

Synthesis of nanocomposites of silica-gold core-shell nanoparticles and gold nanowires with conducting polymers



A thesis submitted towards partial fulfillment of the BS-MS
Dual Degree Program

by

HARJOT KUMAR

Under the guidance of

PROF. DR. SULABHA K. KULKARNI (Supervisor)

&

DR. SURJEET SINGH (Co-Supervisor)

INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH (IISER), PUNE

Certificate

This is to certify that this thesis entitled “*Synthesis of nanocomposites of silica-gold core-shell nanoparticles and Gold nanowires with conducting polymers*” submitted towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research (IISER), Pune represents original research carried out by **Harjot Kumar** at IISER, Pune under the supervision of **Prof. Sulabha K. Kulkarni** and **Dr. Surjeet Singh** during the academic year 2016-2017.

Harjot Kumar

Registration No.: 20121066

Dr. Surjeet Singh

Associate Professor

Committee:

Prof. Sulabha K. Kulkarni (supervisor)

Dr. Surjeet Singh (co-supervisor)

Dr. Nirmalya Ballav (TAC)

Declaration

I hereby declare that the matter embodied in the report entitled “*Synthesis of nanocomposites of silica-gold core-shell nanoparticles and Gold nanowires with conducting polymers*” are the results of the work carried out by me at the Department of Physics, Indian Institute of Science Education and Research, Pune, under the supervision of Prof. Sulabha K. Kulkarni and Dr. Surjeet Singh and the same has not been submitted elsewhere for any other degree.

Harjot Kumar
Registration No.: 20121066

Dr. Surjeet Singh
Associate Professor

Dedicated to my family

Acknowledgements

I express my heartfelt gratitude to my mentor Prof. Dr. Sulabha K. Kulkarni, for her generous guidance, excellent mentorship and constant encouragement. I consider myself very fortunate for being able to work with a very considerate and encouraging professor like her. The supervision and support that she rendered truly helped the progress and smoothness of the project. I also take this opportunity to express a deep sense of gratitude to Dr. Smita Chaturvedi for her cordial support, valuable information and guidance, which helped me in completing this Project. I am indebted to my lab members Abhijit, Kavya and Priyank for their continuous support, support and stimulating discussions.

I am grateful to “Innovation in Science Pursuit for Inspired Research” (INSPIRE) program for continuously providing financial support. I am thankful to IISER, Pune and all faculty members as well as administrative staff for supporting me directly or indirectly in my thesis work. Finally, I extend my gratefulness to one and all who were directly or indirectly involved in the successful completion of this project work.

Abstract

Nanotechnology and nanoscience are a fast evolving field which deals with the properties of the material at the nanoscale level. Harnessing these properties in the form of applications which can aid mankind is nanotechnology. With the properties dependent on size and shapes, discovering methods to synthesize these materials is very essential. The first part of the work focuses on the synthesis of the nanomaterials which include silica-gold core-shell nanoparticles and gold nanowires followed by their characterization.

The second part includes the study and synthesis of conducting polymers. The conducting polymers like polyaniline have been put into many potential applications, for example, gas sensing, etc. This work is focused on characterizing and synthesizing the nanomaterials with certain morphologies and blending them with a conducting polymer to develop new applications and improve the already present ones.

Contents

1 Introduction	9
1.1 Gold	9
1.2 Core-shell nanoparticles	9
1.3 Conducting polymers	10
1.3.1 Polyaniline	11
1.3.2 PEDOT:PSS	12
1.4 Nanowires	12
1.5 Summary	13
2 Experimental techniques	15
2.1 Synthesis of silica spheres	14
2.1.1 Materials	14
2.1.2 Procedure	14
2.2 Synthesis of core-shell nanoparticles	15
2.2.1 Materials	15
2.2.2 Procedure	15
2.2.2.1 Synthesis of gold seeds	15
2.2.2.2 Functionalization of silica spheres	15
2.2.2.3 Attach of gold seed on silica spheres	16
2.2.2.4 Growth of nanowires on silica spheres	16
2.3 Synthesis of gold nanowires	16

2.3.1 Materials.....	16
2.3.2 Procedure.....	16
2.4 Synthesis of Polyaniline.....	17
2.4.1 Materials.....	17
2.4.2 Procedure.....	17
2.5 Analysis Techniques.....	18
2.5.1 UV-Vis absorption spectroscopy.....	19
2.5.2 Field emission scanning electron microscopy.....	20
2.5.3 Fourier transform infrared spectroscopy.....	22
2.5.4 X-ray diffraction.....	23
2.5.5 Field emission transmission electron microscopy.....	24
3 Results and discussions	
3.1 Silica Nanoparticles.....	25
3.1.1 SEM analysis.....	25
3.1.2 UV-Vis analysis.....	26
3.1.3 XRD analysis.....	27
3.2 Core-shell nanoparticles.....	28
3.2.1 SEM analysis.....	28
3.2.2 FTIR analysis.....	30
3.2.3 UV-Vis analysis.....	31
3.2.4 TEM analysis.....	32
3.3 Gold nanowires.....	33
3.3.1 SEM analysis.....	34
3.3.2 XRD analysis.....	35
3.3.3 UV-Vis analysis.....	36
3.4 Nanocomposites.....	36
3.5 Concluding remarks.....	37
4 Summary and future directions.....	38
5 Bibliography.....	40

