Development of Conducting Polyaniline-Gold Nanocomposites

IISER PUNE

Thesis Submitted towards the Partial fulfillment of BS-MS dual degree programme

By

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Dedicated to My Beloved Parents ……….

CERTIFICATE

This is to certify that this dissertation entitled "DEVELOPMENT OF CONDUCTING POLYANILINE-GOLD NANOCOMPOSITES" towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research Pune, represents original research carried out by Anuj Bisht at Department of Chemistry under the Supervision of Dr. M. Jayakannan during the academic year 2011-2012.

Anuj Bisht

Supervisor   **Head of Department of Chemistry**

Date: **Date:**

Place: **Place:**

DECLARATION

I hereby declare that the matter embodied in the report entitled **"DEVELOPMENT OF CONDUCTING POLYANILINE-GOLD NANOCOMPOSITES"** are the results of the investigations carried out by me at the Department of Chemistry, Indian Institute of Science Education and Research (IISER) Pune, under the supervision of Dr. M. Jayakannan and the same has not been submitted elsewhere for any other degree.

Place:Pune   **ANUJ BISHT**

April 2012

ACKNOWLEDGEMENT

ABSTRACT

In the present thesis work, a new renewable resource amphiphilic surfactant was developed and utilized as structure directing agent-cum-dopant for gold nanoparticles, polyaniline nanofibers, gold-polyaniline nanocomposites. Gold and aniline forms self-redox couple, gold was reduced into gold nanoparticles and aniline was simultaneously oxidized to polyaniline nanofibers. Both emulsion and interfacial route were explored for the nanocomposites synthesis. Detailed morphology analysis, photophysical characterization and X-ray diffraction studies revealed that the nanocomposites produced by the interfacial route were more superior than that of the emulsion routes. The nanocomposites produced in the interfacial route were found to be highly crystalline, ordered and showed well-defined lamellar packing in solid state. The approach demonstrated here is a very potential synthetic methodology for the development of conducting polymer-gold nanocomposites which have potential applications in optoelectronics and sensors.

CONTENTS

<u>INTRODUCTION</u>

1.1. Introduction to Nanomaterials

Nanoscience involves the study of behaviour and control of materials and processes at the molecular and atomic levels. One of the fascinating aspects of science at the nanoscale is that the size and shape dependent properties of materials. Properties of nanomaterials are considerably different as compared to those of bulk materials.[1] The larger surface area to volume ration of nanomaterials provide new applications in drug delivery, composite materials, energy storage and chemical reactions, surface based science such as catalysis, which can lead to new science as well as new devices and technologies.[2] The importance and potential of nanosized materials was first pointed out by renowned Physicist Richard Feynman during a lecture entitled "There is plenty of room at the bottom" in 1959.[3] He proposed manipulating individual atoms to create new small structures having completely different properties. For a clear understanding of size ranges a comparison of various commonly encountered objects are given in figure 1.1.
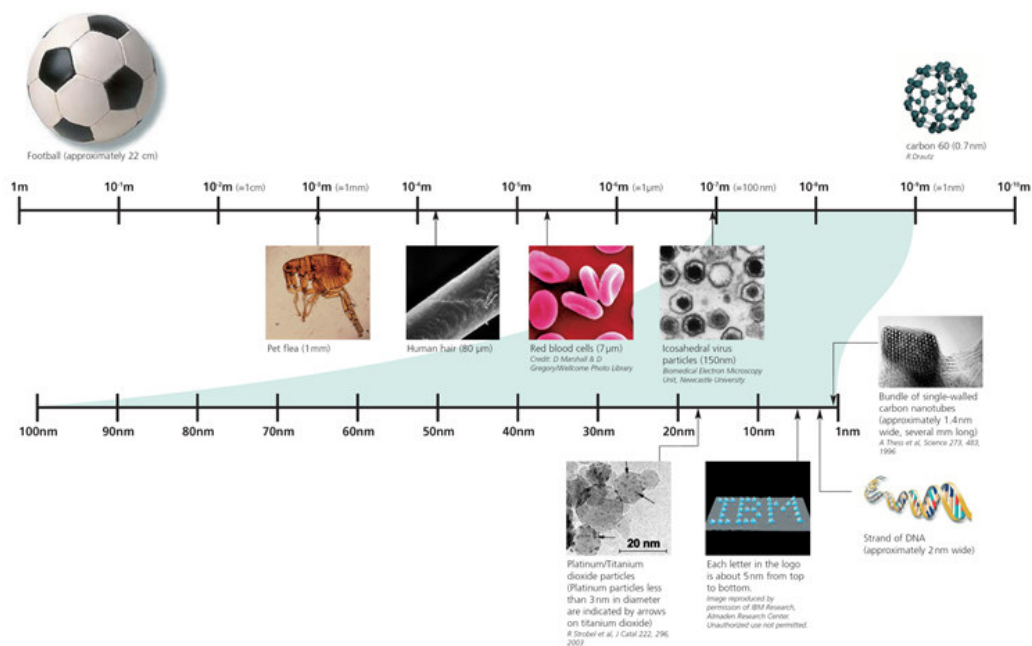
Figure 1.1. *The nano scale – A comparison of the size of some of the common objects with nanomaterials. (adopted from the reference 4)*

A number of physical phenomena become noticeably pronounced as the size of the system decreases. These include statistical mechanical effects, as well as quantum mechanical effects, for example the "quantum size effect" where the electronic properties of solids are altered with great reductions in particle size.[1-4] This

effect does not come into play by going from macro to micro dimensions. However, it becomes dominant when the nanometre size range is reached. Currently nanoscience has grown up to a fully-fledged fascinating interdisciplinary area of research because of the novel quantum and surface phenomena exhibited by these new classes of materials at the nano-scale enabled a wide range of applications in the field of physics, chemistry, biology, material science and engineering. Some examples of nanomaterials are listed in table 1.1.

Table 1.1. *Examples of nanomaterials*

Type	Size	Materials
Quantum dots	Diam. 1-10 nm	Metals, semiconductors
Other nanoparticles	Diam. 1–100 nm	Ceramic oxides
Nanowires	Diam. 1-100 nm	Metals, oxides, sulfides, nitrides
Nanotubes	Diam.1–100 nm	Carbon, metal chalcogenides
Nanoporous solids	Diam. 0.5–10 nm	Zeolites, phosphates etc.
2-Dimensional arrays	2 nm –2 µm	Metals, semiconductors, magnetic materials
Surfaces and thin films	1–1000 nm	A variety of materials (e.g., polymers)
3-D structures (super lattices)	Several nm in the 3-D	Metals, semiconductors, magnetic materials

There are two type of approaches for the synthesis of nanomaterials namely bottom up and top down approach (see figure 1.2). In top down approach, a bulk material break into smaller pieces using mechanical, chemical or other form of energy. The important top down approaches are beam lithography (patterning using light beam), ball-milling (the formation of nanostructure building blocks through controlled mechanical attrition of the bulk starting material). In the bottom up approach, materials are synthesized from atomic or molecular species via chemical reactions, allowing for the precursor particles to grow in size via molecular self assembly (bottom-up)(ref of anil). The well known bottom-up methods are template based self-assembly, supra-molecular self-assembly etc.

One of the oldest nano-sized objects known to us was made of gold. It is not clear when humans first began to take advantage of nanosized materials. It is known that in the fourth-century A.D. Roman glassmakers were fabricating glasses containing nanosized metals. An artefact from this period called the Lycurgus cup resides in the British Museum in London. However, the scientific story of

nanoparticles began much later. In 1856,[5] Faraday prepared the colloidal solution of gold which he called it "divided metal". Nanoparticles does exhibit many unique interesting properties, but it is just a matter of time until more of these properties will be exploited.
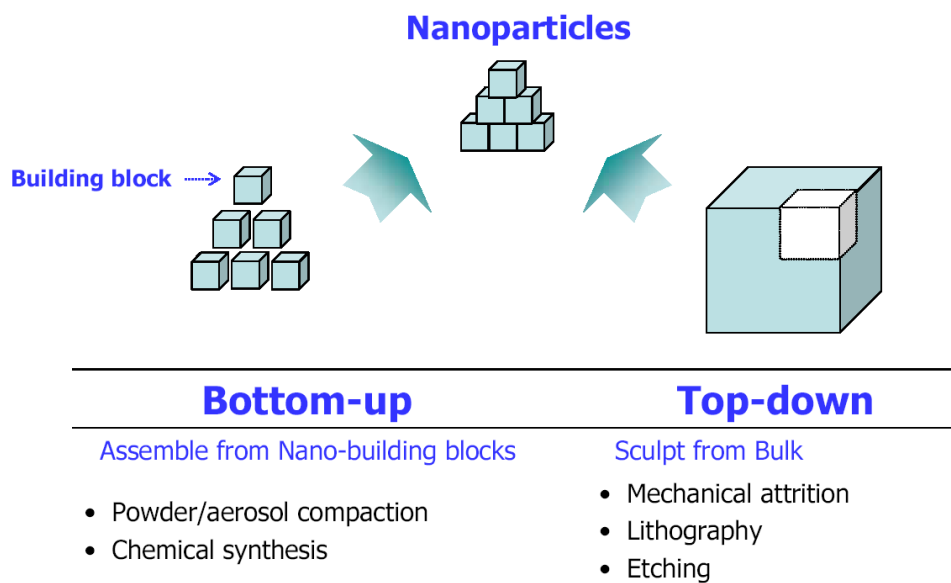
Figure 1.2.*Schematic representation of top down and bottom up methods.*

1.2. Gold Nanoparticles

The importance of gold nanoparticles is mainly due to the new and improved properties observed in nanoscale to the interface which were not seen in individual or bulk atoms. Gold nanoparticles (AuNPs) possess distinct physical and chemical properties that make them excellent material for many potential applications, such as biochemical sensors, electronics, biological imaging and medial therapeutics as well as in catalysis.[6]

Gold nanoparticles are unique because: (1) they can be synthesized easily and can be stabilized in solution, (2) they provide high surface-to-volume ratio, (3) the high surface–to-volume ratio provides optoelectronic properties called surface plasmon resonance and 4) these properties can be tuned by varying their size and shape (see figure 1.3). Multifunctionalization of gold nanoparticles with wide range of organic or biological ligands make them useful for
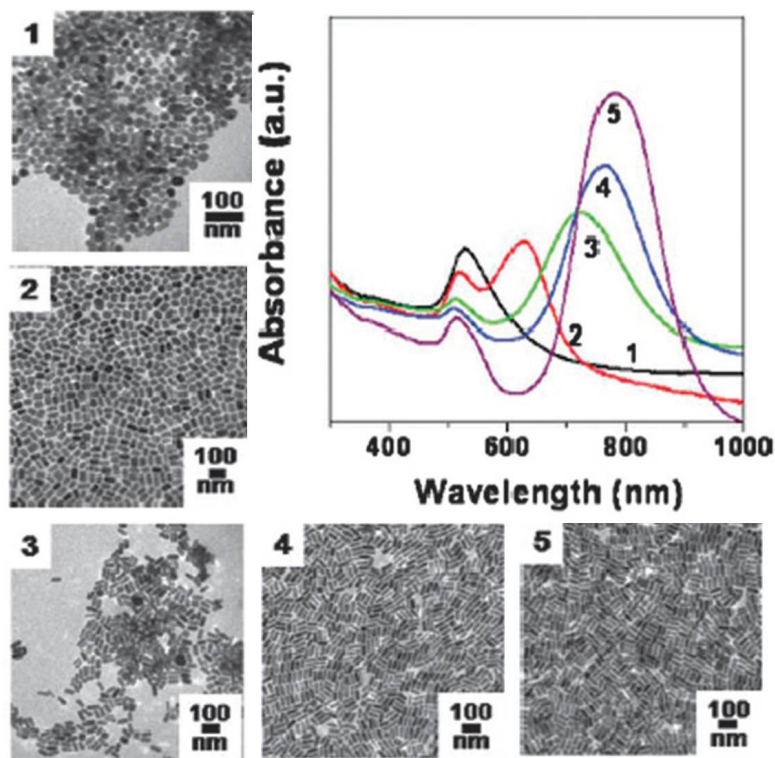
Figure1.3. Effect of anisotropic growth of AuNPs on optical properties (adapted from reference 7.)

selective binding and detection of small molecules and biological targets. There are a large number of ways to synthesize AuNPs most of the time starting from commercial $HAuCl_4$. Citrate reduction of Au(III) to Au(0) in water was introduced by Turkevitch et al. in 1951, a method that is still under practice.[8] Recent modifications of the Turkevitch method have allowed better size distribution and size control within the 9–120 nm range.[9] Brust and Schiffrin in 1994 have reported two phase synthetic strategy utilising strong thiol gold interaction to protect AuNPs with thiol ligands.[10] In this method, $AuCl_4^-$ is transferred from aqueous phase to toluene using tetraoctylammonium bromide (TOAB) and reduced by $NaBH_4$ in presence of dodecanethiol. On addition of $NaBH_4$, a quick colour change from orange to deep brown was observed. The AuNPs are generated in toluene with controlled diameter in the range 1.5 to 5 nm. After this report a diverse anisotropic AuNPs are reported by varying different parameters, and using variety of capping agents (cationic, anionic and neutral surfactants).[11,12] Amphiphilic surfactants such as cetyltrimethyl ammonium bromide (CTAB) with hydrophobic tail and positively charged polar head

are widely used to achieve anisotropy in nanoparticles.[13] The cationic surfactants are generally employed, while there are fewer reports on the use of anionic surfactants as shape directing agent.[14] However, the role of the anionic surfactant structure on the morphology and optoelectronic properties of gold nanoparticles are yet to be understood on fundamental level.

