline is limited particularly because of their poor mechanical properties. However, the composites prepared by mixing of

conducting polymers with conventional polymers can be used in order to improve mechanical properties for all potential usages significantly.

Kivelson *et al.* [36] studied that the electrical transport in polymeric materials has become an area of increasing interest in research because these materials possess a great potential for solid state devices. More over the composite of conducting polymer have attracted considerable interest in recent years because of their numerous applications in variety of electric and electronic devices. It has been found that such composites can exhibit some novel properties and better mechanical properties than pure conducting Polymer. Polypyrrole has been regarded as one of the most studied conducting polymers.

Mohammadi *et al.* [37] reported that the understanding of electrical properties, morphology and crystal structure of polypyrrole composites may be useful in improving the stability characteristics of these materials which are the key factors in governing the device performance. One way of making these composites involves synthesizing the conducting polymer inside the matrices of conventional polymers using chemical or electrochemical polymerization. There are many reports pertaining to the chemical preparation of conducting polymer composites without using any insulating polymer. The most preferred method for synthesis of PPY composites is to use ammonium persulfate as an oxidant.

In this context an early work of Dias *et al.* [38] investigated the preparation of polypyrrole using hydrogen peroxide as the oxidant in the presence of catalytic Fe^{3+} . More interestingly, the electrochemical preparation of polypyrrole has been explored in recent years as a tool for film deposition. Chemical oxidation routes have been reconsidered making use of more environmentally friendly reagents as air, O_2 and H_2O_2 .

Toshima *et al.* [39] reported the polymerization of pyrrole using molecular oxygen in the presence of a rather complex catalytic system, $\text{AlCl}_3\text{-CuCl}$, producing a polymeric material contaminated by organic chlorine, carbonyl and hydroxyl derivatives having a negative effect on the electronic conductivity. The use of a soluble Fe^{3+} catalyst in connection with a water-organic solvent medium resulted in an improved synthesis. Successful use of conventional oxidation catalyst, as supported platinum group metals, using O_2 and H_2O_2 is presently unknown probably owing to

the poisoning effect of the heterocyclic nitrogen on the noble metals [40]. Recently, metallic gold has been proved to be an efficient catalyst in both homogeneous and heterogeneous oxidation. Supported gold showed high efficiency in the oxidation of alcohols, polyols, aldehydes. Among the typical properties of gold catalysis, some of them should be outlined: the first is that only nanometric particles either in form of conventional supported catalyst or as “naked” colloidal nanoparticles, show catalytic activity and the second one is related to the compatibility of gold with nitrogen-containing compounds, as amines. Moreover, in some applications, beside O₂, also H₂O₂ can be used as the oxidant [41]. They have investigated the oxidative polymerization of pyrrole using O₂ and H₂O₂ as the oxidants in aqueous solution under mild conditions in the presence of colloidal gold catalyst [42].

Polypyrrole particles synthesized with K₂Cr₂O₇ and additionally oxidized prior to immobilization of proteins were used for covalent protein *gp51* immobilization. The solution of *gp51* in 0.05 M phosphate buffer, pH 7.0 (10 mg/ml), was added and allowed to react for 30 min at room temperature. For the deactivation of the remaining active carbonyl groups on PPY surface, 1 M ethanolamine hydrochloride was used. The anti-*gp51* antibodies containing blood serum (10 mg/ml) and secondary labeled antibodies diluted with 0.05 M phosphate buffer, pH 7.0 (0.6 mg/ml) were added and allowed to interact with the corresponding affinity agents immobilized and/or formed on the surface of PPY at room temperature for 30 min. After each step the particles were quickly washed, collected by centrifugation and dispersed in phosphate buffer.

CHAPTER 3 EXPERIMENTAL DETAILS

The flow chart showing the systematic experimental work is as follow:

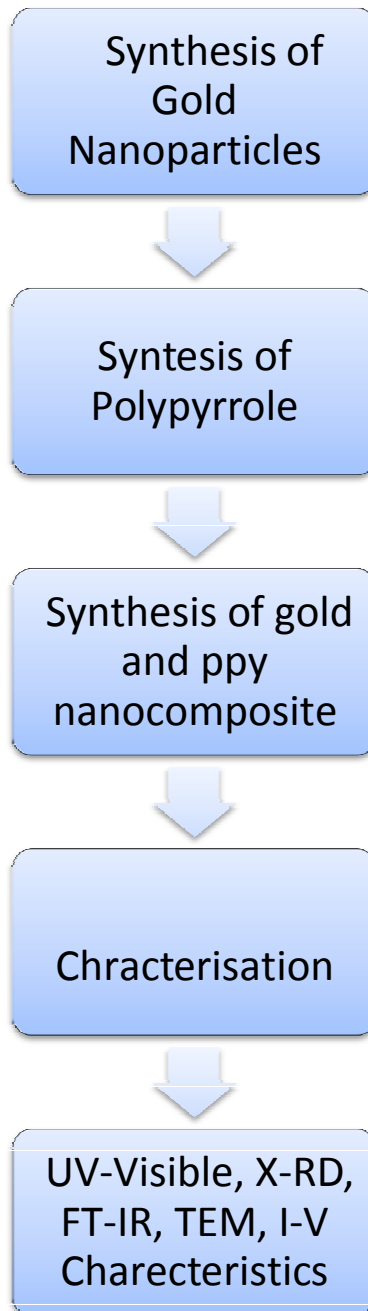


Figure3.1: Flow chart of the various steps of experimental work.

3.1 CHEMICAL DETAILS

The detail of the chemicals given in table 3.1

Table 3.1

Chemical used	Symbol	Source	Molecular weight
Goldchloride	HAuCl ₄	Alfa Aesar	234.5
Ferric Chloride	FeCl ₃	Lambachemie	162.21
PVP(Polyvinyl pyrrolidone)	(C ₆ H ₉ NO) _x	Lamachemie	40000
Hydrazine hydate	H ₆ N ₂ O	RFCL	50.06
Ethanol	CH ₃ CH ₂ OH	Changsitu Yangyuan Chemical China	46.08
Acetone	C ₃ H ₆ O	SISCO	58.08
PPY	C ₄ H ₅ N	Spectrochem PVT .LTD	67.09

3.2 SYNTHESIS OF GOLD NANOPARTICLES

Gold nanoparticles are produced in a liquid ("liquid chemical methods") by reduction of chloroauric acid (HAuCl₄). After dissolving H[AuCl₄], the solution is rapidly stirred while a reducing agent is added. This causes Au³⁺ ions to be reduced to neutral gold atoms. The formation and concentration of gold atoms lead to supersaturated start of liquid supersaturated, and gold gradually starts to precipitate in the form of sub-nanometer particles. The fast stirring of solution is responsible for formation of uniform gold nanoparticlels.