Chapter 1

Introduction

Nanoscience is the study of matter at the nanoscale. Nanomaterials have one of their dimensions in nanometer regime ($1\text{nm} = 10^{-9}\text{ m}$). The average diameter of a human hair is ~ 0.0175 millimeters. With the materials having certain properties in bulk, they start showing different properties as we scale down their size. This difference is mainly attributed to increase in surface area to volume ratio, leading to electron confinement and thus different optical, electrical and magnetic properties. For example, the gold nanoparticles have a different color (red) and melting point (approximately $300\text{ }^{\circ}\text{C}$ for 2.5 nm size) in comparison with normal ones ($1064\text{ }^{\circ}\text{C}$). In 1959, Richard Feynman in his lecture “There’s plenty of room at the bottom” mentioned about the things that could be done at nanoscale level and how this field will make us technologically advance. Nowadays, nanomaterials are everywhere and in great demand because of their potential applications in fuel cells, data storage device, nonlinear photonics, biological applications (e.g. gene and drug delivery), catalysis and nanotechnology.

Nanomaterials can be synthesized using two approaches: Top down and Bottom up. The former approach involves the use of external force to a solid to break it up into smaller particles. We Begin with a pattern generated on a large scale, which is further reduced to the nanoscale. By nature, this approach is not cheap and also slow therefore not suitable for large scale production, e.g. lithography, etc. Bottom Up approach involves building from base i.e. producing nanoparticles starting from atoms of gas or liquids, e.g. Chemical vapor deposition (CVD), Thermal Decomposition, Spray drying, Spray pyrolysis, Sol-gel, Hydrolysis, etc.

This work focuses on the synthesis of nanomaterials like core-shell nanoparticles and gold nanowires. The materials are studied and characterized. The work aims at finding a good application of the synthesized materials by making their nanocomposites with conducting polymers.

1.1 Gold

Gold is seen as a very precious metal. It has atomic number 79 with the melting point of 1064°C. Besides its regular use in ornaments and jewellery, it has many applications in nanoscience and technology. The characteristic yellow sheen of the bulk gold is not observed in the nano-size domain. It shows different optical, magnetic and electrical properties in the nano-size domain. Various morphologies can be created from gold for e.g. gold nanoparticles, gold nanorods, gold nanowires, etc.

Property	Value
Chemical symbol	Au
Atomic number	79
Atomic weight	196.9
Density	19.3 g cm ⁻³
Melting point	1064°C
Boiling point	2970°C
Lattice structure	FCC
oxidation states	5,4,3,2,1,-1

Table 1.1: Bulk gold – Key properties



Figure 1.1: Gold nanoparticles in solution^[1]

1.2 Core-shell nanoparticles

Core-shell nanoparticles are very interesting materials in which one uses the core of one material and coats thin shell of another material.^[2] Such core-shell particles can have interesting properties which can be entirely different compared to their core material nanoparticles or shell material particles separately. These properties also depend on the core to shell ratio. Multi-shell particles

can also synthesized. The one major advantage of the core-shell nanoparticles is that they can be economical as expensive materials can be coated onto inexpensive materials like silica. Core-shell can be synthesized in many combinations for example dielectric-metal,^[3] semiconductor-metal,^[4] metal-metal,^[5] etc. Various techniques can be used for the core-shell nanoparticle synthesis including sol-gel condensation^[6], reverse micelle^[7], precipitation, microemulsion, etc.



Figure 1.2: a) Core-shell nanoparticle b) Multi shell nanoparticle c) Shell particles reduced onto core to form a complete shell

In this work, core-shell nanoparticles with a shell made of gold and core of a dielectric material (SiO_2 -Silica) were prepared. Silica nanoparticles are soluble in water, chemically inert and are highly stable. Silica nanoparticles are also preferred because of their non-coagulating nature. Thus they have very low Van der Waal attraction with the medium hence the low value of Hamaker constant. Core-shell particles of SiO_2 (core) and gold shell have been used in the past for drug delivery, phototherapy, biosensors and as SERS substrates.^{[8],[9]}

1.3 Conducting Polymers

Polymers are a long chain of a repeated molecular unit connected through covalent bonds. Initially, polymers were known to have good insulating properties, but the discovery of conducting polymers totally changed the perception. In 1977, Alan G. MacDiarmid, Hideki Shirakawa, and Alan J. Heeger reported a high conductivity in polyacetylene.^[10] They were awarded the Nobel Prize in chemistry in the year 2000 for ‘the discovery and development of conductive polymers.’ For the polymers to become conducting they needed to have free electrons as in metals. The way

out was doping. Shirakawa et al. used halogen doping for making the polyacetylene conductive.^[10] Oxidation with iodine leaves a positive charge along the polymer. Thus imparting the polyacetylene its conductivity. Widely used conducting polymers include polyaniline, polypyrrole, polythiophene, etc.