### 1.3. Electrically Conducting Polymer

Conducting polymers are organic polymers that can conduct electricity. This class of polymers has a highly delocalized π-electron system with alternative single and double bonds (conjugated) in the polymer backbone. It was discovered in 1977 by Mac-Diarmid, Heeger and Shirakawa that the conjugated polyacetylene conduct electricity upon exposure to iodine vapour.[15,16] This discovery initiated a substantial amount of effort in understanding these new classes of polymers and recognized by 2000 Nobel Prize. In conducting polymers the π-conjugation of the polymer chain generates high energy occupied (HOMO) and low energy unoccupied molecular orbitals (LUMO) leading to a system that can be readily oxidized or reduced.[17] Their electronic conductivity is called intrinsic as it is caused by the presence of conjugated electrons in the polymer backbone which enables electric charges to
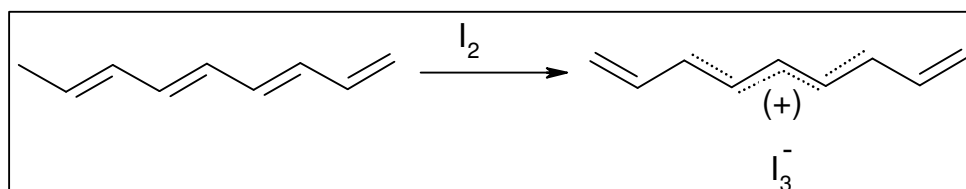
Figure 1.4. *Doping in conducting Polyacetylene.*

move around without any added conducting materials (e.g. metals, graphite). In most of the cases, these polymers are insulators in their neutral state and they become conducting only after introduction of electron acceptors/donors by a process known as 'doping' (see figure 1.4). Conducting polymers can provide the conduction of electric charges through movement of electrons in unoccupied energy states or movement of holes in filled energy states. The creation of conductive holes in polymer by oxidation is called p-type doping and the creation of free electrons by reduction is called n-type doping. The first discovered conducting polymer

polyacetylene has a high conductivity, but its poor environmental stability hampers practical applications. This has led to the discovery of a variety of other conducting polymers such as polypyrrole (PPy), polythiophene, poly-p-phenylene, poly-p-phenylenevinylene (PPV), polyaniline (PANI) etc.[16,18] shown in figure 1.5. The electrical behaviour of these polymers and their derivatives are similar to that of polyacetylene, but they showed higher stability and better processability.
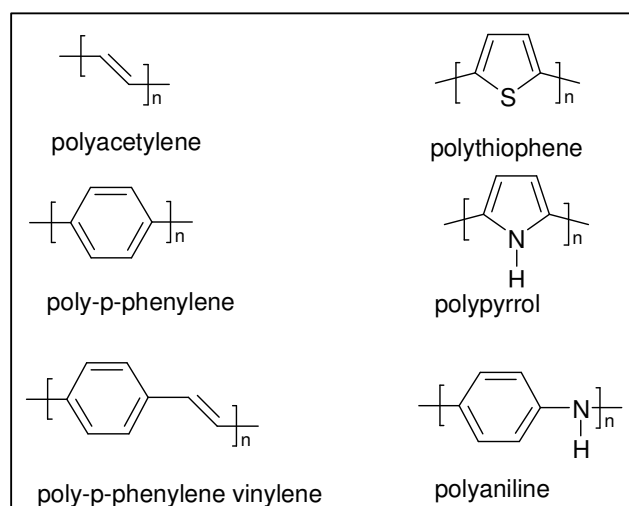
Figure 1.5. *Various types of conducting polymers.*

1.4. Polyaniline Nanomaterials

Among the conducting polymers polyaniline is unique due to its wide range of conductivity from insulating to metallic regime, redox tunability, good environmental stability, low cost, ease of synthesis, and promising applications in various fields, such as metallic corrosion protection, electromagnetic interference shielding, electrostatic discharge, sensors, actuators etc.[15,19] Polyaniline and its derivatives are generally synthesized by chemical or electrochemical oxidative polymerization of the aniline monomers in acidic aqueous media.[19,20] Polyaniline has three different oxidation states. They are fully reduced colourless leucoemeraldine form; half oxidized blue coloured emeraldine base form and fully oxidized brown coloured pernigraniline form.[21,22] These oxidations states can be reversibly change from one to other by means of chemical or electrochemical means (see figure 1.6). All these three forms are found to be insulators of electricity in normal conditions.[23] But the emeraldine base form on protonation will yield green coloured emeraldine salt, which is a highly conducting material. When polyaniline is prepared by the conventional

chemical oxidative polymerization from aniline monomer in acidic media, emeraldine salt (protonated form) can be obtained that can then be converted into the emeraldine base form by treating with base. The conductivity change between emeraldine salt ($\sigma \geq 1$ S cm^{-1}) and emeraldine base ($\sigma \leq 10^{-10}$ Scm^{-1}) states can be greater than ten orders of magnitude.
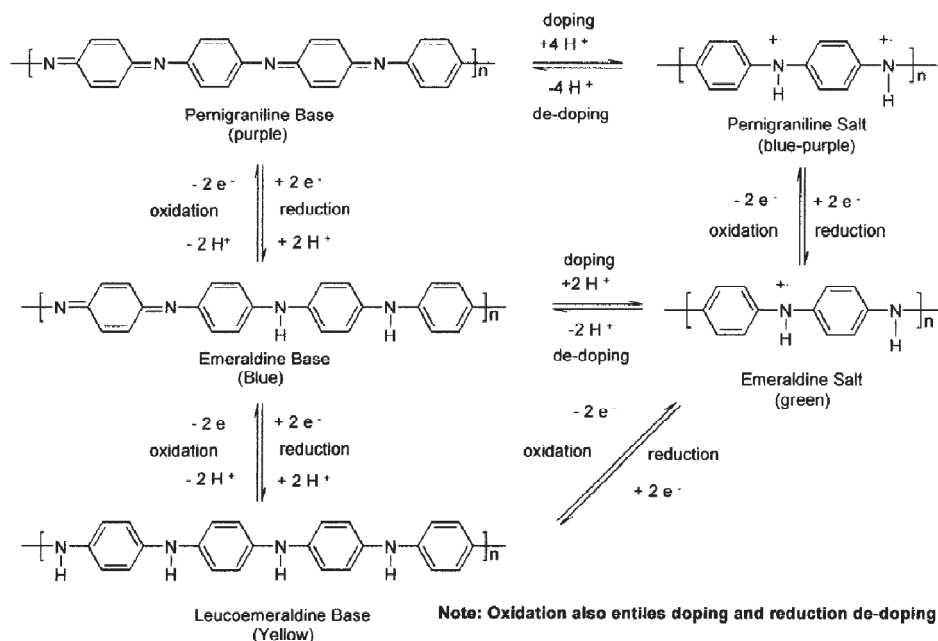
Figure 1.6. *Various oxidation states of polyaniline and their redox tenability (adopted from reference 58)*

Number of attempts has been carried out to synthesize polyaniline nanomaterial and explore its novel properties.[24,25] The first developed and straight forward methods for the synthesis of nano-polyaniline were physical routes like electro spinning and mechanical stretching.[15] But these techniques are not suitable for making nanostructures of <100 nm dimension. So the interest shifted to develop in situ synthetic approaches for nano-dimensional polyaniline. This chemical approach was again categorized namely the template synthesis and the no-template synthesis, with respect to whether template is used or not. The template based methods were subdivided into hard template (physical template) and soft template (chemical template) synthesis approach according to the solubility of the templates in the reaction media.[25,26] Hard template synthesis for architecting conducting polymers were developed by Martin et al. , which make use of the pores, channels of hard materials such as polymer membranes , zeolites, anodic aluminium oxide etc. as

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template for polymer growth.[27,28] Here the monomer was filled in pores of template and upon polymerising the polymer formed will take the shape of the channel. The main advantage of this approach is by selecting suitable template characteristics it is possible to precisely tune the morphological features like diameter, length etc. However, the main drawback of the method is that a rather tedious post-synthesis process is required in order to remove the templates and also the nano-structure may be destroyed or form undesirable aggregated structures after released from the templates.

1.4.1. Soft template synthesis

The soft template or self-assembly method is an easy and widely used scalable method pioneered by Wan and co-workers.[29-34] This process involves the use of structure-directing molecules such as surfactants, functional dopants, amphiphilic polymers, liquid crystals, supramolecular assemblies as templates for production of the one-dimensional nanomaterials of polyaniline and polypyrrole. The widely used
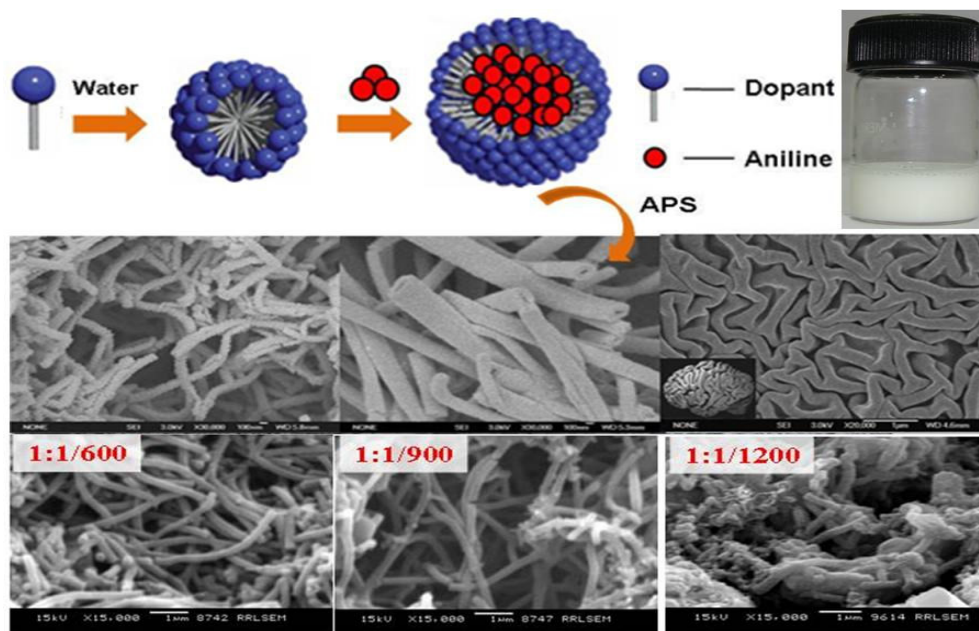
Figure 1.7. *A schematic representation of soft template approach and various polyaniline morphologies synthesised this route (adapted from reference-35).*

functional dopants are naphthalenesulfonic acid (NSA), camphorsulfonic acid (CSA), azobenzenesulfonic acid (ABSA), 2-acrylamido-2-methyl-1-propanesulfonicacid (AMPSA) and the polyelectrolytes include poly (acrylicacid), poly (styrene

sulphonicacid) etc. This method is free of post synthesis processing since these molecules are good dopants for polyaniline. In a typical synthesis, aniline and functional dopant with different molar ratios were added to a certain amount of distilled water and stirred to result the formation of aniline-dopant complex. This soft template was oxidised by oxidants like ammonium per sulphate to get nanomaterials (see figure 1.7). The formation of the one-dimensional nano-structured polyaniline depended on the reaction conditions, such as the concentration of aniline, the molar ratio of aniline to oxidant, the soft template etc.[36,37] By adopting soft template approach a variety of nanostructures including nanofibers, nanotubes, nanorods, nanospheres and nanoleaves etc were synthesised. So by selectively tuning the self-assembly properties of the dopant template it is possible to create a variety of nanostructures. Another important advantage of this process is that after synthesis of nanostructures it is possible to employ any dopant by a dedoping–redoping procedure without significantly changing the morphologies and diameters of the nanostructures.
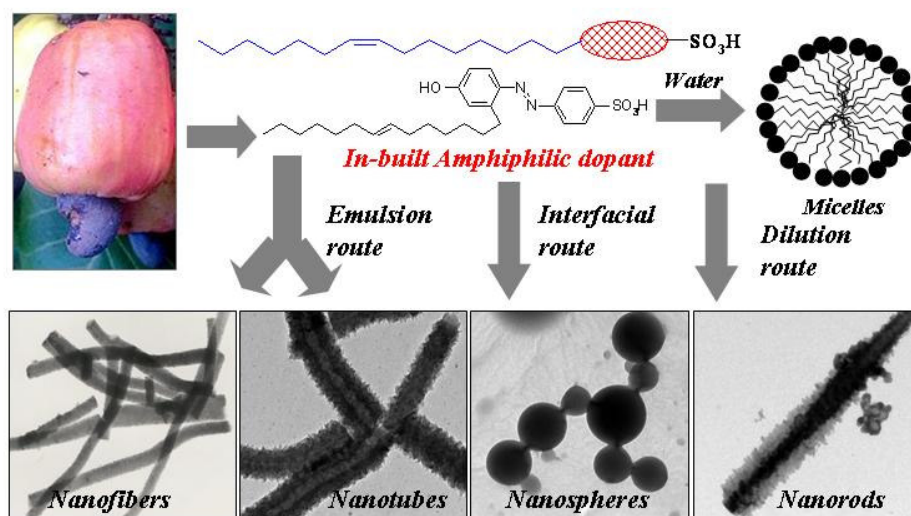
Figure 1.8.*Synthesis of Polyaniline nanostructures using different methods of polymerisation route (adapted from [Anilkumar, et al 2009]).*