Procedure involves boiling of HAuCl₄ (auric acid) salt in desired volume, followed by addition of sodium citrate with constant heating for about half an hour. Gradually, the colour of the solution changes from faint yellowish color to grey to purple to deep purple, until settling on wine red. The solution will be allowed to cool at room temperature. This procedure produces monodispersed particles.

To prevent the agglomeration of nanoparticles stabilizing agent is required that sticks to the nanoparticle surface. They can be functionalized with various organic ligands to create organic-inorganic hybrids with advanced functionality.

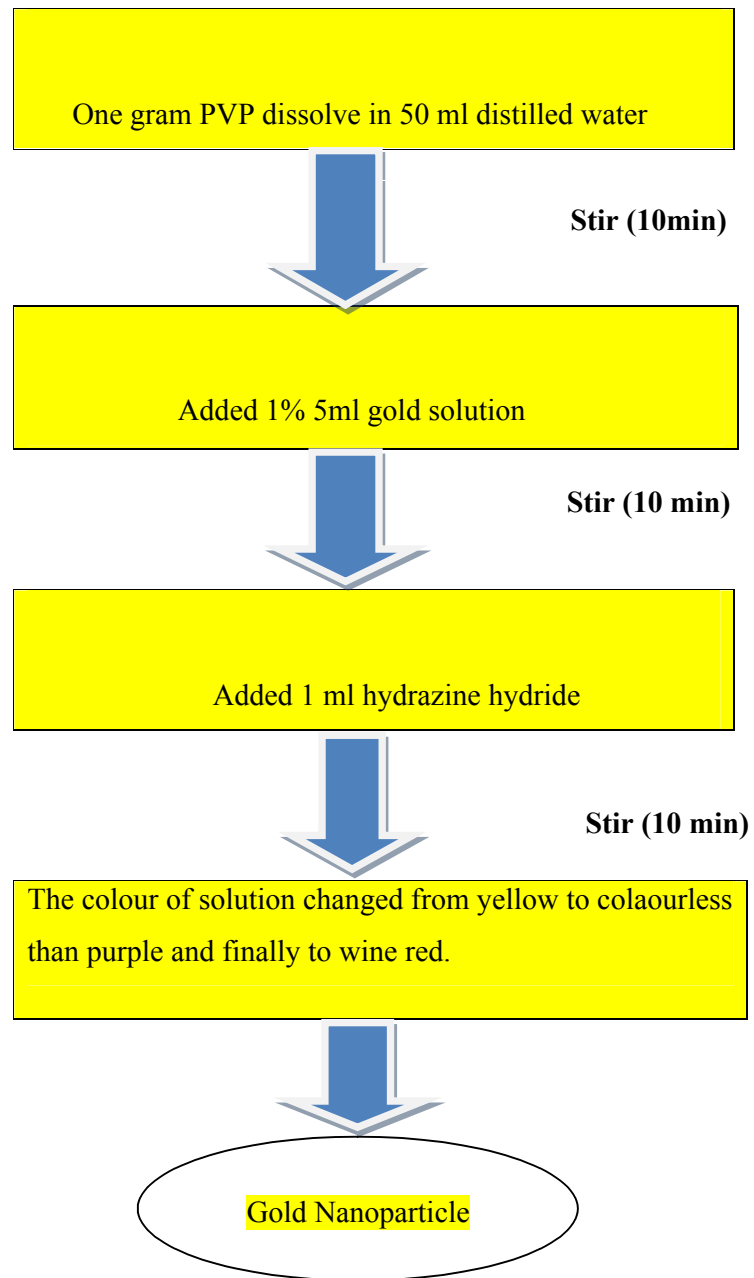


Figure 3.2: Synthesis of Gold Nanoparticles.

3.3 SYNTESIS OF POLYPYRROLE

One milliliter of pyrrole was added via syringe in 100 ml of distilled water stirred solution containing 9.74 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at room temperature. The Fe^{3+} /pyrrole molar ratio was 2.5. The solution was stirred for 24 hrs with magnetic stirrer, which gives rise to the formation of a black precipitate. The resulting black precipitate was filtered in vacuum. The precipitate was washed with copious amount of triply distilled water until the washing was cleared. The polypyrrole so obtained was soft jet black powder, dried in desiccators overnight and again dried in an oven at 25°C .

3.4 SYNTHESIS OF PPY GOLD NANO COMPOSITE

The 9.74 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added in 100 ml distilled water put in volumetric flask. 10 ml gold solution was added in volumetric flask and finally added 1 ml of polypyrrole via syringe. Stirred the reaction mixture by magnetic stirrer for 24 h, the reaction mixture was filtered in vacuum. A black colored precipitate was obtained. Obtained precipitated was washed with distilled water. The material so obtained was first dried in desiccators overnight and then in oven at 25°C . The obtained powder is black in colour and soft.