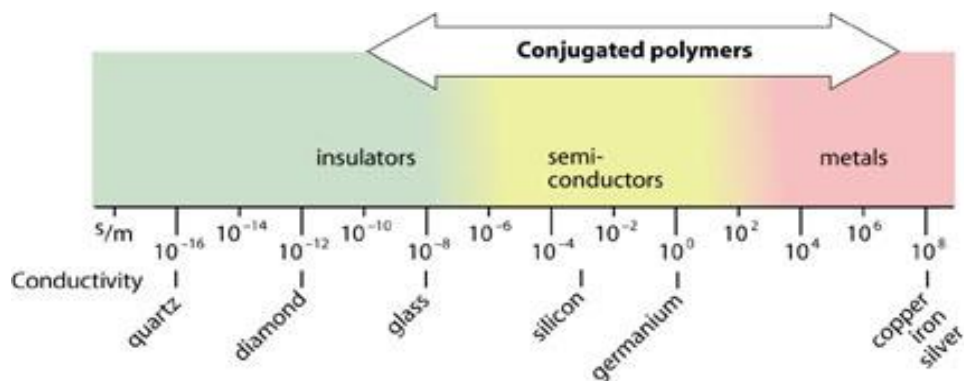


Figure 1.3: Conductivity comparison between conductive polymers and other materials^[11]

The potential applications of conductive polymers include electronic nanodevices (field effect transistors and diodes), sensors (gas sensors, optical sensors, and biosensors), solar cells, supercapacitors, electromagnetic frequency interference (EMI) shielding, etc.^{[12],[13]}

1.3.1 Polyaniline

First discovered in the 19th century, polyaniline (PANI) came to light with the discovery of conductive polymers in the 1980s.

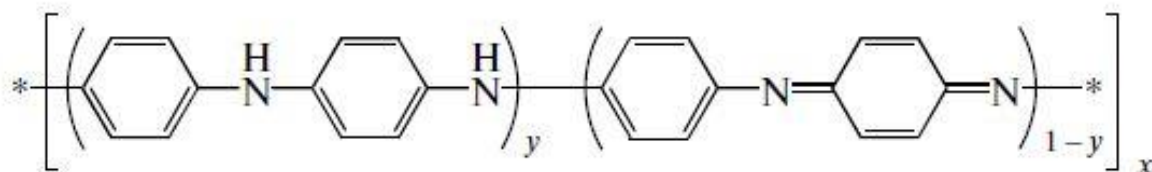


Figure 1.4: Building blocks of polyaniline: reduced (y) and oxidized (1-y)^[12]

Built from aniline monomer, polyaniline contains, figure 1.4 reduced (y) and oxidized blocks (1-y). Redox state of the polymer is determined by the value of 'y'. For the value of y = 0.5, it occurs

as emeraldine form, for the value of $y = 1$, it occurs as leucoemeraldine form which is the fully reduced form and for the value of $y = 0$, it occurs as pernigraniline form which is fully oxidized form. Polyaniline is most conducting in its emeraldine (salt) form while the others forms have poor conductivities. Emeraldine salt form is dark green in colour. Polyaniline can be synthesized through various synthesis routes which are electrochemical polymerization (give the purest form of polyaniline), chemical polymerization (easy and simple), gas phase plasma method, etc.^[12]

1.3.2 PEDOT:PSS

Poly alkylene dioxythiophene polystyrene sulfonate (PEDOT:PSS) is a polymer composed of two ionomers: Poly (3,4 ethylene dioxythiophene) (PEDOT) and polystyrene sulfonate (PSS). PEDOT is a conducting polymer and its electrical conductivity can be further increased by oxidation. In 1980s PEDOT was initially developed in Bayer AG labs but the polymer was found to be insoluble.^[14] On doping PEDOT with PSS, a polyelectrolyte complex is created which is stable, soluble, reproducible and have many applications. PEDOT:PSS has many applications like as an anti-static layer in photographic films, as an electrode, in LEDs, etc.^[15]

1.4 Nanowire

A nanowire is a 1-D nanostructure, with the diameter of the order of a nanometer. While the diameter of nanowires is negligible, the length can go up till micrometers and can even become visible to naked eye. Such a unique characteristic of having a very small diameter (nm) as compared to the length (micrometers) give rise to a very high value of the aspect ratio which is the ratio of width to height. Nanowires also have high surface area to volume ratio and this property can be put into use for sensing purposes. Extremely high surface area provide more space to the detecting molecule/binder to get attached to the nanowires and detect even a very small change. Nanowires are categorized into various categories based on the material for e.g. metallic (Au), semiconducting (GaN), superconducting (YBCO) and insulating (TiO₂).