Anilkumar *et al* from our group have reported the synthesis of polyaniline nanofiber using renewable resource cardanol derived surfactant for the synthesis of polyaniline nanofibers via emulsion route see figure1.8. [aAnilkumar*et al* 2006]. Detail investigation reveals that nanofibers were formed due to the oxidation of self assembled aniline + surfactant cylindrical template. The nanofiber formation was

facile for wide range of [aniline]/ [surfactant] concentration which was rarely reported in literature for synthesis of polyanilinenanofibers. Interfacial polymerisation was also carried out using the same anionic surfactant + oxidant in aqueous layer and aniline in organic layer resulted formation of nanospheres [^{c}Anilkumar*et al* 2008]. The formation of the spherical aggregates between surfactant and oxidant ammonium persulfate and subsequent monomer intake at the interface created the polyaniline nanospheres. In general, the sound knowledge of the polyaniline structure and chemical properties, with reasonably good solubility and processability, thermal and environmental stability, and facile nanomaterial formation makes this polymer front runner in conducting polymer nanomaterials.

1.5.   Aim of the thesis

The organic/inorganic nanocomposites with different combinations of the two components have gained attention because of their interesting physical properties and potential applications.[40] The incorporation of metallic or semiconducting nanoparticles such as polypyrrole and polyaniline is of interest because of the strong electronic interaction between then a nanoparticles and polymer matrixes.[41,42] The ability to control the shape and size of nanocomposites is an important factor for defining their properties, such as the electronic band gap conductivity, catalytic efficiency and light-emission efficiency.[43,44] The schematic representation of the PANI/Au nanocomposite formation is shown in figure 1.9.

Gold Nanoparticles   Polyaniline Nano-fibres   Gold-PANI Nanocomposites
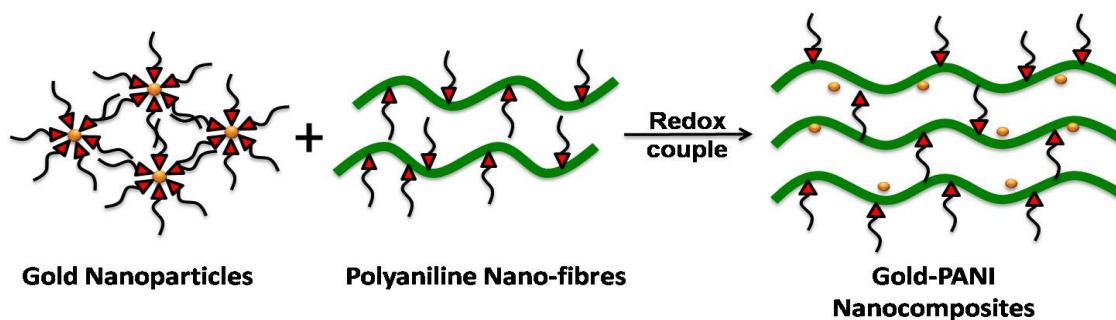
Figure 1.9.*Schematic representation for PANI/Au nanocomposite formation.*

As we discussed above amongst the conducting polymers, polyaniline has been extensively studied because of its ease of synthesis by simple oxidation reaction, controllable electrical conductivity and interesting redox properties

associated with the polymeric chain. On the other hand, among the metal nanoparticles gold has been extensively studied due to its easy synthesis by reduction of its precursor like $HAuCl_4$, their unique optical and catalytic properties. Thus, a gold-polyaniline composite would acquire quality through the combination of both components. Recently few reports documents the development of PANI/Au nanocomposites using surfactants and the resultant nanocomposites possess improvement in their properties like good stability, high conductivity and the unique optical behaviour.[45-47] However, role of the surfactant structure, polymerisation methodology and the characterisation of PANI/Au nanocomposite, understanding at the premature level.

In this thesis work, renewable resource surfactant was employed as a dual surfactant for stabilizing gold as well as PANI nanomaterials and PANI/Au nanocomposites. Further efforts has been taken to trace the role of the composition of the gold & PANI in polymerization process, oxidising agent, reducing agent in details to correlate their structure-property relationship. The novelties of the thesis work are pointed as follows:

(i) A renewable resource dopant containing aliphatic tail and hydrophilic -SO_3H polar head was custom designed through tailor made approach.

(ii) Gold nanoparticles of 50 nm were successfully synthesized using the renewable resource surfactant.

(iii) The surfactant was also employed as dopant for synthesizing PANI nanofibers.

(iv) A self-redox coupling of gold and aniline in the presence of renewable resource surfactant produced well defined PANI/Au nanocomposites.

(v) The role of the polymerization methodology such as emulsion and interfacial on the properties of nanocomposites were investigated in details.

(vi) The resultant nanocomposites were characterized by HR-TEM, WXRD, DLS, UV-Spectrophotometer, etc.

Finally, the important outcome of the thesis work is summarized in the last chapter.

EXPERIMENTAL SECTION

2.1. Materials:

3-Pentadecylphenol, 1, 4-butanesultone, potassium tertiary butoxide, chloroauric acid ($HAuCl_4.3H_2O$, 99.9%), sodiumborohydride ($NaBH_4$, 95 %), ammoniumpersulfate (APS) were purchased from Sigma Aldrich chemicals. For gold nanoparticles synthesis, 18 MΩ deionized water (Milli Q) was used. Glassware were cleaned with aqua regia and rinsed with water prior to use.

2.2. Measurements:

Purity of the synthesized surfactant was confirmed by NMR (Jeol NMR spectrophotometer, 400 MHz) using d_6-DMSO as solvent containing small amount of TMS as internal standard. Infrared spectrum of the surfactant was also recorded by using Thermo-Scientific Nicolet 6700 FT-IR spectrophotometer. The nanoparticles were characterized by Perkin-Elmer Lambda-45absoption spectrophotometer.Morphology of nanomaterials was studied by using FEI Technai T30 Stwin, 300kV TEM instrument and JEOL JSM-6360A SEM instrument. X-ray diffraction patterns were recorded on BrukerAdvace D80 (Cu Kα radiation) instrument.

2.3. General Procedures:

2.3.1. Synthesis of 4-(3-Pentadecylphenoxy)butane-1-sulfonic acid (PDP-C₄SO₃H):

3-Pentadecylphenol (5.0 g, 16.5 mmol) was added into a flask containing potassium tertiarybutoxide (3.7 g, 33.0 mmol) in dry ethanol (50 ml). This solution was heated at 60 ºC for 30 min under nitrogen atmosphere. The contents were cooled and 1,4-butanesultone (4.5 g, 33.0 mmol) was added drop wise. The reaction was continued by refluxing for 40 hours under nitrogen atmosphere. It was cooled and white solid mass was isolated by suction filtration. The white potassium salt of the product was suspended in water (20 ml) and acidified by 5M HCl to get sulfonic acid as white precipitate. The solid was further purified by passing through silica gel column using 15/85 methanol/DCM (v/v) as eluent. Yield = 6.9 g (97 %). Melting point: 79-83 ℃. ^{1}H-NMR (d_6-DMSO)δ: 7.14 ppm (t, 1H, Ar-**H**), 6.70 ppm (m, 3H, Ar-**H**), 3.90 ppm (t, 2H, Ar-O-**CH₂**), 2.50 ppm (t, 2H, HO₃S-**CH₂**), 1.72 ppm (m, 4H, -**CH₂**-**CH₂**-CH₂-SO₃H), 2.49 ppm (m, 2H, Ar-**CH₂**-C₁₄H₂₉), 1.25 ppm (m, 24H, aliphatic

side chain), 0.84 ppm (t, 3H, -CH$_3$), ^{13}C-NMR (d_6-DMSO)δ: 158.7, 143.9, 129.2, 120.4, 114.4, 111.5, 67.1, 51.1, 35.2, 31.35, 29.1, 28.7, 22.1, 21.9, and 14.0. FT-IR (KBr): 3490, 2916, 2849, 1612, 1581, 1471, 1450, 1296, 1245, 1158, 1058, 969, 864, 778, 752, 718,688, 621, 595, and 529. MALDI-TOF-TOF (MW: 440.0): m/z = 479.1 (as MK$^+$ ion).

2.3.2. Synthesis of gold nanoparticles:

Gold nanoparticles were synthesized by reduction of chloroauric acid with sodium borohydride in an aqueous surfactant solution. In a typical synthesis, 0.1 M HAuCl$_4$(50µL) and of 0.1M ice-cold aqueous NaBH$_4$ (60µL) were added to of 0.01mM surfactant solution (19.89ml) under stirring at room temperature. The solution turned purple immediately on addition of NaBH$_4$. Solution was left to stand at room temperature after stirring for 30 minutes. The removal of the water destabilized the Au-nanoparticles, and therefore, it was directly used for TEM, UV-vis and WXRD analysis and the data are provided in the results and discussion part.

2.3.3. Preparation of polyaniline nanomaterial via emulsion route:

Typical procedure for the emulsion polymerization for polyaniline nanomaterial is explained in detail for PDP-C$_4$-SO$_3$H assisted process. Similar synthetic procedure is adopted for other dopants unless specified separately. PDP-C$_4$-SO$_3$H (96.4 mg, 0.22 mmol for 1:1/50 composition) was taken in distilled water (20 mL) and stirred under sonication for 15 minutes. Distilled aniline (1.0 mL, 11.0 mmol) was added to the surfactant solution and stirred under sonication for 1 h. At the end of sonication, the polymerization mixture turned into a pale yellow thick emulsion. APS(1.35M aqueous solution, 5.0 mL) was added drop wise at 0℃ to the above solution and continued the stirring under sonication for 1h. The polymerization was continued without disturbance for 15 h at 5°C. The polymer was filtered, washed with water and methanol till the filtrate become colourless. The green polymer was dried under vacuum oven for 24h at 60°C (0.01 mmHg). Yield = 240 mg (24 %).^{1}H-NMR (400 MHz, d_6-DMSO) δ: 7.40 ppm (m, 2H, Ar-**H**, Pani), 7.44 ppm (m, 2H, Ar-**H**, Pani), 7.78 ppm (s, 4H, Ar-**H** Dopant). FT-IR (KBr, cm^{-1}): 1570, 1500, 1300, 1140, 1030, 818 & 694. UV-visible (in water, nm) λ max: 297, 427 and broad peak at 838 nm.

2.3.4. Synthesis of Polyaniline nanomaterials via interfacial route:

Aniline (1mL) was diluted in 100ml of toluene.PDP-C_4-SO_3H (96.4mg, 2.19×10^{-4} mol) and APS (2.77g, 1.21×10^{-2} mol) were dissolved in 100ml of Millipore water in a 250ml beaker. Aniline solution was added gently along the sides of the beaker to the above aqueous mixture. The resulting two-phase system was covered to minimize solvent evaporation and left undisturbed for 24h. The reaction mixture was filtered and the dark green precipitate washed repeatedly with acetone (10 x 25ml) until the filtrate becomes colourless. The green powder was dried in vacuum oven at 60°C for 13h.FT-IR (in cm^{-1}): 1570, 1480, 1300, 1110, 802, 694, and 617. UV-visible (in water, nm) λ max: 328, 449 and free carrier tail >700.

2.3.5. Synthesis of PANI/Au Nanocomposite via emulsion route

In a typical experiment, PDP-C_4SO_3H (96.4 mg) was dissolved in Millipore water (20 mL); the solution was heated and sonicated for 30 min. To that, aniline (1 mL) was added and sonicated it for 10-15 min, yielding a milky white emulsion at room temperature. The milky white emulsion was divided into 4 aliquots (5 mL each) for the following experiments.

Composition-1: (H_2O+PDP-C_4-SO_3H+Aniline)+$HAuCl_4$: The milky white emulsion (4.7 mL) was taken in glass vial and 0.1M $HAuCl_4$ (0.27 mL) solution was added drop wise. After addition, stirring continued for 30 min at room temperature and then kept undisturbed for 15h for complete growth of nanocomposite.