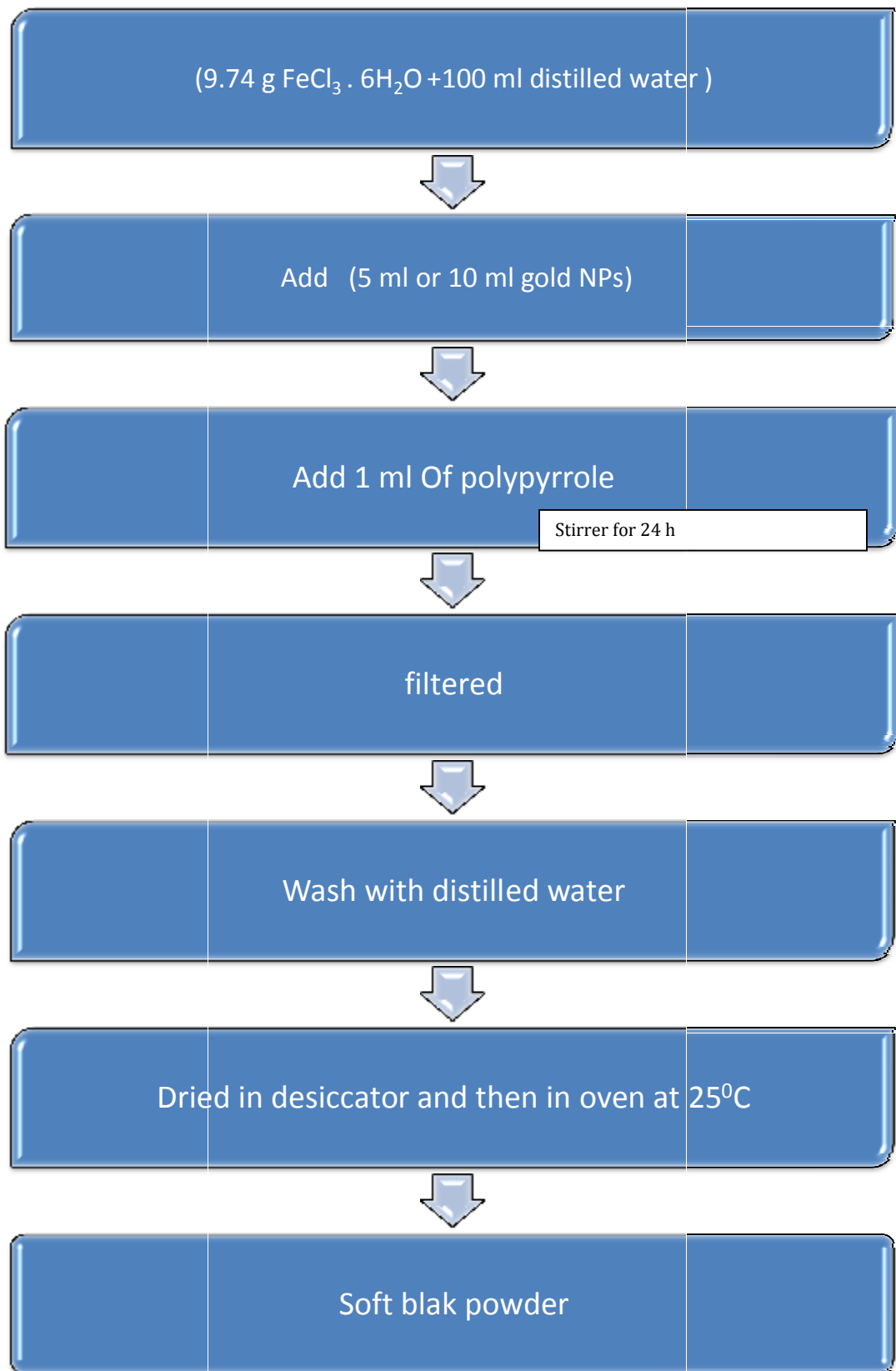


Figure 3.3: Flow chart of Synthesis PPY-Au nanocomposite

3.5 PALLETS OF COMPOSITE POWDER

The composite powders were pressed to form pellets of 10 mm diameter and 2–2.5 mm thickness by applying pressure of 90MPa in hydraulic press. The pellets of PPY and its composites were coated with silver paste on either side. These pellets use for characterization for I-V.

3.6 CHARACTERISATION TECHNIQUES

Various techniques are used to characterize the gold nanoparticles as well as nanocomposite. The working principle and technical details of these techniques are given below:

3.6.1 X-ray diffraction

XRD pattern were recorded with a X'PERT PANALYTICAL diffractometer using Cu ($K\alpha$) radiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature. This technique is based on the Braggs law of diffraction. The compact X-ray diffraction instrument is shown in figure 3.4.



Figure 3.4 Compact XRD Unit.

An X-ray tube generates X-rays by focusing an electron beam that has been accelerated across a high voltage field and bombards the stationary rotating solid target. As electrons collide with atoms in the target and slow down, a continuous spectrum of X-rays are emitted, which is termed as Bremsstrahlung radiation. The high energy electrons also eject inner shell electrons in atoms through the ionization process. When a free electron fills the shell, an X-ray photon with energy characteristic to the target material is emitted. Common targets used in X-ray tubes include Cu and Mo, which emit 8 keV and 14 keV with corresponding wavelength of 1.54 \AA and 0.8 \AA , respectively. X-rays primarily interact with electrons in atoms. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystal, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern allows us to deduce the distance between the crystal planes [43].

3.6.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of the prepared samples were recorded in KBr powder using Perkin Elmer RX-1 FTIR spectrophotometer in the range 500 cm^{-1} to 3500 cm^{-1} . The instrument is shown in figure 3.5.



Figure 3.5 FTIR Spectrophotometer.

Infra-red spectroscopy is particularly applicable to the study of orientation in polymers. Infra-red absorbance is due to the interaction between the electric field vector and the molecule dipole transition moments due to molecular vibrations. The absorbance is at a maximum when the electric field vector and the transition moment are parallel to each other, and zero when the orientation is perpendicular. The orientation of molecular components can be characterized by using the dichroic ratio which is defined as $A_{//}/A_{\perp}$ where $A_{//}$ is the absorbance parallel to the chain axis and A_{\perp} is the perpendicular direction [44].

Different alignment of the molecules results in changes in the intensity of a number of infra-red modes because each interatomic bond may vibrate in several different modes (stretching or bending). Individual bond may absorb at more than one IR frequency. Stretching absorptions usually produce stronger peaks than bending, however the weaker bending absorptions can be useful in differentiating similar type of bonds (e.g. aromatic substitution). It is also important to note that symmetrical vibrations do not cause absorption of IR radiation. In general, the most important factors determining where a chemical bond will absorb or not are the bond order and type of atoms joined by the bond. Conjugation and nearby atoms shift the frequency to a lesser degree. Therefore, the same or similar functional group in different molecules will typically absorb within the same and specific frequency range. Hooke's law states that the IR frequency at which a chemical bond absorbs is inversely proportional to the square root of the reduced mass of the bonded atoms.

3.6.3 Thermal Analysis instrument

TGA-DSC analysis was carried out using Water model SDT-Q-600MENT. During experiment the heating rate kept 5 °C/min in the temperature range of 30- 1000 °C and all experiment performed in nitrogen atmosphere. This instrument is shown in figure 3.6.

This instrument provides simultaneous measurement of weight change (TGA) and differential heat flow (DSC) from ambient to 1500 °C. SDT technology features a dual beam thermo balance that compensates for beam growth and buoyancy contributions to baseline drift; thermocouples that provide differential temperature measurements (DTA) within the dual ceramic beams; and a purge gas system with

digital mass flow control, gas switching capability and a separate gas inlet for the option to deliver reactive gas to the sample. For analyzing samples that tend to lose weight during heating, the new Q600 technology provides improved DSC accuracy when the instantaneous weight, rather than the initial sample weight, is used in heat flow integration. The DSC signal is also useful in providing higher temperature solid state phase and melting transitions where no weight loss occurs.