Nanowires can be put into many applications including pressure sensors, electronic devices (for transistors), conducting thin films, etc.^[16] Metal nanowires also show remarkable optical properties. We all know that the optical properties of a material depend on its dielectric constant

and for gold which is a conductor it depends on the incident wavelength. According to Mie theory, (1908) for spherical particles which have size smaller than the wavelength which is incident upon them, resonant absorption is size independent.^[17] For the anisotropic nanomaterials like nanowire, Richard Gans proposed a theory (1912), which gave the dependence of resonant absorption of the energy based on the aspect ratio of the particles.^[18] Later, Drude described conduction electrons in metals and how they respond (collective oscillation) to the incident energy and term Plasmon was coined which is defined as the quasiparticle denoting the collective oscillation of all the free electrons. In nanomaterials, when the frequency of incident light matches with the surface plasmon frequency of the material to be studied, resonant absorption take place, termed as surface plasmon resonance (SPR).

Gold nanowires being anisotropic, their optical behavior toward the incident light is given by Gans theory. For anisotropic nanostructures, their exist two resonant surface plasmon modes: Transverse surface plasmons resonance (TSPR, when the polarization of incident beam perpendicular to long axis of the specimen) and Longitudinal surface plasmons resonance (LSPR, when the polarization of incident beam parallel to long axis of the specimen). In case of nanowires, TSPR is observed at 520-530 nm and LSPR occurs in IR region.

1.5 Summary

Nanotechnology has become an integral part of today's world, the world Feynman dreamt of in his legendary lecture "There's plenty of room in the bottom". In this chapter, we briefly discussed the methods for synthesizing nano materials. Brief discussion on gold and its importance was included followed by a short introduction on core-shell nanoparticles. Conducting polymers along with a small historical mention, their applications and brief introduction of polyaniline was included. Nanocomposites composed of nanomaterials like silica gold core shell nano particles with conducting polymers can be put into many possible applications. All such applications including gas sensing was studied.

Chapter 2

Experimental Techniques

This section discusses the synthesis procedures of silica spheres, gold seeds, functionalization of silica spheres, attachment of gold seeds on the silica sphere, growth of nanowires on silica spheres, gold nanowires and polyaniline. Working principle of the characterization and analysis techniques employed for e.g. FESEM, UV-Vis, transmission electron microscopy (TEM), etc. is also discussed.

2.1 Synthesis of silica spheres

2.1.1 Materials

Tetra ethyl ortho silicate (TEOS) and ethanol were bought from Sigma Aldrich. Ammonia was bought from Fisher Scientific. All the above mentioned chemicals were used as provided by the supplier without any further refinement. Milli-Q water was utilized in all the Experiments.

2.1.2 Procedure

Silica spheres were synthesized using Stöber method.^[19] In a typical synthesis, absolute alcohol (25 ml) is mixed with ammonia (2 ml, 30 wt%) and Milli-Q (1.13 ml) water solution, followed by a dropwise addition of Tetra ethyl ortho silicate (TEOS) (0.75 ml) under vigorous stirring. After sometime, the colour of the solution changes to opaque white. Solution was mixed gently overnight and later the silica spheres were collected using centrifugation and dissolved in ethanol. It is a sol-gel method involving hydrolysis (Si-O chains are created) followed by condensation in a alcoholic

medium giving amorphous silica particles. The advantages of the Stöber method are monodisperse and high purity silica nanoparticles. Overall reaction is easy to setup and operates at room temperature without any requirement of the heating device.

2.2 Synthesis of core-shell nanoparticles

2.2.1 Materials

Absolute ethanol, tetraethyl orthosilicate (TEOS), 3-aminopropyl triethoxysilane (APTES), Gold chloride hydrate ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$), L-ascorbic acid and 4-mercaptobenzoic acid (MBA) were purchased from Sigma Aldrich. Sodium citrate tribasic dehydrate was purchased from Alfa Aesar. Sodium borohydride (NaBH_4) was purchased from Sisco Research Laboratories (SRL), Mumbai, India. Ammonia solution (NH_4OH) was purchased from Fisher Scientific. Chemicals were utilised without any further refinement. Milli-Q water was used for all the experiments.

2.2.2 Procedure

Synthesis of silica gold core shell nanoparticles is done in various steps. All the steps are mentioned below briefly.^[20]

2.2.2.1 Synthesis of Gold seeds

HAuCl_4 (0.250 mM, 10ml) was mixed with sodium citrate (0.25 mM, 10 ml). Then, sodium borohydride (0.3 ml, 10 mM) was added to the solution under vigorous stirring. Upon complete decomposition of sodium borohydride, a pink color solution was obtained indicating the successful formation of gold seeds.