Composition-2: (H_2O+PDP-C_4-SO_3H+Aniline)+$HAuCl_4$+$NaBH_4$: The milky white emulsion (4.4 mL) was taken in glass vial and 0.1 M $HAuCl_4$ (0.274 mL) was added to it. Then, freshly prepared 0.1M $NaBH_4$ (0.3 mL) was added drop-wise (in cold condition) into the solution. After addition, stirring continued for 30 min at room temperature.

Composition-3: (H_2O+PDP-C_4-SO_3H+Aniline)+$HAuCl_4$+APS: The milky white emulsion (4.7 mL) was taken in glass vial; 0.1M $HAuCl_4$ (0.27 mL) was added to it. Then, APS (0.17 g) was added to the solution. After addition, stirring continued for 30 min at room temperature. Reaction mixture kept undisturbed for 15 h for complete growth of nanocomposite.

Composition-4: (H$_2$O+PDP-C$_4$-SO$_3$H+Aniline)+HAuCl$_4$+NaBH$_4$+APS: The milky white (4.4 mL) emulsion was taken in glass vial and 0.1M HAuCl$_4$ (0.27 mL) was added to it. Then, freshly prepared 0.1M NaBH$_4$ (0.3 mL) was added drop-wise (in cold condition) into the solution. APS (0.17 g) was added to the above reaction mixture. After addition, stirring continued for 30min at room temperature.

After the completion of the reaction all the four samples were centrifuged for 30 min at 5000 rpm. Supernatant was removed and precipitate was re-dispersed in water. The removal of the water destabilized the nano-composites, and therefore, the nano-composite was directly used for TEM, UV-vis and WXRD analysis and the data are provided in the results and discussion part.

2.3.6. Synthesis of PANI/Au nanocomposite by using against the gravity approach:

 PDP-C$_4$-SO$_3$H (96.4 mg, 0.219 mmol) was dissolved in 100 mL of Millipore water. The solution was then placed into a pre-heated water bath at 45°C for 10min and also sonicated for 10 min. Aniline (1 mL, 10.96 mmol) was dissolved in DCM (100 mL).In a 250-mL beaker, Aniline-DCM solution was added first because of higher density and then PDP-C$_4$-SO$_3$H solution was added gently with minimal agitation along the sides of the beaker to the solution. 0.1MHAuCl$_4$ (1.0 mL, representing a mole ratio of ~1:1/100 Aniline toHAuCl$_4$) solution was injected very slowly to the top layer (aqueous layer) along the sides of the beaker. The resulting two phase system was covered to minimize solvent evaporation and left undisturbed for 24 h. After the completion of the reaction, the nano-composite dispersed in the aqueous medium was collected separately. The removal of the water destabilized the nano-composites, and therefore, the nano-composite was directly used for TEM, UV-vis and WXRD analysis and the data are provided in the results and discussion part.

2.3.7. Synthesis of PANI/Au composite by using towards the gravity approach

Aniline (1 mL, 10.96 mmol) was diluted in toluene (100 mL). PDP-C$_4$-SO$_3$H (96.4 mg, 0.219 mmol) was dissolved in 100mL of water in another 100ml conical flask. Sonicated and heated it for 15 min. In a 250-ml beaker, PDP-C$_4$-SO$_3$H solution

was added first because of higher density and then toluene-aniline solution was added gently and with minimal agitation along the sides of the beaker to the solution. $0.1 M HAuCl_4$(1.0 mL, representing a mole ratio of ~1:1/100 Aniline to $HAuCl_4$) solution was injected very slowly to the bottom layer (aqueous layer).The resulting two-phase system was covered to minimize solvent evaporation and left undisturbed for 30 h. Top organic layer was removed using dropper, and the nanocomposites in the aqueous medium was stored. The removal of the water destabilized the nano-composites, and therefore, the nano-composite was directly used for TEM, UV-vis and WXRD analysis and the data are provided in the results and discussion part.

RESULTS AND DISCUSSIONS

3.1 Synthesis of Surfactant and PANI-Nanofibers

Ring opening of 1,4-butanesultones with naturally occurring alkyl chain substituted phenols {Pentadecyl phenol (PDP)} from cashew nutshell yielded an amphiphillic as PDP-C_4-SO_3H as shown in the reaction scheme in figure 3.1 .
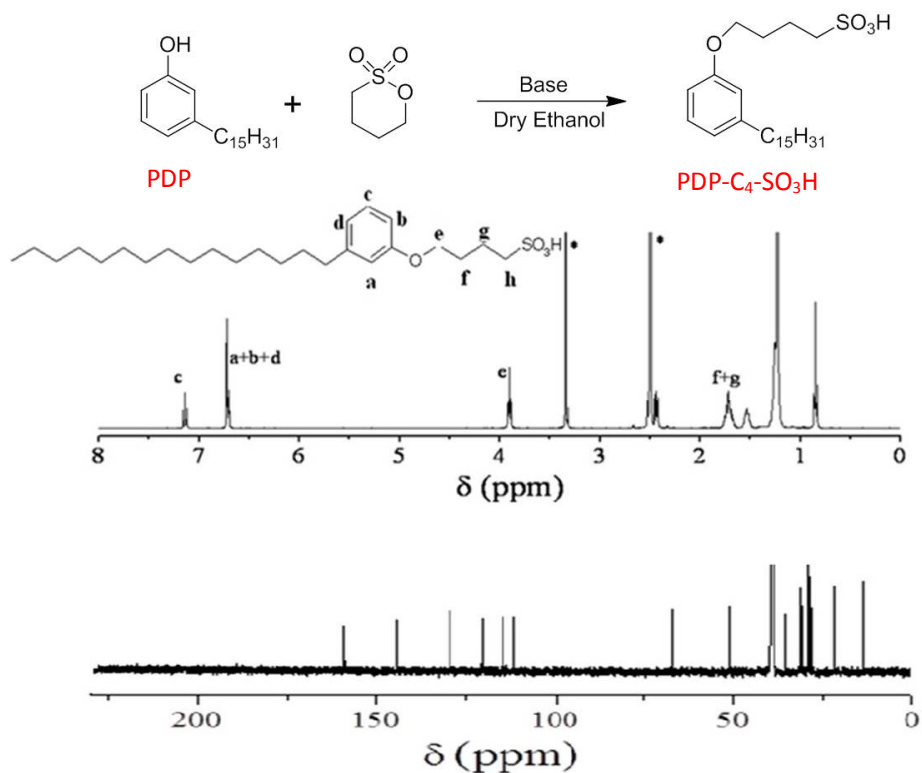
Figure 3.1.*Synthesis of PDP-C4-SO3H surfactant –cum-dopant molecule, its ^{1}H-NMR and ^{13}C-NMR.*

The purity of PDP-C_4-SO_3H was confirmed by ^{1}H-NMR and ^{13}C-NMR spectra of the dopants in d_6-DMSO (see figure 3.1). Various types of protons are assigned with alphabets corresponding to their struture. The four aromatic protons in PDP-C_4-SO_3H appeared at 7.14 ppm (for c-proton) and 6.70 ppm (for a+b+d protons together). Protons with respect to Ar-O-**CH₂** appeared at 3.9 ppm. The other two protons from the sultone part (f and g) appeared at 1.72 ppm. Ar-**CH₂** and **CH₂**-SO_3H are merged with DMSO solvent peak at 2.5 ppm. The peak intensities are in accordance with expected structure, which confirms the formation of new renewable resource amphiphilic dopants. The ^{13}C-NMR spectra of the dopants showed peaks corresponding to their aliphatic and aromatic carbons.

The newly synthesized amphiphilic molecule (PDP-C$_4$-SO$_3$H) is soluble in water and undergoes self-assembly to form spherical micelles of 5.4 nm size which was studied in detail by using DLS and surface tension measurement earlier in our group[48]. Aniline in micellar solution of PDP-C$_4$-SO$_3$H prefers to stay in hydrophobic core of the micelle which forms white thick emulsion. Emulsion is soft template which on subsequent oxidation by adding ammonium persulphate forms polyaniline nanomaterial. Morphology studies by SEM and TEM microscopy revealed the formation of PANI nanofibers (see figure 3.2).
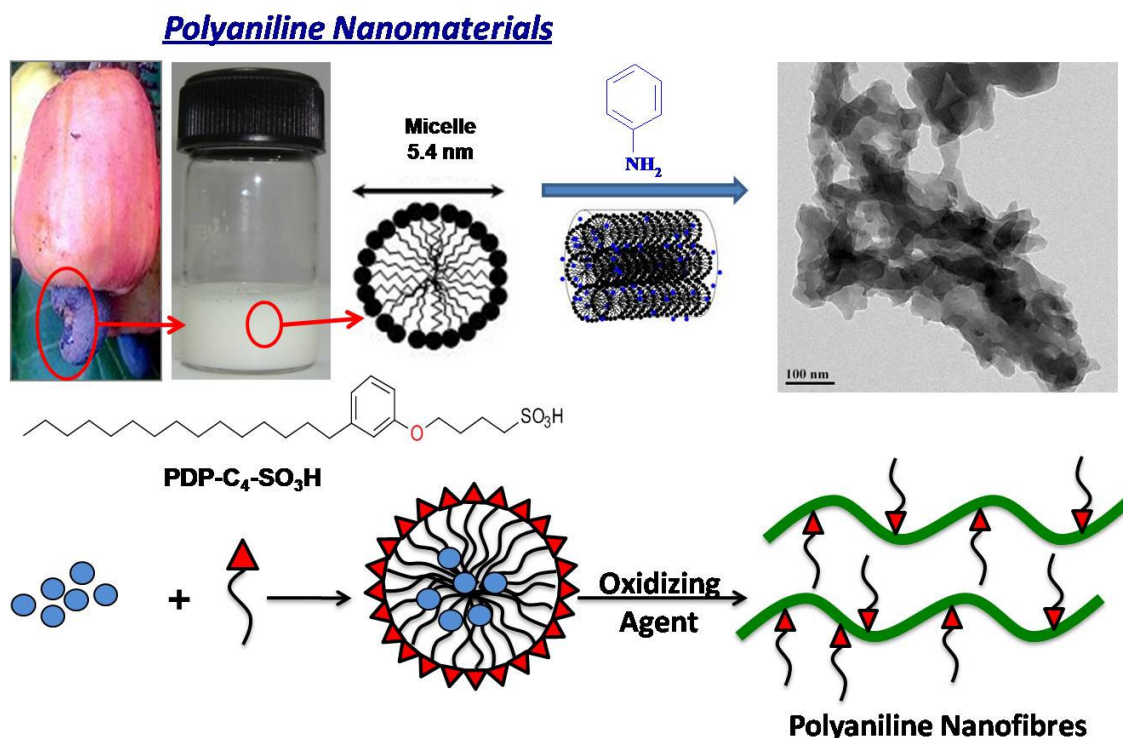

Figure 3.2. *PANI nanofiber synthesis by using PDP-C$_4$-SO$_3$H as dopant via emulsion route and its TEM image*

3.2. Synthesis of Gold Nanoparticles

The PDP-C$_4$-SO$_3$H molecule behaves as typical amphiphile through hydrophilic sulphonic acid as a polar head and the long alkyl chain as a hydrophobic tail. Gold nanoparticles were synthesized by using PDP-C$_4$-SO$_3$H as stabiliser in water. The precursor of gold i.e. HAuCl$_4$ in micellar solution of PDP-C$_4$-SO$_3$H was reduced by using NaBH$_4$. Reaction mixture containing HAuCl$_4$ and PDP-C$_4$-SO$_3$H was yellow coloured which on reduction with NaBH$_4$ gave purple solution as shown in figure 3.3. Gold nanoparticle formation was confirmed by colour change from