Figure 3.6 TGA-DSC Instrument.

Calorimet Thermogravimetry analysis (TGA) is a technique by which the mass of a material is measured as a function of temperature while the material is subjected to a controlled temperature program. On the TGA curves the mass is normally plotted on the Y-axis and temperature is on X-axis increasing from left to right. (DSC) is a technique to measure the heat flow through the sample as the sample is heated at a controlled heating rate. Heat flow is dependent on sample morphology. If the material is amorphous, a shift in the base line will be observed when the amorphous chains are given enough thermal energy to facilitate movement of chains. Thus, the material changes from rigid glassy state to rubbery state as the chains become more flexible and a change in heat capacity occurs. The temperature at which this change in material properties occurs is referred to as the glass transition temperature. If the material is crystalline, a peak in the heat flow occurs as the crystals melt or crystallize [45].

3.6.4 Transmission Electron Microscope (TEM)

TEM measurements were performed on a JEOL-1200EX TEM instrument operated at 120 kV. This instrument was used to see the smaller features of the composite material and the nanoparticles. The TEM micrographs were taken for the composite PANI/NiCo and NiCo composite.

For preparation of samples for TEM analysis, a portion of composite film was scratched and was dispersed in an ethanol solution and deposited on carbon-coated Cu-TEM grids. The film on the TEM grid was allowed to stand for some time to allow the liquid to evaporate. After drying, the specimen is transferred in the microscope column for imaging at different magnification and the electron diffraction patterns were recorded [46].

TEM images are formed using transmitted electrons (instead of the visible light) which can produce magnification details up to 1,000,00X with resolution better than 10 \AA . The images can be resolved over a fluorescent screen or a photographic film. Furthermore the analysis of the X-ray produced by the interaction between the accelerated electrons with the sample allows determining the elemental composition of the sample with high spatial resolution. At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.

It has a fully automated vacuum system. The state of the art electronic circuits, logical and compact design facilitate both operation and maintenance. For example, start up shut down and photography can be executed by a simple push button operation. Magnification and camera length can be directly readout regardless of any change in the accelerating voltage and recorded together with the film number on the film. Moreover the microscope provides very stable and excellent images at low to high magnification and a variety of diffraction patterns instantly. The available attachments can permit the specimen to be heated, cooled, tilted in-situ and also enable various signals from the specimen to be observed. The column of the microscope consists of

an electron gun, two-stage condenser lens, an interlocking two-stage beam deflector, specimen chamber, and the image forming system, which is normally composed of an objective lens, two-stage intermediate lens and projector lens. Viewing chamber and camera chamber are also the parts of the column. The specimen chamber has a side entry stage. The specimen exchange device contains an airlock mechanism so that the specimen can be exchanged without breaking the column vacuum. The specimen holder has a capacity of holding two specimens. The specimen movement range in X and Y directions are $\pm 1\text{mm}$ while along Z direction it is $\pm 0.5\text{mm}$. The specimen can be tilted by an angle of $\pm 30^\circ$ (X-tilt). The viewing chamber consists of a viewing window to see image of the specimen formed on the fluorescent screen. A binocular with a clear field of view is also installed with it to see the ten times enlarged image and also for image focusing purposes. The approximate size of an individual particle in the image of the specimen on the photographic screen can also be estimated with the help of small scale provided on the photographic screen. This instrument has a fully automatic camera complete with a data-recording device and its specially designed automatic exposure mechanism ensures optimum exposure. Since this camera is equipped with an air lock mechanism, rapid film exchange can be executed without breaking the vacuum of the column. The camera chamber has films loading capacity up to 50. The cut films having size 65mm X 90mm, supplied by Eastman Kodak Company U.S.A. were used for recording purpose



Figure. 3.7 Photograph of Transmission Electron Microscope

3.5.5 UV-Visible Spectrophotometer

UV-Visible absorption spectra of colloidal gold nanoparticles was acquired on Perkin Elmer (Lambda 35) spectrophotometer

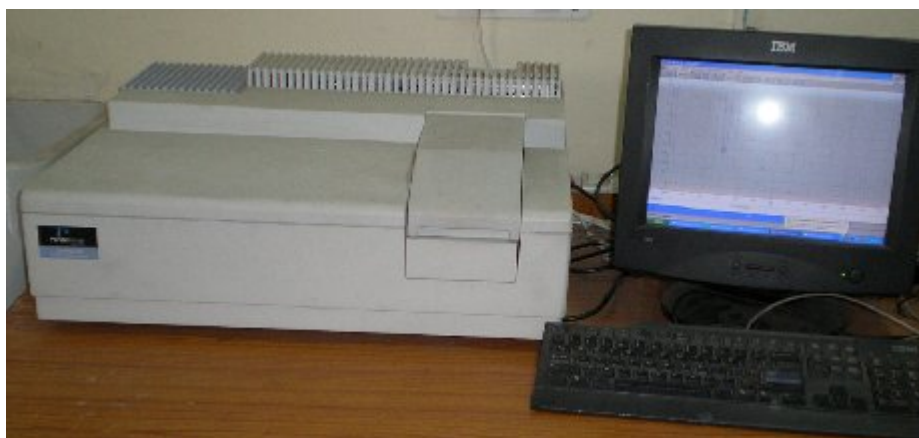


Figure 3.8: Photograph of UV-Vis Spectrophotometer

4.1 UV-VISIBLE STUDIES

The UV-Vis spectra of polypyrrole-gold at different stages are shown in Figure 4.2 a-b. Because polypyrrole absorbs at wavelengths close to those where Au absorbs, it is difficult to detect the presence of Au nanoparticles with UV-Vis spectroscopy. The absence of absorption peaks corresponding to Au nanoparticles in the resulting nanocomposites can be explained on the basis of strongly acidic environment of the solutions, reduce oscillator strength. Consequently, absorption peak can be absent in the U.V spectra. This may also be due to overlap of the absorption of polymers matrix and metal nanoparticles. Absorption peak could not appear even in pH neutralized solutions. Therefore, it seems that the main reason for the absence of peaks corresponding to Au nanoparticles is due to overlapping. The UV-Vis spectra of polypyrrole-gold (4.2b), obtained during initial stages of polymerization, clearly shows a broad peak of around 450 nm, confirming the formation of Au nanoparticles.