2.2.2.2 Functionalization of silica spheres

Silica spheres were re-dispersed in ethanol (10 ml) and Milli –Q water (520 μl) was added. To this, ammonium hydroxide (200 μl) was added followed by the addition of 3-aminopropyl triethoxysilane (APTES 32 μl) under vigorous stirring.

The solution was stirred for 2 hours at room temperature and subsequently at 70°C for 1.5 h. The solution was centrifuged (2000 rpm, 8 min.) and obtained precipitate was dissolved in ethanol (10 ml).

2.2.2.3 Attachment of gold seed on silica spheres

Functionalized silica spheres (0.346 ml) were added to the gold seeds (10 ml) and the solution was stirred gently for 3 hour at room temperature. The particles were centrifuged (2000 rpm, 10min.) and dissolved in distilled water (1.2 ml).

2.2.2.4 Growth of nanowires on silica spheres

MBA (0.275 mM) and H_{Au}Cl₄ (0.825 mM) were added in ethanol/water solution (10 ml, 3:1 v/v). followed by addition of Au-primed silica (0.55 ml). The solution was gently stirred for 15 sec. and then L-ascorbic acid (0.488 mL, 42 mM) was added. The solution was stirred for 5 sec and left undisturbed for 15 minutes, followed by centrifugation (2000 rpm, 8 min.) and redispersion in ethanol (2ml).

Overall the process involved the surface modification of the silica nanoparticles with APTES. APTES covalently attaches to the silica nanoparticles through –OH group and leaves the surface with –NH terminating group. Gold seeds particles attach to the silica nanoparticles through this –NH group, followed by the growth of gold nanowires giving core-shell nanoparticles.

2.3 Synthesis of gold nanowires

2.3.1 Materials

Gold chloride hydrate (H_{Au}Cl₄.xH₂O), Oleylamine (OA) and Tri-isopropylsilane (TIPS) were purchased from Sigma Aldrich. Hexane was purchased from Rankem. All the chemicals were used as provided by the supplier without any further refinement. Milli-Q water was utilized in all the Experiments.

2.3.2 Procedure

Single step wet chemical method was employed for the synthesis of the gold nanowires.^[21] In typical reaction, HAuCl_4 is dissolved in hexane (2.5 ml) followed by addition of Oleylamine (100 μl) and TIPS (150 μl). A yellow color solution is obtained. The solution is left undisturbed for overnight and color of the solution gradually changed from yellow to dark pink, as shown in figure 2.1. The solution is washed with ethanol for the removal of excess Oleylamine and the precipitate is re-dispersed in hexane (2 ml). Oleylamine plays the role of stabilizer and one-dimensional growth template, thus forming a polymeric chain. TIPS reduces Au from Au (3) to Au (0), giving gold nanowires with Oleylamine capping.

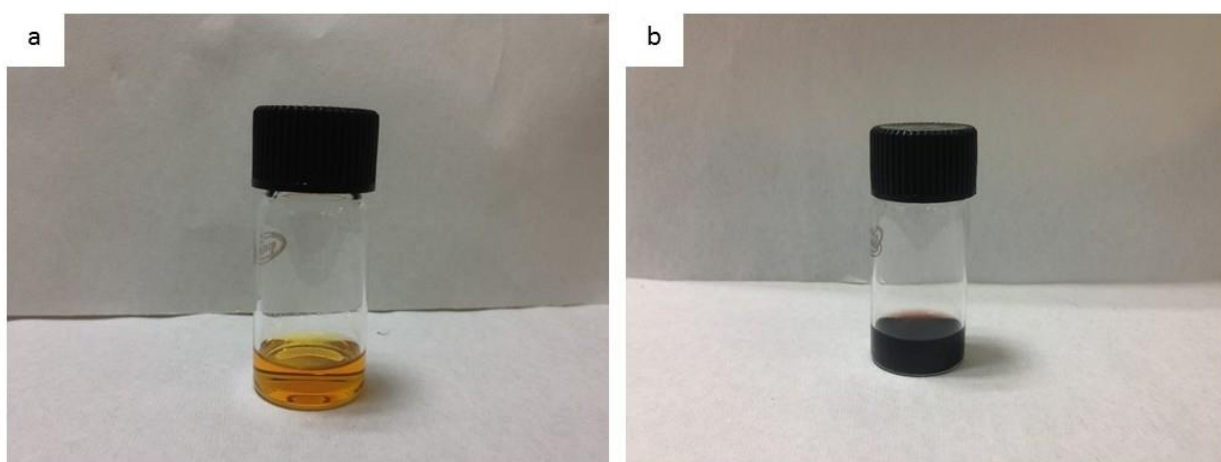


Figure 2.1: a) Yellow color solution obtained after the mixing of HAuCl_4 , oleylamine and TIPS in hexane. b) Dark pink color solution after 12 hours of reaction time

2.4 Synthesis of polyaniline

2.4.1 Materials

Aniline was purchased from S.D. fine chemicals (SDFCL) Limited, Mumbai, India. Hydrochloric acid (HCl) was purchased from Thomas Baker Pvt. Limited, Mumbai, India. Ammonium peroxydisulphate (APS) was purchased from Fisher Scientific. All the chemicals were used as it is without any further refinement. Milli- Q water was utilized in all the experiments.