yellow to purple. The AuNPs are stable as colloid and do not phase separate. TEM analysis of stable colloid shows uniformly distributed spherical nanoparticles of 6 nm size (see figure-3.3). This indicates that the PDP-C_4-SO_3H plays important role in controlling shape and stabilising AuNPs. Selective Area Diffraction (SAD) image of AuNP showed the well defined ring-spot pattern giving conformation of face centred cubic crystal lattice.ng PDP-C_4-SO_3H arrangement of PDP-C_4-SO_3H around AuNP spheres for stabilization.
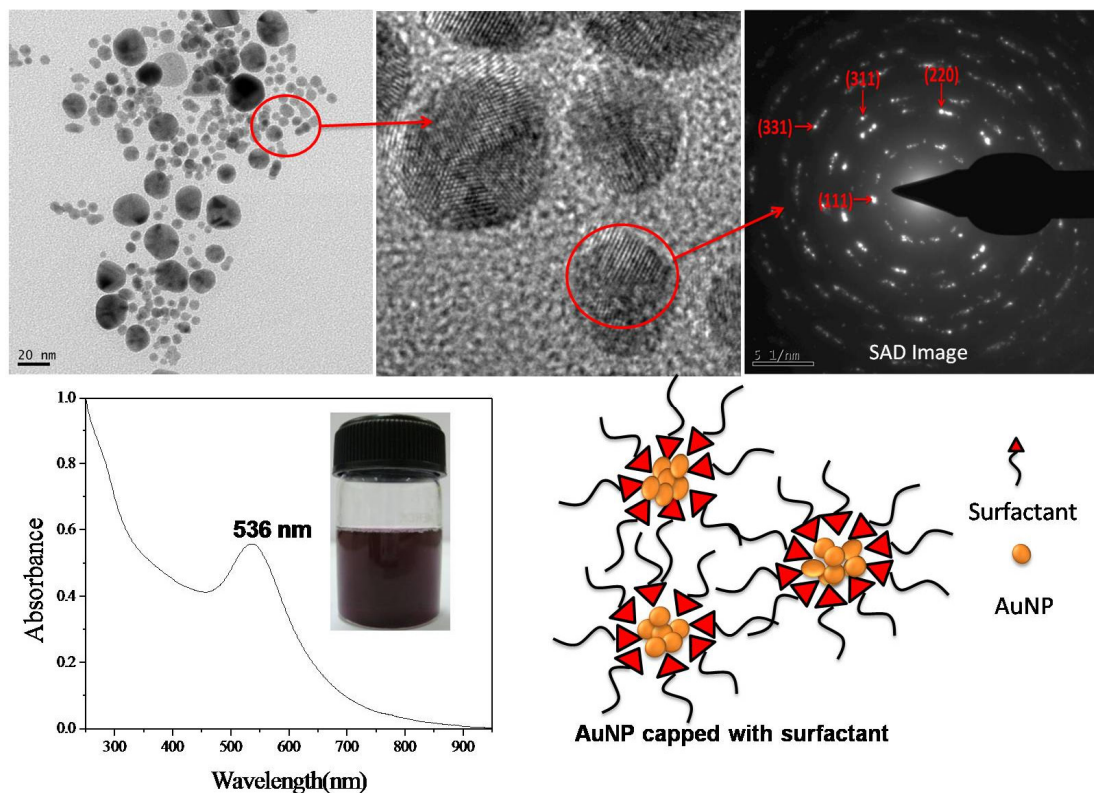

Figure 3.3.*Morphology of AuNPs synthesized by using PDP-C_4-SO_3H arrangement of PDP-C_4-SO_3H around AuNP spheres for stabilization.*

3.3. Synthesis of PANI/Au Nanocomposites in Emulsion route

From above discussion it is understood that by careful selection of surfactant-cum-dopant we can synthesize PANI nanofibers and isotropic AuNPs. The two concepts of synthesizing PANI nanomaterial and AuNPs by using common micellar template of suitable surfactant-cum-dopant can be introduced to synthesize PANI/Au composite. Chemical synthesis of a PANI/Au composite is based on the redox properties of chloroauric acid and aniline. $HAuCl_4$ is reduced from Au(III) to Au(0) by aniline accompanying the simultaneous oxidation and polymerisation of aniline to

polyaniline. The important issue for reaction to proceed is that the reduction potential for HAuCl$_4$ to form its Au(0) state should be lower than the aniline. It is studied that in aqueous solution the reduction potential for HAuCl$_4$ is 0.853 V (vs SHE) and oxidising potential for aniline is 1.183 V (vs SHE). So that in presence of each other in water the HAuCl$_4$ reduction to Au(0) and the corresponding amine oxidation reaction to its radical cation is irreversible.[49] The concept of synthesis of PANI/Au nanocomposites by using PDP-C$_4$-SO$_3$H via redox coupling between aniline and HAuCl$_4$ were performed as shown in figure 3.4.

## Pani-Gold Nanocomposities
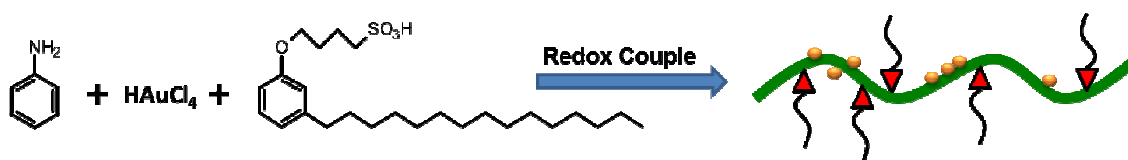
Figure 3.4.*Schematic representation of PANI/Au nanocomposite formation.*

Typically aniline+surfactant in water produced milky emulsion which was further used for the synthesis of nano-composites. PANI/Au nanocomposites were synthesized by four different ways:

(i)   Aniline + HAuCl$_4$ (Redox Couple)

(ii)   Aniline + HAuCl$_4$ + Reducing Agent (NaBH$_4$)

(iii)   Aniline + HAuCl$_4$ + Oxidizing Agent (APS)

(iv)   Aniline + HAuCl$_4$ + Reducing Agent (NaBH$_4$) + Oxidizing Agent (APS)

(i) Addition of HAuCl$_4$ in emulsion changes colour from white to pink and then immidiately to green. Homogeneous green coloured solution was stable for long time and the phase separation did not occur. TEM image of PANI/Au nanocomposite showed fibrilar polyaniline matrix with trapped gold nanospheres (see dark spots in figure 3.5). This shows that individual morphology of PANI (fiber) and AuNPs (spheres) in the nanocomposite has been retained as observed in above reactions. Under this reaction gold acted as oxidizing agent for aniline and aniline oxidized into anilinium radical which subsequently polymerize to form polyaniline. Au(III) will get

reduced to Au(0) and the particles were stabilized by both the surfactant and polymer chain.
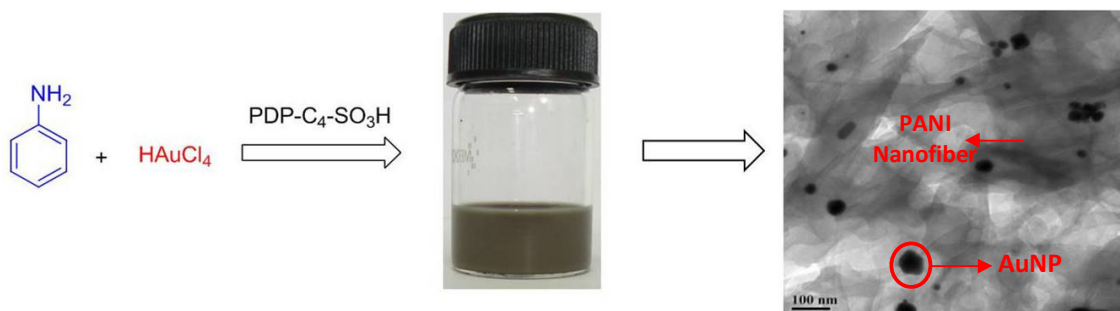
Figure.3.5. *PANI/Au nanocomposite synthesis by using PDP-C$_4$-SO$_3$H as dopant-cum-surfactant via emulsion route for composition and its TEM image.*

(ii) In this process, excess APS (oxidising agent) was added into the redox couple (Aniline+Au), so that the role of oxidising agent could be understood. After addition of HAuCl$_4$ to the emulsion (aniline+dopant) a stable green coloured solution obtained. Addition of excess APS induced phase separation as shown in figure 3.6. The phase separation of the product is due to fast polymerization of aniline by the APS rather than by Au. The image showed the matrix of PANI fibers only and no AuNP was observed (see figure 3.6). The Presence of PANI fibers showed the dominance of PANI nanomaterial rather than PANI/Au nanocomposites.
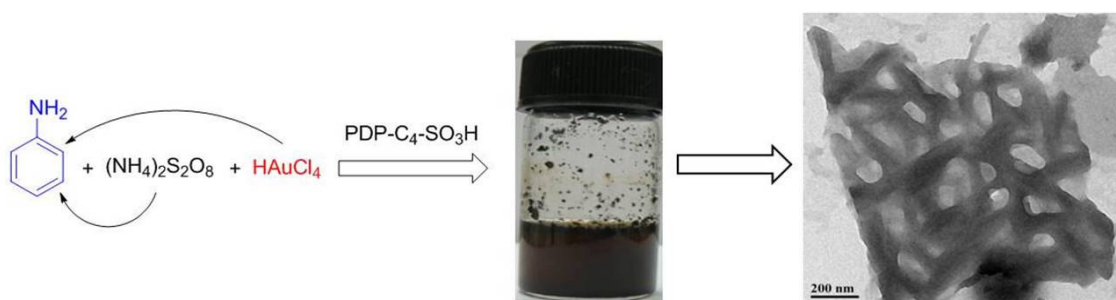
Figure 3.6. *PANI/Au nanocomposite synthesis by using PDP-C$_4$-SO$_3$H as dopant.*

(iii) In this process, excess of NaBH$_4$ (reducing agent) was added into the redox couple (Aniline+Au), so that the role of reducing agent could be understood. After Addition of HAuCl$_4$ in emulsion (aniline+dopant) a stable green coloured solution obtained. Addition of excess NaBH$_4$ did not affect the stability of colloid.
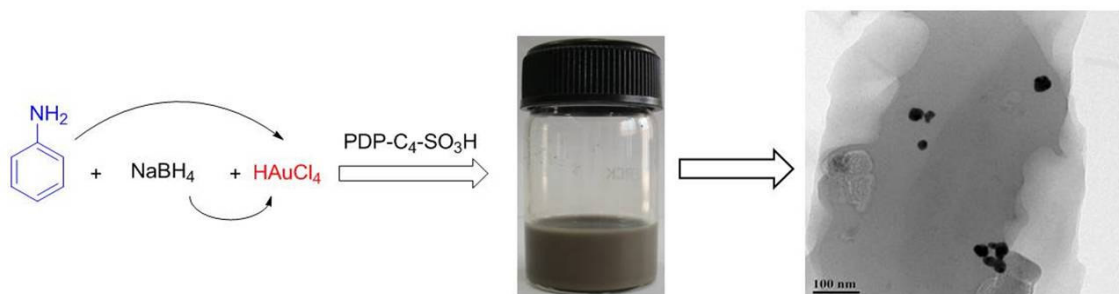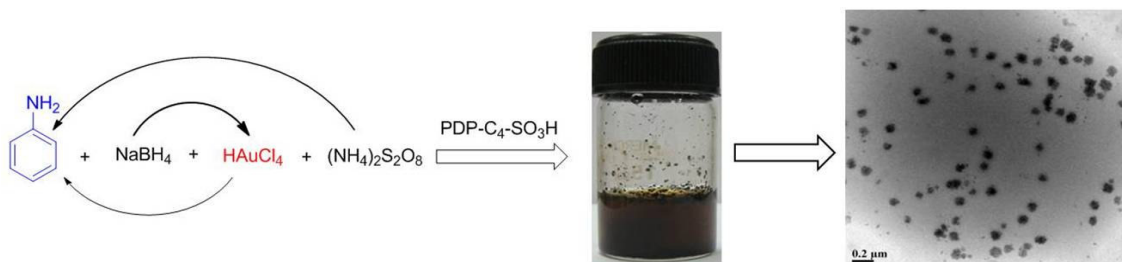
Figure 3.7.*PANI/Au nanocomposite synthesis by using PDP-C$_4$-SO$_3$H as dopant-cum-surfactant via emulsion route for composition-3 and its TEM image.*

There is a competition reaction between aniline and NaBH$_4$ to reduce HAuCl$_4$ to AuNPs. In this composition PANI and AuNP components were, but the morphology for PANI was not retained. The TEM images showed polymeric sheet for PANI associated with agglomerated spherical AuNPs (see figure 3.7).

(iv) In this process both the oxidising and reducing agent were added to redox couple (Aniline+Au), so that, the role of both oxidising & reducing agent could be understood. After adding both oxidising and reducing agent to the redox couple complete phase separation was seen, similar to APS case as shown in figure 3.8. TEM image of the resultant product showed aggregated nanocomposites which were not uniform (see figure 3.8), which revealed that this composition has no specificity for any component formation in PANI/Au nanocomposite.