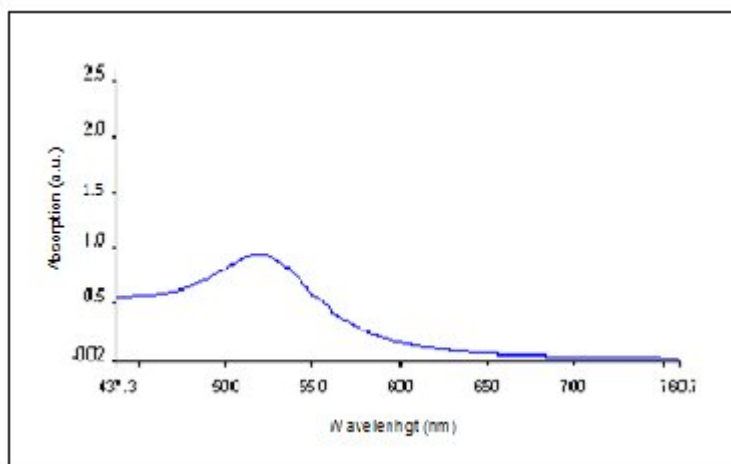


Figure 4.1a: UV-Visible spectra of gold nanoparticles

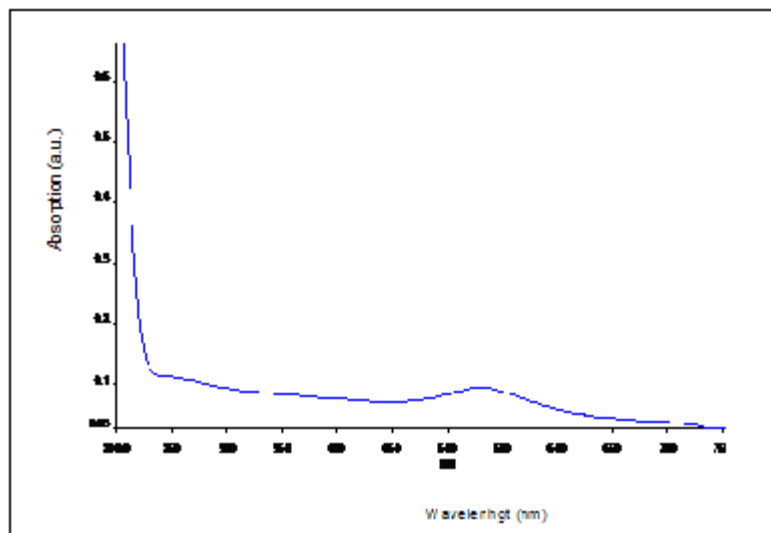


Figure 4.1b: UV-Visible spectra of PPY-Au nanocomposite

4.2 XRD ANALYSIS

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of material.

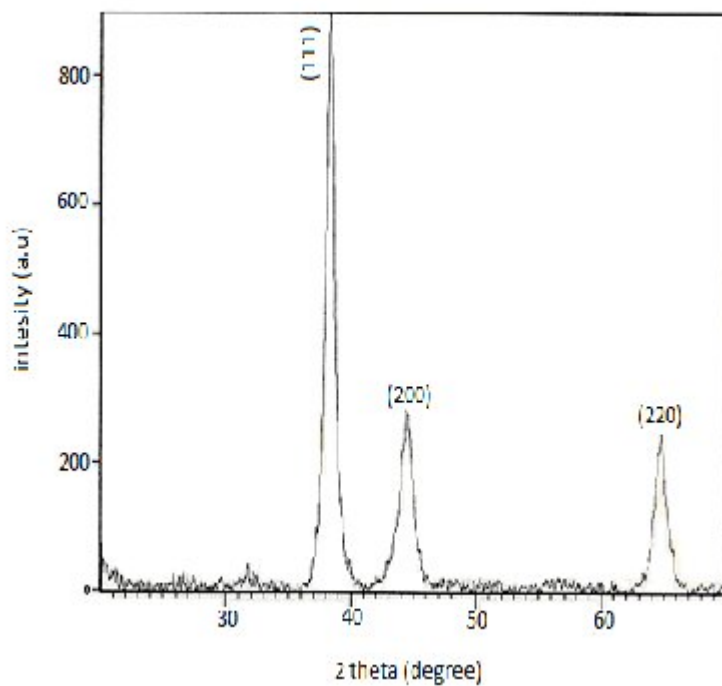


Figure 4.2 (a): XRD pattern of gold nanoparticles

The XRD patterns of Gold, PPY and PPY-Gold are shown in fig 4.3 (a-c). The XRD of Gold exhibit prominent broad peaks. The all XRD peaks are index with fcc structure. The Scherer's formula is used to calculate the particle size of Gold nanoparticles. The particle size is calculated as follows:

$$t = \frac{\lambda k}{\beta \cos\theta}$$

Where, t = thickness of crystallite

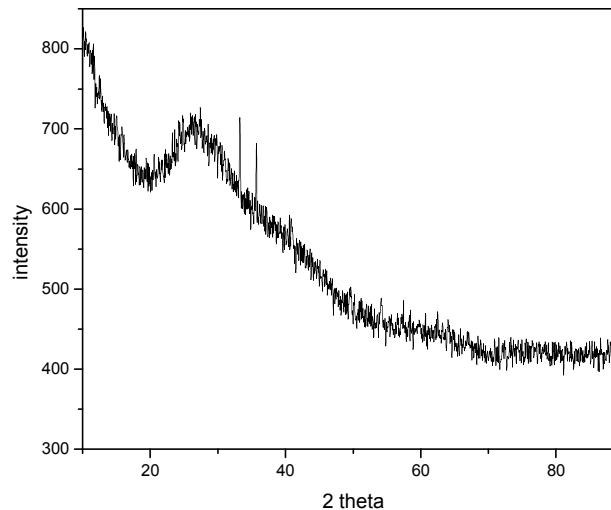
k = constant dependent on crystallite shape (0.89)

$\lambda = 1.54 \text{ \AA}$, (x-ray wavelength)

β = FWHM (full width at half max) or integral breadth

θ = Bragg angle

On the other hand, the XRD pattern of polypyrrole shows a broad hump around 23-32° which is clearly manifest of amorphous nature of the sample. However, in case of nanocomposite exhibit sharp XRD peak along with broad hump. In addition to this peak are shifted to the lower angle.