2.4.2 Procedure

Polyaniline (PANI) was synthesized using modified Stejskal et al.^[22] Round bottom flask (250 ml) is maintained at 0°C, distilled aniline (300 μ l) and HCl (30ml, 1M) are added. The solution is stirred for 35 minutes. Later, ammonium peroxydisulphate (0.1 M in 20 ml of 1M HCl) is added. A dark green colored solution is obtained after 30-40 minutes and stirred overnight.

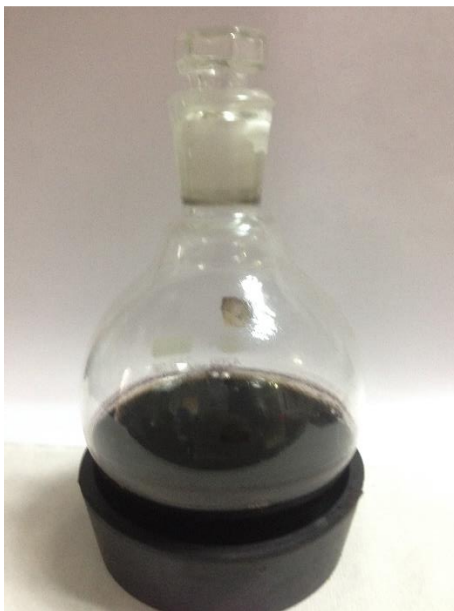


Figure 2.2: Synthesized polyaniline (Green) in a round bottom flask

2.5 Synthesis of Nanocomposites

Nanocomposites of the conducting polymers e.g. polyaniline, PEDOT:PSS, etc. and nanomaterials e.g. silica gold core shell nanoparticles, gold nanowires, etc. were synthesized. Polyaniline was obtained in the powder form by vacuum drying. 2mg of polyaniline was dissolved in 1ml of dimethyl formamide. Solution was sonicated well. Silica-gold core shell nanoparticles in different ratios were added to the solution to obtain various samples, then the samples were spin coated onto a clean glass slide for obtaining a thin film. Other techniques like drop-casting, dip coating were also used for obtaining thin films. Similar nano composites with gold nanowires instead of silica-gold core shell nanoparticles were also synthesized.

At present, the work on finding a good application of the synthesized nanocomposites is on its way. One such good application is gas sensing, and the samples are being prepared and optimized

for getting a good gas sensing application. Nanocomposites with other conducting polymers like PDOT:SS are being prepared.

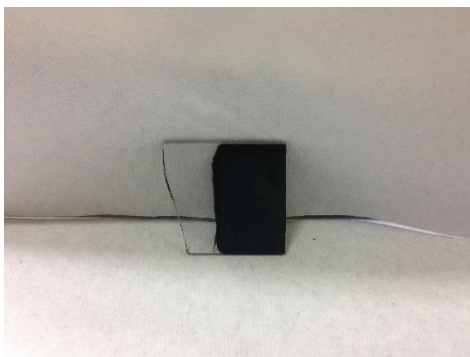


Figure 2.3: Polyaniline thin film obtained by dip coating

2.6 Analysis techniques

2.6.1 UV-Vis absorption spectroscopy

Absorption spectroscopy involves illuminating the sample with a light of certain intensity and measuring the transmitted intensity. The change in intensity is due to absorbance and scattering. Whenever the energy of the incident beam matches with the electronic transition of the molecules, absorbance take place. The transmittance is defined as

$$T = I/I_0$$

Where I = Intensity of incident beam, I_0 = Intensity of transmitted beam

Absorbance is directly related to concentration of the sample and path length

$$A = \log (I/I_0) = \epsilon l c$$

Here, ϵ is molar absorptivity, l is the path length and c is the concentration of the sample

In a typical spectrometer, the sample is kept in a cuvette which has calibrated dimensions and optical parameters. A reference cuvette filled with dispersing medium is also kept to remove any absorption by the dispersing medium. Two lamps for getting the whole UV-Vis range are employed. One is Deuterium (D_2) lamp which act as UV source, for the wavelengths less than 320 nm and other is Tungsten lamp for visible NIR regions of the spectrum. For detection of the

transmitted beam, two detectors including photomultiplier tube and Peltier cooled PbS detector (for $\lambda > 860$ nm) are employed. Standard UV-Vis plot includes absorbance as a function of wavelength of the incident beam. Perkin Elmer Lambda 950 UV-Vis Spectrometer was used for the UV-Vis analysis and working schematic of the instrument is shown in figure 2.2.