Figure 3.8.*PANI/Au nanocomposite synthesis by using PDP-C$_4$-SO$_3$H as dopant-cum-surfactant via emulsion route for composition-4 and its TEM image.*

Collectively if we compare all possibilities, compositions in which APS was used showed fast polymerization which lead to the phase separation of resultant material. Morphology of corresponding material showed that the polymer formation was more dominant over AuNPs formation. The addition of both APS and NaBH$_4$ formed aggregated nanocomposites which were not uniform. Therefore, self-redox

couple of HAuCl$_4$+Aniline was the most suitable combination for PANI/Au nanocomposites formation. The mechanistic pathway for emulsion polymerization is shown in figure 3.9. In the emulsion polymerization, surfactant–cum-dopant molecule self-assembles to form spherical micelle. Resultant spherical micelle accommodates aniline monomer in their hydrophobic core to form emulsion. There are two types of
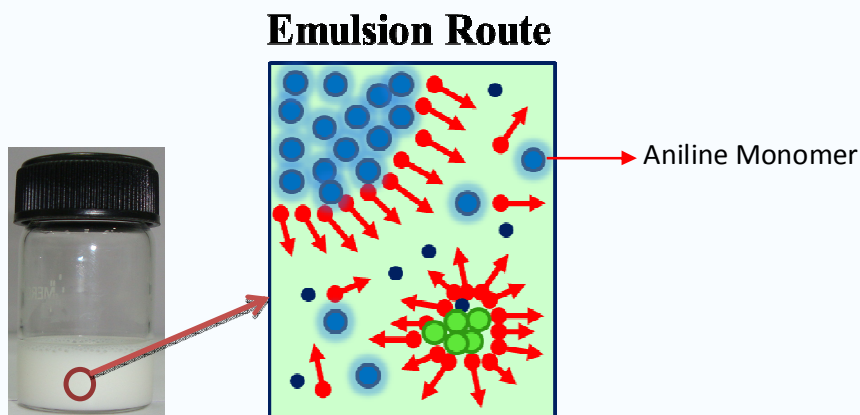
Figure 3.9. *Pictorial representation of mechanism for emulsion route for nanomaterial synthesis.*

aggregates possible: (i) larger micrometer size oil drops stabilized by the dopants and (ii) small nano-reactors constituted by the tiny micelles of the dopants. The larger surface area to volume ratio in the tiny micelles attracts the oxidant. Subsequently, the polymerization proceeds in the hydrophobic middle core where aniline monomer is present. The charged polyaniline chains possessed higher affinity towards water; as the consequence the micelles dissociate and the polymers get absorbed in water. The dopant molecules again associate to form new micelles with aniline supplied form the big oil droplets encapsulated in the hydrophobic core and new reaction starts and so on.[50] Formation of polyaniline in this route does not have uniform growth as monomer for chain growth is available in same environment leading to branching in polymer.

. Though PANI/Au nanocomposite was successfully prepared using the renewable resource surfactant, yield of the nanocomposites was found to be less than 5%. Additionally during the purification of nanocomposite, the removal of unreacted aniline destabilizes the nanocomposite. As a consequence, emulsion polymerization turned to be not a robust methodology for making large quantity of composites in pure form. Further, emulsion route synthesized PANI nanomaterial

contains defects in terms of their solid state packing and hence, consequently poor conductivity. Therefore new methodology such as interfacial polymerization route was adopted.

3.4. Interfacial Polymerization

In the interfacial synthesis, the aniline monomers get absorbed at the aqueous-organic interface and get oxidized by the oxidising agent present at the interface in the aqueous medium as shown in figure 3.10. The high water affinity of the polymer chains enhances their presence in water rather than in organic phase. At the interface new reaction cites are created for growing new polymer chains and
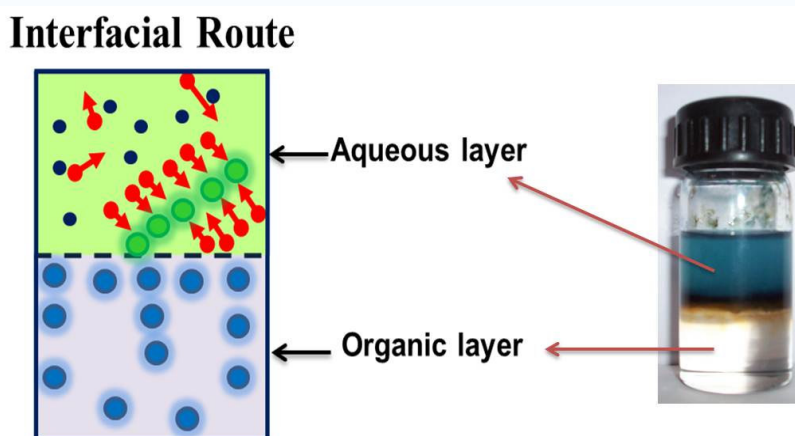
Figure 3.10. *Pictorial representation of mechanism for interfacial route for nanomaterial synthesis.*

the process continues tills the end of the polymerization. As a net effect, the interfacial route provides aniline monomers uni-directional chain growth at the interface. This unidirectional growth of PANI/Au nanocomposite may result in more improved chemical and physical properties for different applications.

Nanocomposite of PANI/Au has been synthesized via interfacial route to study the effect of reaction mechanism on properties of resultant nanocomposite. Aqueous layer was prepared by dissolving $HAuCl_4$ and $PDP-C_4-SO_3H$ while aniline was dissolved in organic solvent (DCM or toluene) to prepare organic layer. The schematic representation of this concept is shown in figure 3.11. By appropriate selection of solvent two approaches have been attempted i.e. against gravity approach and towards gravity approach with respect to the movement of aniline
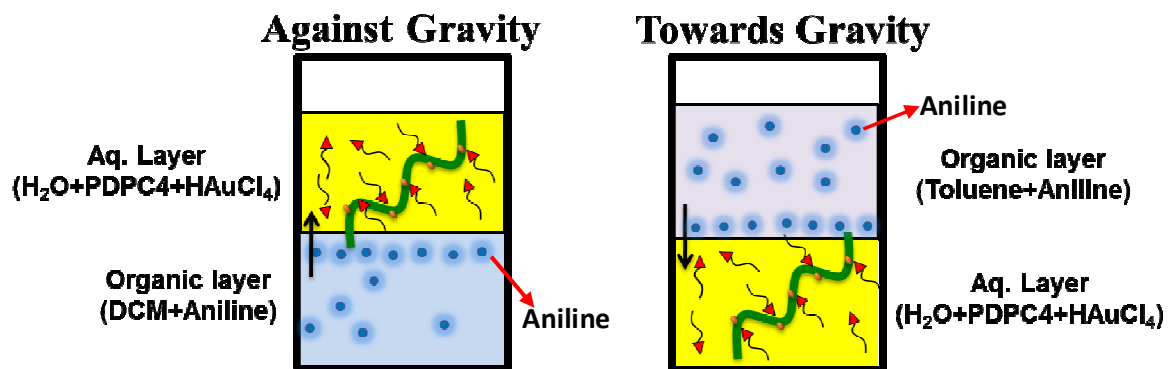
Figure 3.11.*Pictorial representation of plausible mechanism for interfacial route for nanocomposite synthesis.*

monomer. The experiments are shown in figure 3.12. In case of against gravity approach DCM-Water solvent combination was used, as the density of DCM is more than water. DCM layer containing aniline forms at bottom and aqueous layer forms at top layer containing PDP-C_4-SO_3H and $HAuCl_4$ precursor. At the interface the aniline

| 0 sec | 30 sec | 3 min | 20 min | 4 hours |
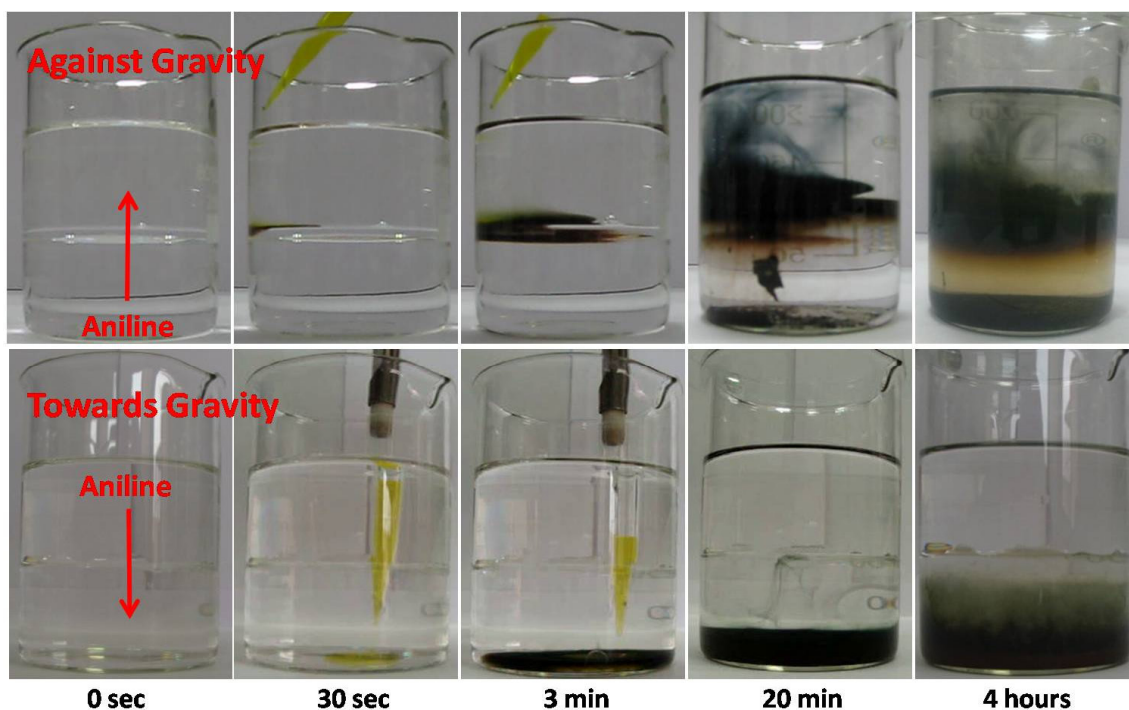
Figure 3.12.*Photographs for interfacial route synthesis of PANI/Au nanocomposite by against and towards gravity approach.*

monomer comes in contact with gold precursor by diffusion phenomenon which initiates the polymerisation of aniline and subsequently the reduction of $HAuCl_4$ to

form gold nanoparticles. Polyaniline nanomaterial has affinity to water and the polymer obtained at interface of DCM and water prefers to stabilise in aqueous layer.

In case of towards gravity approach toluene-water solvent combination was used, as the density of toluene is lower than water. Aqueous layer prefer to form at bottom while toluene layer forms on top. After the initiation of redox coupling between aniline and $HAuCl_4$ the resultant PANI/Au composite enters in aqueous phase. In this case the formation of nanocomposite was expected to be good, as redox couple reaction continues in aqueous layer. The green coloured nanocomposite was further subjected to their physical characterization.

3.5. Morphology characterisation of PANI/Au nanocomposite

Nanocomposites synthesized by against gravity approach (DCM-Water) were subjected for SEM and TEM analysis. SEM image showed globular morphology of nanocomposite, but this image do not give much information. TEM image showed
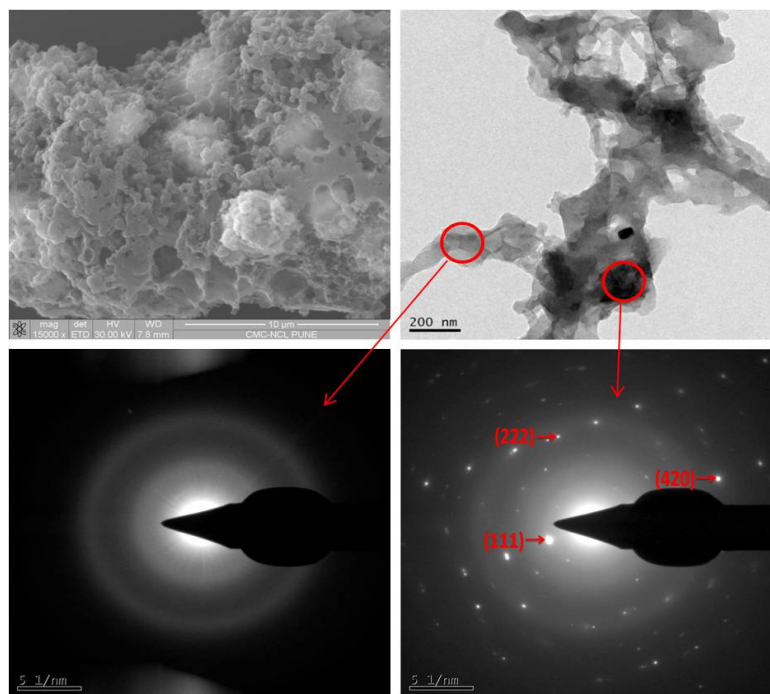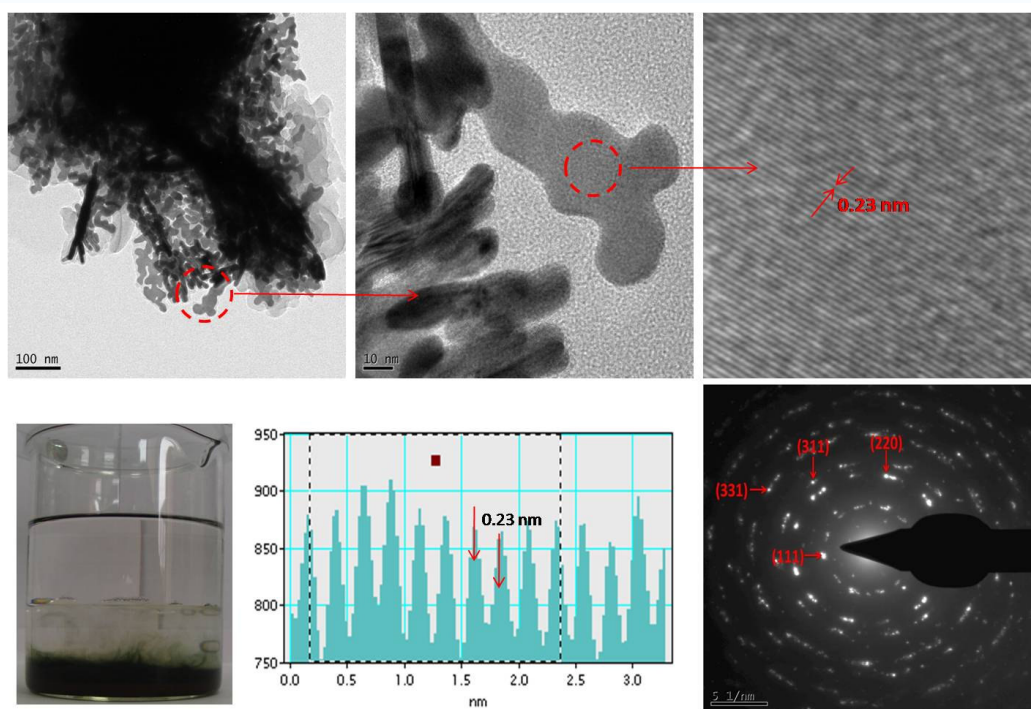