4.2 (b): XRD of pure polypyrrole

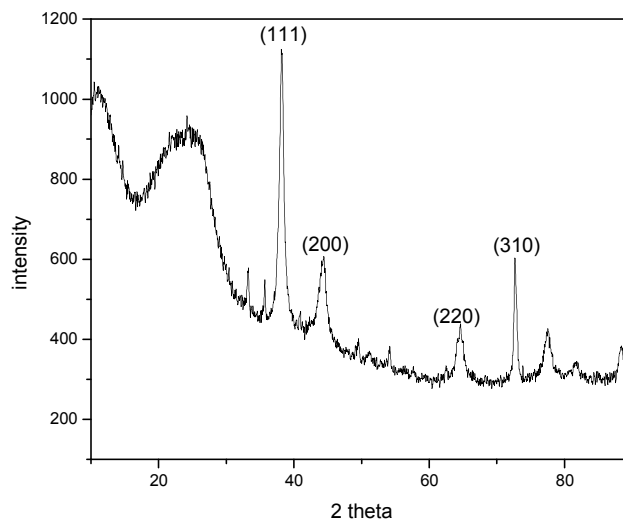


Fig 4.2 (c): Polypyrrole-gold nanocomposite

As shown in Figure 4.3c, peaks due to (111), (200) (220) and (310) Bragg reflections of Au nanoparticles can be clearly observed in nanocomposite sample. The particle size of Au nanocomposite are calculated using Scherer's formula and summarized in the Table 4.1.

Table 4.1

[°2Th.]	Plane	Crystallite size (nm)	Average crystallite size (nm)
38.1886	(111)	14.93	18.50
44.4246	(200)	16.76	
64.5947	(220)	10.20	
72.6453	(310)	32.12	

4.3 FT-IR Analysis:

The Spectrum of the PPY- Gold Composite clearly exhibit some shifts in the characteristic absorption peaks of PPY Figs 4.4 a-c showing the insertion of gold in polymer matrix. In the FT-IR spectra of both polypyrrole and polypyrrole gold composites, absorption peaks corresponding to bipolaron bands were observed at 904 and 1170 cm^{-1} in good agreement with spectroscopic characterization of polypyrrole. The shift in position of the peak at 1536 and 1642 cm^{-1} , corresponding to $-\text{C}-\text{N}$

stretch to higher wave numbers in the spectra, indicates an effective charge transfer between the Au and polypyrrole. The absorption peak at 1536 cm^{-1} corresponding to the C-C and C=C stretching vibrations in PPY has shifted to 1642 cm^{-1} . However, in PPY-Au nanocomposite weak bond at 1530 cm^{-1} is observed in PPY sample because of C-N stretching. This bond shifted to 1536 cm^{-1} in the PPY-Au nanocomposite. The appearance of absorption peaks at 1170 cm^{-1} is due to C-H and C-H plane deforming modes in pure PPY.

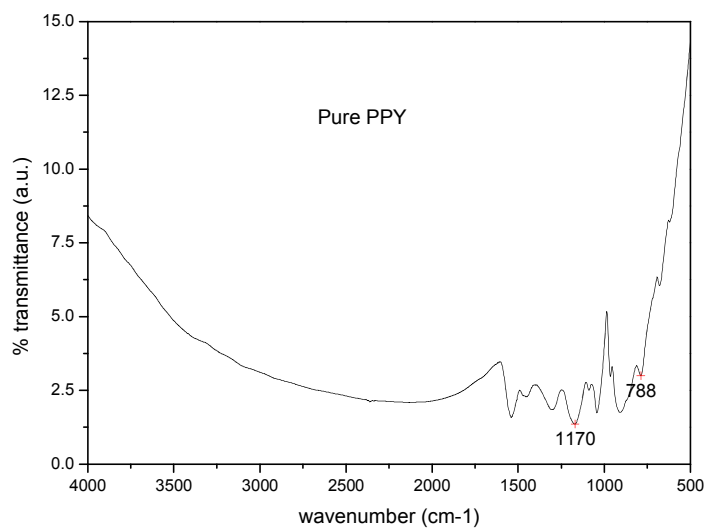


Figure 4.3 (a) FT-IR of Polypyrrole.

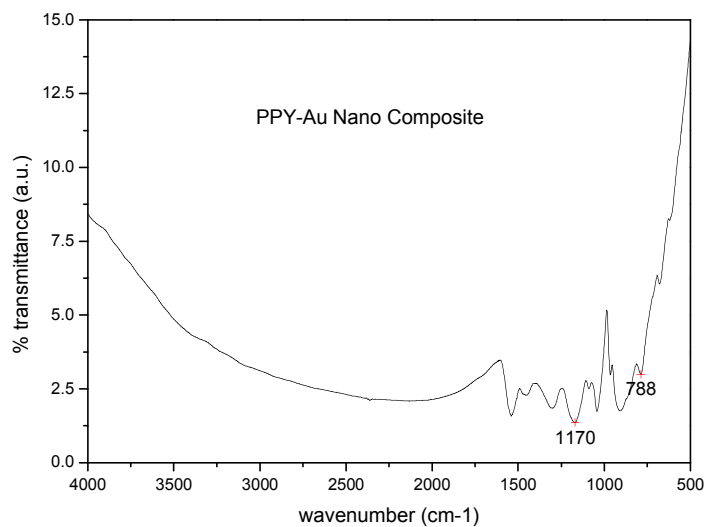


Figure 4.3 (b) FT-IR of PPY-Gold nanoparticle.

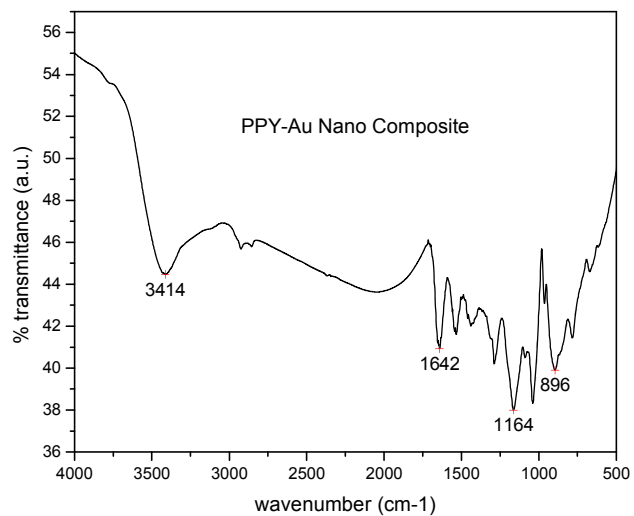


Figure 4.3 (c) FT-IR of PPY-Gold nanocomposite

4.4 TEM STUDIES

In the transmission electron microscopic study of the polypyrrole-Au nanocomposites, most of the gold nanoparticle was found attached to the polypyrrole matrix. The size

of the Au nanoparticles in the polypyrrole-gold composites is around 10 nm. The size of Au metal particles, calculated from TEM and from XRD, is in close agreement with each other.