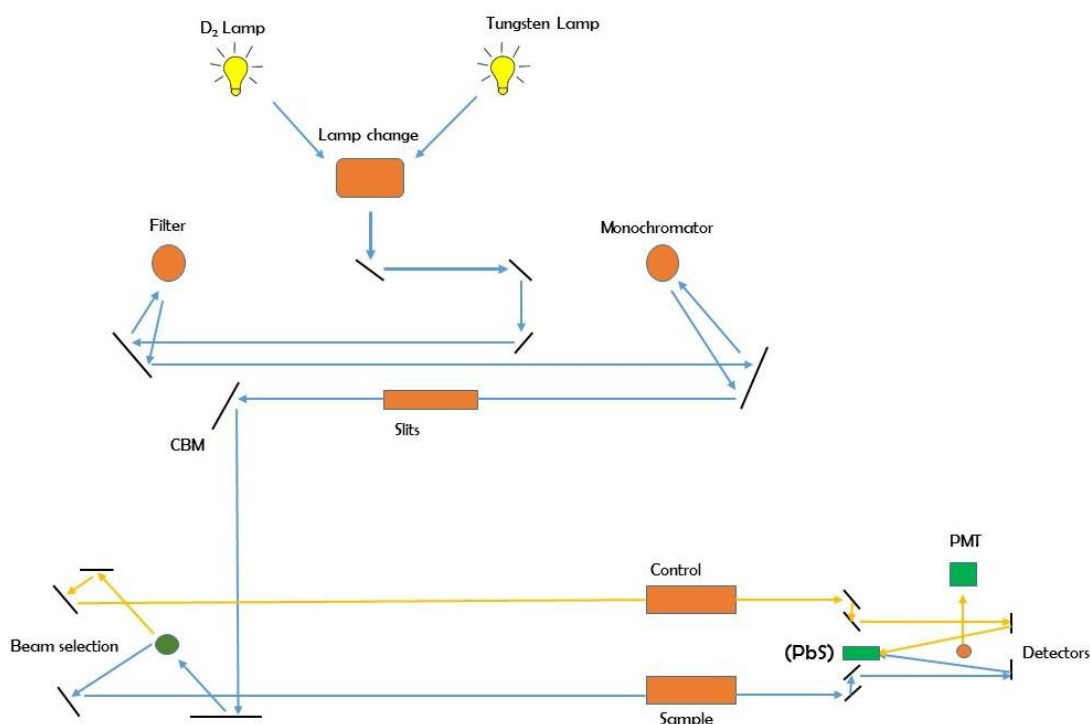


Figure 2.4: Schematic of the UV-Vis spectrometer

UV-Vis spectroscopy is a simple yet very powerful tool. With the properties of the material changing with size and concentration, it is very useful for nanoscience and can tell a lot about the synthesized material/molecule.

2.6.2 Field emission scanning electron microscopy (FESEM)

Starting from first compound microscope in 1590's to first electron microscope in 1933. Humans have always tried to see the small things better and better. With the limitation on spatial resolution offered by the optical microscopes (~200 nm), which is due to diffraction, in scanning electron

microscopy, electron beam with high energy is used to get better resolution. Wavelength of electron beam can be calculated using the de Broglie relation,

$$\lambda = h/(2mE)^{1/2}$$

where m is electron rest mass and h is Planck's constant

A focused and high energy electron beam is used for imaging and its wavelength can be tuned by changing the energy value. The electrons are generated using hot tungsten/ZrO cathode or from cold filament (using electric field), followed by acceleration using electric field gradient. The beam is focused using electrostatic lenses. Electron beam interact with the specimen under very complex phenomenon, producing back scattered electrons, UV light, visible light, Auger electrons and X-rays. SEM uses secondary or back scattered electrons for imaging. The velocity and angle of the secondary electrons is used to construct an image with the help of detectors and amplifiers.

Sample preparation includes drop-casting the sample solution (~15 μ l) on a clean silicon wafer. One of the limitations of the SEM is that the insulating samples cannot be viewed directly. A thin coating of gold (<10 nm) is done on the sample for imaging. The schematic of the Zeiss™ Ultra Plus FESEM used for the sample analysis is shown in figure 2.3.