Figure 3.13.*SEM image and TEM image of PANI/Au nanocomposite synthesized by against gravity approach, SAD image for PANI fibre and AuNP region.*

the fibril polymer network with gold nanoparticle trapped inside. To distinguish between polymer matrix and AuNPs, selected area diffraction (SAD) images were

taken at polymer matrix and AuNP nanosphere region respectively. SAD image of polymer region gives ring pattern showing amorphous nature, while SAD image of dark AuNP region showed spot pattern indicating the crystalline nature. By using Gatan software the d-spacing values for spots in each ring were calculated and then compared with JCPDS database to obtain (h, k, l) values. The spots in each ring are labelled with corresponding (h, k, l) values representing presence of gold domain (see figure 3.13). Their SAD images clearly showed that two nanomaterials (PANI and AuNP) were nicely formed compact structure in nanocomposite.

In case of towards gravity approach (Toluene-Water), the TEM image showed branched sheets of AuNP over PANI domain as shown in figure 3.14. High magnification image of one of the branch of AuNP showed fringes, which indicates

Figure 3.14._TEM image of PANI/Au nanocomposite synthesized by towards gravity approach, SAD image for PANI fiber and AuNP region._

the effective alignment of gold atoms. SAD pattern of the gold region shows spot pattern with more number of bright spots than against gravity approach. Fringes of AuNP region and more number of bright spot in SAD pattern indicated high crystallinity compared to against gravity approach (see figure 3.13). By using Gatan software the d-spacing between two adjacent planes was calculated. Small area

selection of fringes gives peak pattern in graph. The distance between two adjacent peaks is the d-spacing value for corresponding adjacent planes. The d-spacing value obtained was 0.23 nm which on comparing with JCPDS universal datasheet gives confirmation of presence of gold domain in the form of face centred cubic crystal lattice.[51]

The values of d-spacing and (h, k, l) planes are compared in table number 3.1. It can be observed that the number of spots available for calculating d-spacing are less in case of against gravity approach, while the nanocomposite synthesized by towards gravity approach showed more number of spots. Hence the approach of towards gravitational movement of aniline monomer was good for PANI/Au nanocomposite synthesis.

Table 3.1. Comparison of d-spacing and (h, k, l) data of AuNPs, PANI/Au nanocomposite synthesized via interfacial route.

Sample	d-spacing (Å)	(h, k, l) values	Remarks
Gold Nanoparticles	2.65	(111)	FCC
	1.87	(200)	
	1.60	(220)	
	1.20	(311)	
PANI/Au Nanocomposites (Against Gravity)	2.75	(111)	FCC, Crystallinity pattern was not uniform
	1.13	(222)	
	0.92	(420)	
PANI/Au Nanocomposites (Towards Gravity)	2.38	(111)	FCC, Well defined diffraction rings, having strong spot pattern
	1.44	(220)	
	1.24	(311)	
	0.92	(331)	

3.6. Photophysical Characterization

Absorption spectra of all synthesized nanomaterials were measured to understand their electronic behaviour. Absorption spectra were recorded in water as solvent. Emulsion route synthesized polyaniline nanomaterials using PDP-C_4-SO_3H showed three transitions at 300 nm, 420 nm, and a broad peak at 850 nm with

respect to π-π* transition, polaron to conducting band, valence band to polaron band respectively.[52] The peak like nature for the valence band to polaron transition is due to coiled like conformation of PANI chain. AuNPs stabilised with PDP-C_4-SO_3H showed a single absorption band at 536 nm as shown in figure 3.15. This peak is corresponding to the spherical morphology of AuNPs as per the surface plasmon resonance phenomenon. Surface Plasmon Resonance (SPR) in gold nanoparticles is well known and the effect of anisotropy in the shape of nanoparticles is well studied. Surface Plasmon Resonance (SPR) is one of the unique optical properties shown by gold nanoparticles. The word Plasmon means collective oscillation of free
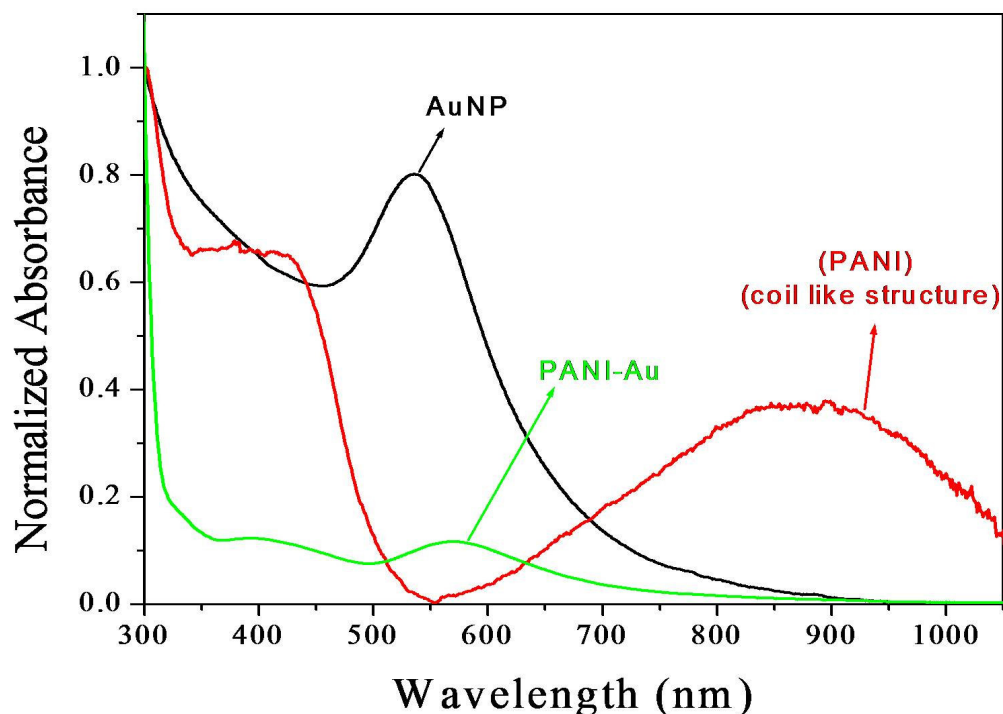
Figure 3.15. *Absorption spectra of PANI, AuNPs and PANI/Au nanocomposite synthesized via emulsion route.*

electron gas density, often at optical frequencies; "Surface Plasmon" means plasmon confined to the surface and interacts with the light resulting in polarization. When the size of the nanoparticles is much smaller as compared to wavelength of light, coherent oscillation of the conduction band electrons induced by interaction with an electromagnetic field.[53] This resonance is called Surface Plasmon Resonance (SPR) which is shown in figure 3.16.
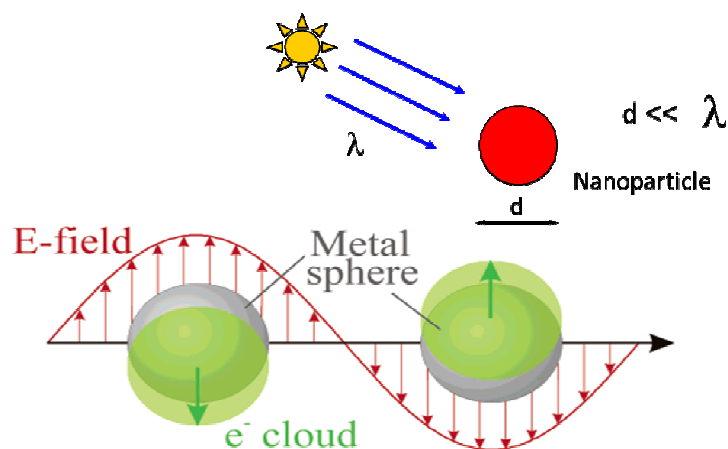
Figure 3.16.*Surface plasmon resonance effect of gold nanoparticles.*

Nanospheres of gold give rise to a single absorption band, while anisotropic particles such as nanorods, nanobipyramids, nanoplates and nanoprisms exhibit more complex patterns. Nanorods possess two absorption bands, one at a lower wavelength corresponding to the width of the rods and the other at a longer wavelength corresponding to their length. These are transverse surface plasmon resonance (TSPR) and longitudinal surface plasmon resonance (LSPR) bands respectively. Absorption spectra of nanocomposite showed two peaks at 405 nm and 570 nm corresponding to PANI and AuNP sphere respectively as shown in figure 3.15. The presence of absorption peaks for PANI and AuNPs sphere indicated the formation of nanocomposite efficiently.

Absorption spectra of PANI synthesize via interfacial route using PDP-C_4-SO_3H showed same absorption spectra as emulsion route except free carrier tailing above 800 nm with high optical density which is shown in figure 3.17. The free carrier tailing above 800 nm corresponds to expanded chain like conformation of polymer backbone leading to increase in electron mobility along the chain. Nanocomposite obtained by both against gravity and towards gravity showed absorption band at ~430 nm and~ 540 nm corresponding to polaron to conduction band of PANI and AuNP nanospheres respectively. However, the intensity for both the absorption band is less for against gravity approach than towards gravity approach respectively. These observations showed that the formation of nanocomposite in against gravity approach is not efficient.
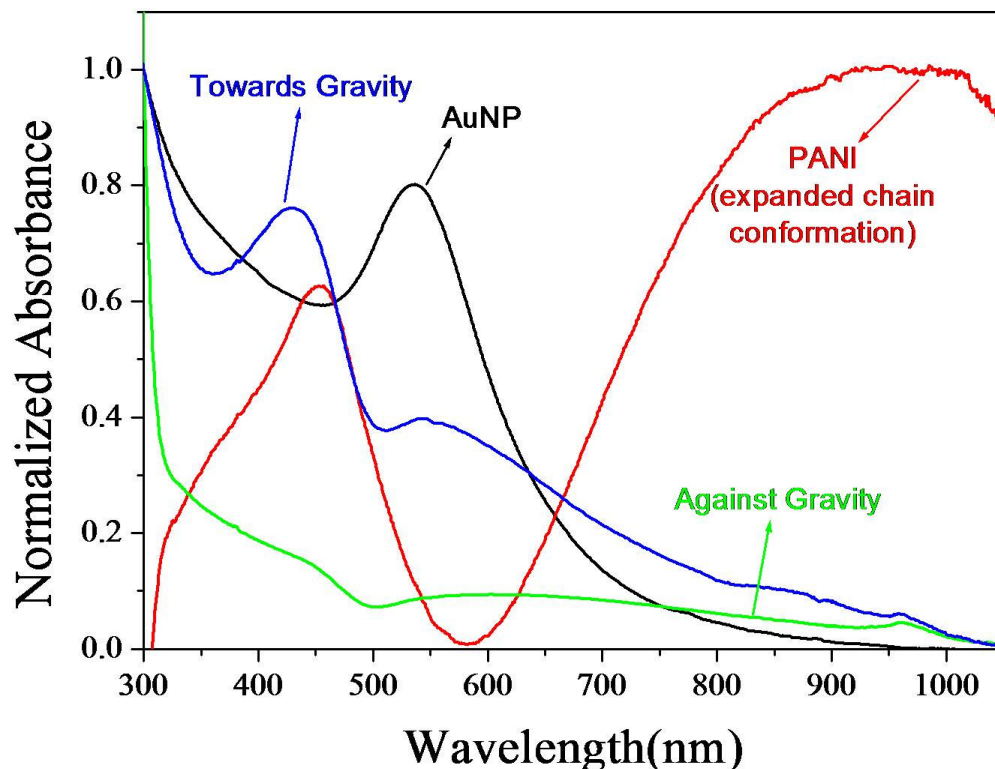
Figure 3.17.*Absorption spectra of PANI, AuNPs and PANI/Au nanocomposite synthesized via towards the gravity and against the gravity interfacial route.*