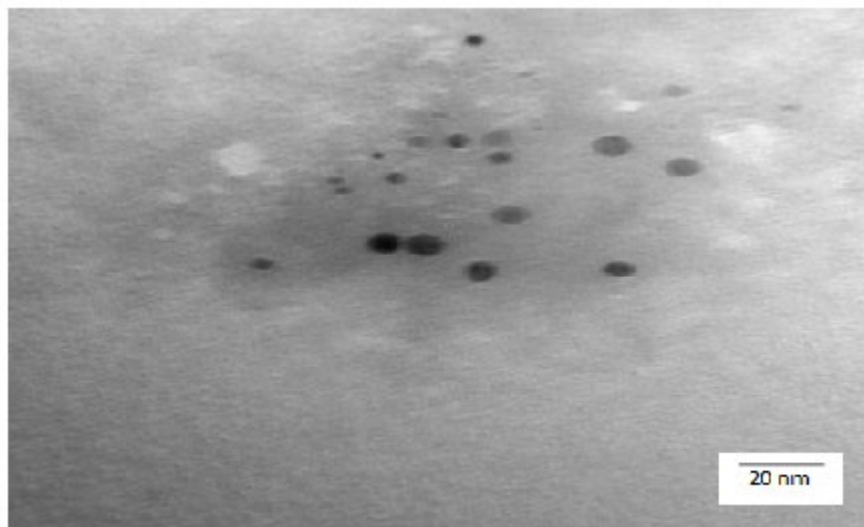


Figure 4.4 TEM Image of PPY-Au Composite

4.5 CONDUCTIVITY STUDIES

I-V characteristics of pure PPY and PPY-Au nanocomposite shown in Fig. 4.5(a) & Fig. 4.5(b) respectively. The I-V characteristics are taken on the silver coated pellets using two probe methods. The copper electrodes were placed on the both surface of coated samples. The electric conductivity of the polypyrrole gold nanoparticle composite powder is measured by the tow- point probe technique. The I-V characteristic of a palette of PPY and PPY-Au Composite in light. The pellets of PPY and its composites were coated with silver paste on either side. Copper electrodes were placed on both the surfaces to obtain a better contact. The value of the conductivity of nanocomposite is found $\sim 10^{-5} \text{ Scm}^{-1}$ because gold is a conductor, the higher conductivity of the nanocomposites should be ascribed to the combination of gold in the nanocomposites. It is clearly evident from the conductivity values that the dispersion of gold nanoparticles decrease the resitivity of the sample as compare to the polypyrrol due to metallic nature of gold nanoperticles.

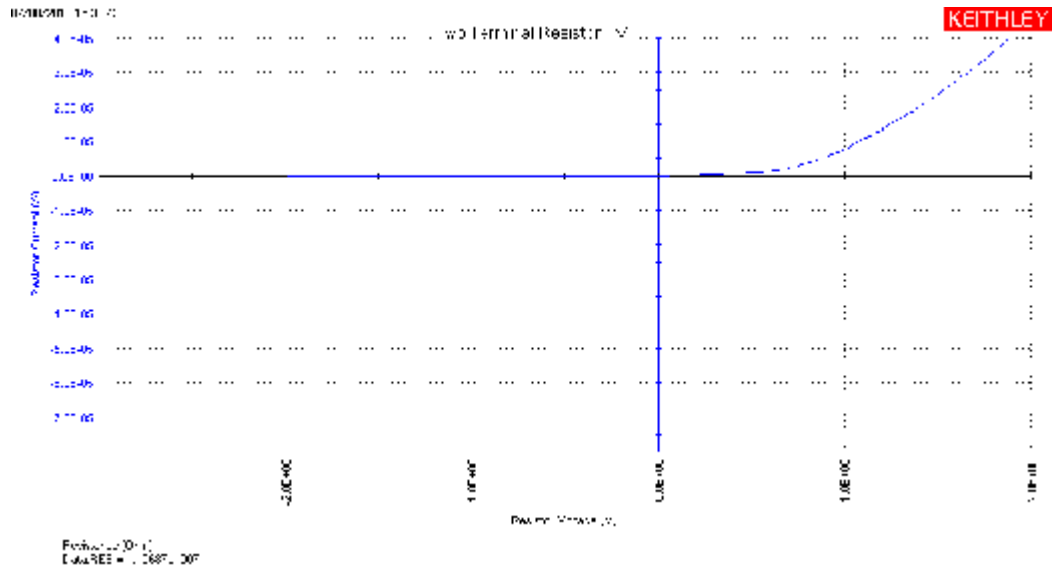


Figure 4.5(a) I-V Characteristics of Pure PPY

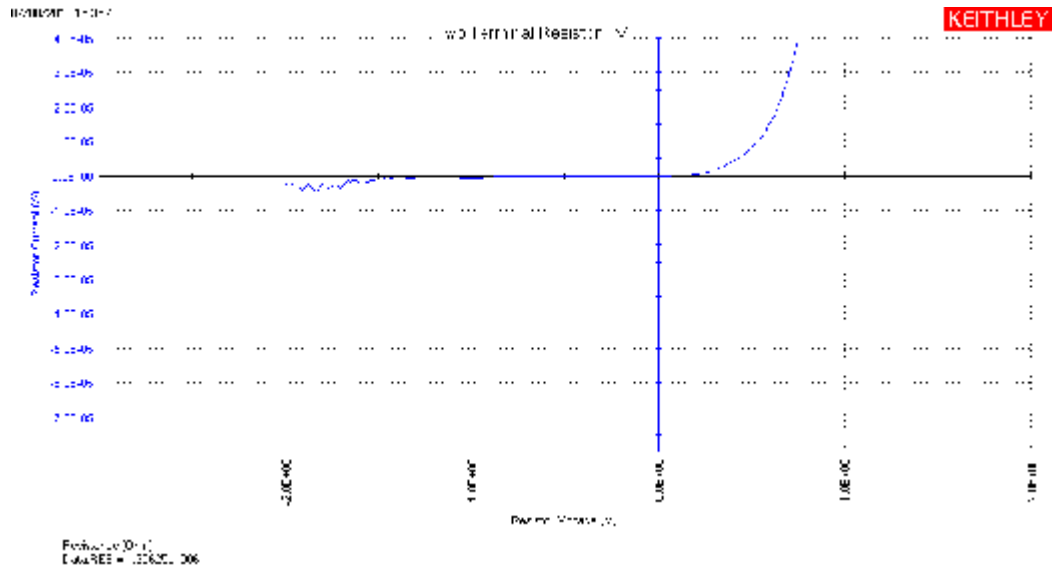


Figure 4.5(b) I-V Characteristics of PPY-Au Composite

CONCLUSIONS

The gold nanoparticles and polypyrrol are synthesis by chemical route. The particle size of the nanoparticle is calculated using Scherer formula i.e. 10nm. These nanoparticles disperse in polypyrrol polymer matrix in different ratio. The nanocomposite shows few order high conductivity then pure polypyrrol. The XRD and FTIR results of nanocomposite show well attachment of the nanoparticles with the polypyrrol matrix. However the particles of nanoparticles increase after dispersion in polymer matrix i.e. 35 nm (average).

In the depth study is required to understand the conductivity phenomena in nanocomposite using simulations. Number of samples synthesis with different concentration of gold nanoparticles in polymer, so that systematically the effect of gold nanoparticle can be observed.

REFERENCES

- [1] Hei R, Qian X, Yin J, Zhu Z, J. Mater. Chem. 12 (2002) pp 3783.
- [2] Kelsall R, Hamley I, Geoghegan M, Nano Science (2005) pp 278.
- [3] WILSON M, KANNANGARA K, SMITH M, RAGUSE B, NANOTECHNOLOGY BASICS SCIENCE (2005) PP 2378.
- [4] Daniel M and Astruc D, Chem. Rev. 104 (2004), pp 293.
- [5] Terasaki N, Yamamoto N, Biochem. Biophys. (2007) pp 345.
- [6] Murphy CJ, Sau TK, Gole AM, Li T, J. Phys. Chem. (2005), pp. 13857.
- [7] Cushing BL, Kolesnichenko VL and O'Connor CJ, Chem. Rev. (2004), pp. 3893.
- [8] Hussain I, Graham S, Wang Z, Tan B, Sherrington DC, Rannard SP, Cooper AI and Brust M, J. Am. Chem. Soc. (2005), pp. 16398.
- [9] Wilcoxon JP and Provencio PP, J. Am. Chem. Soc. (2004), pp. 6402.
- [10] Mafune F, Kohno J, Takeda Y and Kondow T, J. Phys. Chem. B (2001), pp 5114.
- [11] Bruchez M, Moronne M, Gin P, Weiss S, Semiconductor nanocrystals as fluorescent biological labels. *Science* (1998) pp 2013-2016.
- [12] Chan WCW, Nie SM Quantum dot bioconjugates for ultrasensitive nonisotopic detection. *Science* (1998) pp 2016-2018.
- [13] Mah C, Zolotukhin I, Fraites TJ, Dobson J, Batich C, Byrne BJ Mol Therapy (2000), pp S239.
- [14] Evgenia G. Matveeva, Tanya Shtoyko, Ignacy Gryczynski, Irina Akopova, and Zygmunt Gryczynski. J. Chem Phys. (2009) pp 85–90.
- [15] Bond G.C, Thomson D.T, Catalysis by Gold (2006) pp 567.
- [16] Jacob D. Gibson, Bishnu P. Khanal, chem. (2007), pp 129.
- [17] Qian, Ximei. Nature Biotechnology. 26 (2008) pp 123.
- [18] Lu X, Tuan HY, Korgel BA, Xia Y, Chem. Eur. J. (2008) pp 1584 – 1591.
- [19] H. Shirakawa, Angewandte Chemie – International Edition 40 (2001) pp 257.
- [20] Huang T, and Murray RW, American Chemical Society. 18 (2002), pp 7077-7081.
- [21] Carotenuto G and Nicolais L J. Mater. Chem., 13, (2003) pp 1038–1041.
- [22] Michael S.Fruend and Bhavana Deore Self doped conducting polymers (2007) pp 20-25.

- [23] Shirakawa H, Louis E. J., MacDiarmid A. G., Chiang C. K., *Chemical Communications* (1977) pp 578.
- [24] Heeger A. J., *Angewandte Chemie – International Edition* 40 (2001) pp 2591.
- [25] Liang Z , Zhang J, Wang L, Song S, Fan C, Li G J. *Mol. Sci.*((2007) pp 526-532 13.
- [26] Sarathy KV, Narayan KS, Kim J, *thin films Elsevier Science* (1999) pp 345.
- [27] Lin, J.S, Carpenter EE, and Connor CJO, *Journal of Solid State Chemistry* 159 (2001), pp 26-31.
- [28] Aslam M, Fu L, Su M, Vijayamohanan K and Dravid VP, *J. Mater. Chem*, (2004) pp 1795 – 1797, pp 2979 – 2980.
- [29] Fang F, Zhang YF *Journal of Materials Science* 40 (2005) pp
- [30] Liu H, Zhou Q, Liang Y, Yin G, Xu Z, *J mater sci* 41 (2006) pp 3657–3662.
- [31] Liang Z , Zhang J, Wang L, Song S, Fan C, Li G J. *Mol. Sci.*((2007) pp 526-532 13.
- [32] A. O. Patil, A. J. Heeger, F. Wudl, *Chemical Reviews* 88 (1988) pp 183.
- [33] Ahirwal GK and Mitra CK *journal Sensors* 2009, 9, pp 881-894.
- [34] Chen J, Hass O, *Journal of Materials Science* 1997
- [35] Lee L, Mueller, K. *Phy.Rev.*(2001) pp 345
- [36] Singh R, Tandon R P, Panwar V S and Chandra S *J. Appl. Phys.* (1991) pp 2504.
- [37] Mohammadi A, Lundstrom, I *Polymer Sci* (1993) pp 395.
- [38] Rasika Dias H.V, Fianchini M., *Polymer* (2006) pp 47, 7349.
- [39] Toshima N., Tayanagi J, *Chem. Lett.* (1990) pp 1369.
- [40] Freifeldel M, *Practical Catalytic Hydrogenation* (1971) pp 39.
- [41] Comotti M, Della Pina C., Matarrese R., Rossi M, *Angew. Chem. Int. Ed* (2004) pp 43, 5812.
- [42] M. Comotti, C. Della Pina, E. Falletta, M. Rossi, *J. Catal.* (2006) pp 244, 89.
- [43] Alexander L. E, *X-ray Diffraction in Polymer Science"*, (1969). pp 453.
- [44] Painter P. C., Coleman M. M., J. Koenig L., “*The Theory of Vibrational Spectroscopy and its Application to the Polymeric Materials* (1982) pp 567.
- [45] Wan, M.; Wei, W.; Zhang, Z.; Zhang, L.; Huang, K.; Yang, Y. *Synth. Met.* (2003) pp 135-136, 175.