3.7. Wide angle X-ray diffraction study

Polyaniline nanomaterial, AuNPs, PANI/Au nanocomposite, and PDP-C$_4$-SO$_3$H were subjected for W-XRD measurement and their spectra are given in figure 3.18. Surfactant showed diffraction peaks below $2\theta = 25°$ corresponding to its aromatic ring and aliphatic chain packing. Emulsion route synthesized polymers showed broad peaks at $2\theta = 19.2°$ (d-spacing= 4.6 Å) and $2\theta = 25.9°$ (d-spacing = 3.4 Å) corresponding to aromatic chain interaction[54]. These nanomaterials also showed lower angle peak at $2\theta = 6.5°$ (d-spacing = 13.5 Å) attributed to inter digitations of long tail substituted dopants into the polyaniline matrix. Diffraction pattern for AuNPs showed four peaks at $2\theta = 37.9°$ (d-spacing = 2.37 Å), $2\theta = 44.1$ (d-spacing = 2.05 Å), $2\theta = 64.3°$ (d-spacing = 1.45 Å), $2\theta = 77.3°$ (d-spacing = 1.23 Å). The d-spacing values were compared with JCPDS universal database which reveals the presence of gold domain. The indexing of the diffraction pattern gives (h,k,l) values for
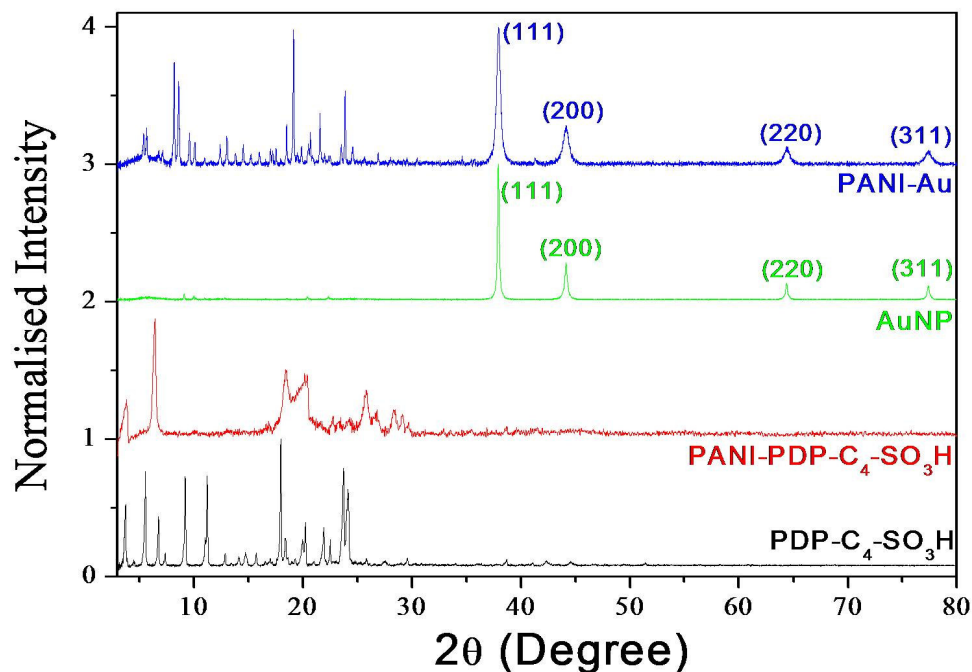
Figure 3.18. *W-XRD pattern for PDP-C4-SO3H, PANI, AuNPs, and PANI/Au nanocomposite synthesized via emulsion route.*

corresponding plane which are labelled in figure 3.18. The indexing of XRD pattern showed formation of face centre cubic (FCC) crystal lattice.[55] In diffraction pattern of nanocomposite, peaks below $2\theta = 25°$ corresponds to PANI and PDP-C$_4$-SO$_3$H while four intense gold peaks are present above $2\theta = 25°$. The presence of diffraction peaks corresponding to PANI, surfactant and AuNPs confirmed the formation of nanocomposite.

The diffraction patterns for nanomaterials synthesized via interfacial route are provided in figure 3.19. The PANI nanomaterial synthesized by using the PDP-C$_4$-SO$_3$H dopants showed broad peaks at $2\theta = 19.2°$ (d-spacing= 4.6 Å) and $2\theta = 25.9°$ (d-spacing = 3.4 Å) corresponding to aromatic interaction. Highly ordered sharp lower angle peak at $2\theta = 6.5°$ (d-spacing = 13.5 Å) indicates high solid state ordering in the polyaniline nanomaterials. Nanocomposites synthesized by against gravity approach showed intense peaks for AuNP, while diffraction peaks corresponding to PANI and PDP-C$_4$-SO$_3$H were absent. The presence of intense AuNP diffraction peak indicates the dominance of more crystalline AuNP domain over amorphous PANI domain. In towards gravity approach all expected diffraction peaks of PANI
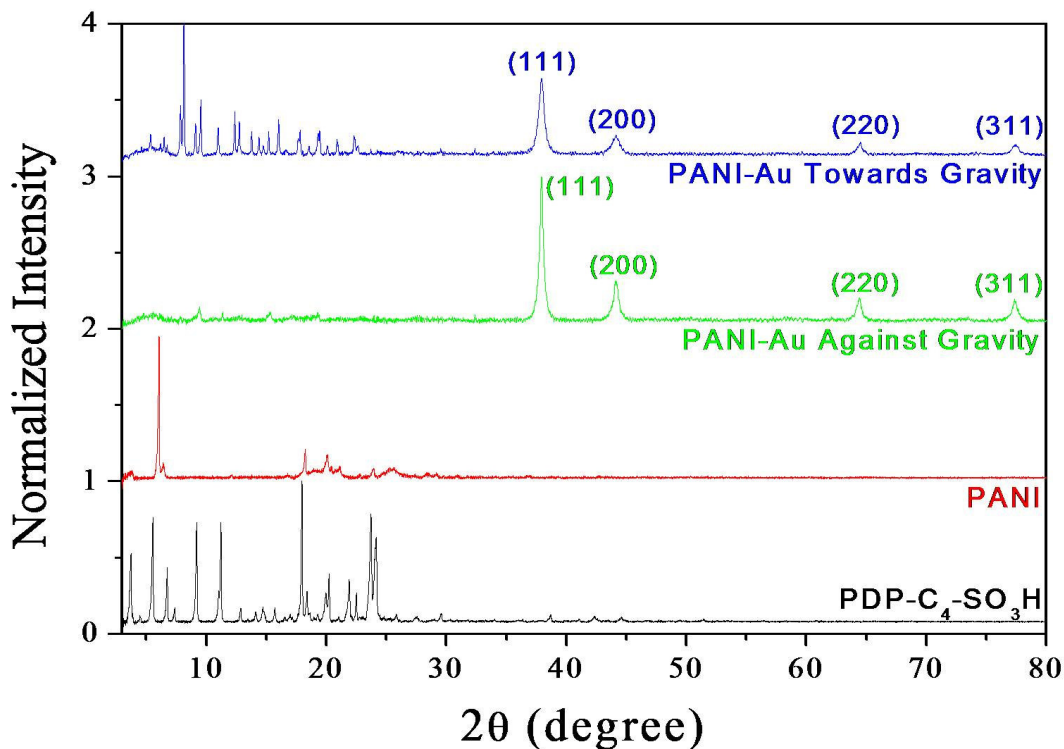
Figure 3.19. *W-XRD pattern for PDP-C4-SO₃H, PANI, and PANI/Au nanocomposite synthesized via interfacial and via towards gravity and against gravity approach.*

domain. In towards gravity approach all expected diffraction peaks for PANI, PDP-C_4-SO_3H and AuNPs were present which indicates formation of both the domains efficiently. The indexing for AuNP diffraction peaks were performed by using JCPDS universal database to achieve the (h, k, l) values for corresponding planes. The values for (h, k, l) are labelled in figure 3.19. The indexing for gold peaks indicated the formation of FCC crystal lattice structure.

Based on morphological analysis, photophysical characterization and WXRD pattern of the PANI/Au nanocomposite, the mechanism for the nanocomposite formation proposed in figure 3.20.

In general, in the present case, PDP-C_4-SO_3H played dual role in stabilising AuNPs, and doping of PANI and PANI/Au nanocomposite. PANI/Au nanocomposite synthesized via interfacial route was more efficiently formed rather than emulsion route. It is clear from WXRD, absorption and morphological studies, that in the case

of interfacial route synthesized PANI/Au nanocomposite was more ordered compared with emulsion route. The reason for the enhanced ordering in the interfacial route was attributed to the unidirectional growth of nanomaterials at the interface.

Emulsion Route   **Interfacial Route**

Coil- like structure   Expanded chain conformation
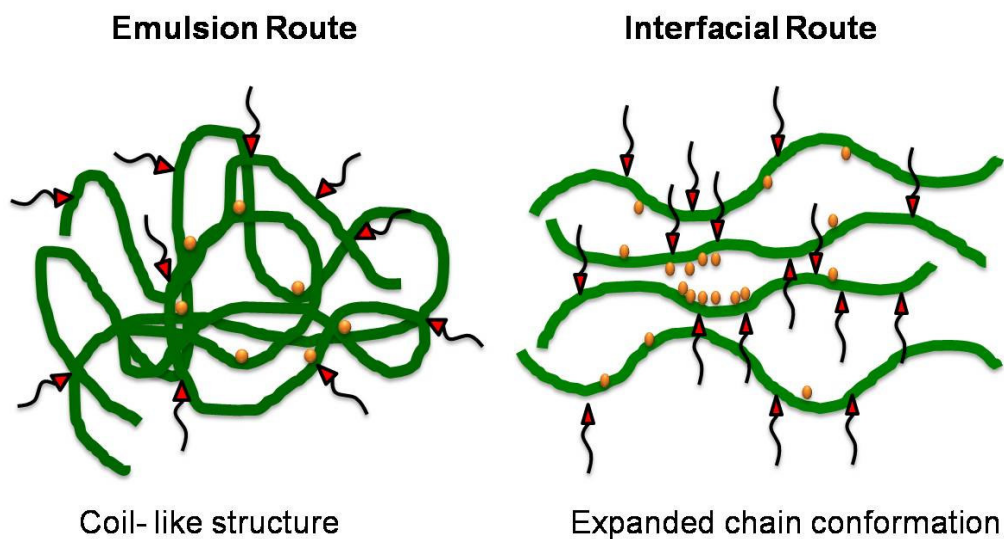
Figure 3.20.*Schematic representation of PANI/Au nanocomposite synthesised via emulsion and interfacial route.*

In a nutshell, in the present thesis work renewable resource dopant was successfully utilized for the synthesis of PANI/Au nanocomposites and tuning their materials properties.

CONCLUSION

Conclusion:

We have synthesized surfactant-cum-dopant from renewable resource from cashew and utilized for AuNPs, PANI and PANI/Au nanocomposites. The important advantages of this work are mention point wise as follows: (i) Renewable resource based surfactant-cum-dopant i.e PDP-C$_4$-SO$_3$H was synthesised by ring opening reaction with 1,4-butane sultone in presence of base. Newly synthesized surfactant-cum-dopant was nicely soluble in water which formed spherical micelles, (ii) The micellar solution of PDP-C$_4$-SO$_3$H was used to synthesize the gold nanoparticles which on morphological studies revealed the formation of nanospheres exclusively, (iii) Aniline in PDP-C$_4$-SO$_3$H micellar solution formed emulsion which on subsequent oxidation with APS formed polyaniline nanomaterial. The TEM analysis of the PANI nanomaterial showed the formation of nanofibers, (iv) The two reactions of AuNP formation by reduction of HAuCl$_4$ and PANI nanomaterial formation by oxidation of aniline were utilised for synthesis of PANI/Au nanocomposite by using PDP-C$_4$-SO$_3$H as common template, (v) Emulsion route was employed for nanocomposite synthesis, where different compositions were taken to find out the appropriate reaction condition for PANI/Au nanocomposite, (vi) Emulsion route possesses drawback of non directional growth of nanoparticles which effects the solid state ordering and conductivity of resultant nanocomposite. Also the absorption spectra showed coiled like conformation, (vii) Interfacial route was employed because of unidirectional growth of nanomaterials at interface which gives rise to ordering in resultant nanocomposite formed. The expanded chain conformation was observed in absorption spectra, (viii) Morphological studies, W-XRD, and absorption study confirms that the interfacial route is more prominent for the synthesis of PANI/Au nanocomposite rather than emulsion route, (ix) Mechanism for resultant nanocomposite synthesis is proposed in which the efficient packing of gold and PANI chains observed in interfacial route synthesized nanocomposite.

The present investigation clearly demonstrated the importance of surfactant selection and polymerization process for producing excellent Conducting Polymer-Gold nanocomposites. Au-Pani nanocomposites synthesized in the present investigations could be very useful for applications in electronics, chemical and biosensors.

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