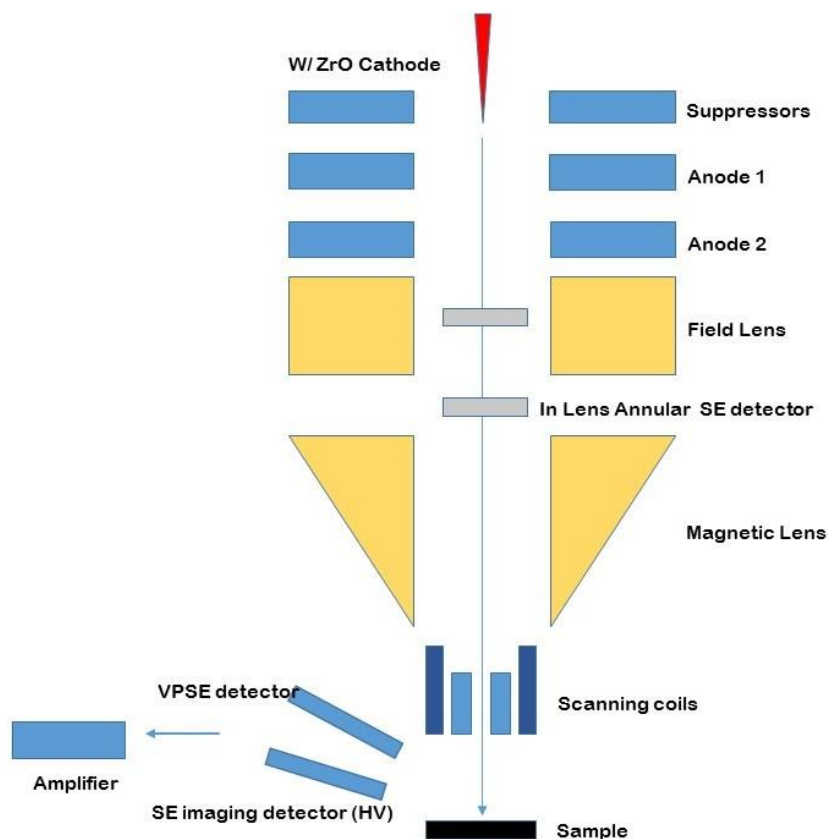


Figure 2.5: Schematic of scanning electron microscope (SEM)

Transmission electron microscopy (TEM) is other electron microscopy technique, which uses very high energy electron beam (usually > 50 keV) for imaging. The electron beam transmits through the sample and gives an image.

2.6.3 Fourier transform infrared spectroscopy (FTIR)

FTIR is used for the identification of the type of bonds present in the sample. Each functional group has its own characteristic absorption band in the infrared region, thus when the sample is illuminated with infrared light, transition between the vibrational energy levels of the molecule take place. Energy of the vibrations is given as

$$E_n = (n+1/2)h\nu_0$$

Here n is vibration quantum number, ν_0 is oscillator frequency, h is Planck's constant. The molecule should possess dipole moment for the absorption to take place. Bruker alpha spectrometer was used for the analysis.

2.6.4 X-ray diffraction

X-rays have their wavelength comparable to interatomic distance thus they are diffracted by the atoms. This scattering of the X-rays by the atoms can tell us about their arrangement. When the X-rays interact with the atoms they are re-emitted and these re-emitted waves then interfere producing a diffraction pattern. X-rays interact with the electrons present in the atom. Electrons oscillate on interaction and later scatter the absorbed energy. When the waves interfere constructively Bragg condition is met and relation between the wavelength of the X-ray used (λ), scattering angle (Θ) and interplanar distance (d) is given as

$$n\lambda = 2d\sin\Theta$$

The scattered intensity depends on the nature of the atom and the crystal structure (crystal factor). More the number of electrons, more is the scattered intensity. Intensity also depends on wavelength of the X-ray used and the scattering angle. Thus scattering power of an atom is defined as

$$f = Z\sin\Theta/\lambda$$

Where, f is atomic scattering factor, Z is atomic number and Θ is the angle of scattering

Bruker D8 X-ray diffractometer was used for obtaining the diffraction pattern of the samples. The main components of the diffractometer include X-ray tube, goniometer and detector. X-rays are generated in X-ray tube. Detector counts the scattered electrons, which is generally Geiger Muller tube or scintillation counter.

Single crystals have sharp peaks in the diffraction pattern. The broadening in the case of the single crystals is mainly attributed to the instrumental limitations. In the case of polycrystalline materials, the broadening is mainly attributed to the grain size. XRD analysis of the nanomaterials are done under certain conditions. Nanomaterials as compared to polycrystalline materials don't possess grain boundaries, but still the broadening of the diffraction peaks is observed. The broadening is attributed to the limited number of lattice planes present in the nanomaterials as compared to the infinite number of lattice planes present in single or polycrystalline materials. The broadening is related to the thickness of the sample and the relation is given by Scherrer formula.

$$t = K \lambda / \beta \cos(\Theta_B)$$

Where, t is thickness of the crystal, K is the shape factor (typical value is 0.9), λ is the X-ray wavelength, β is the broadening (full width half maximum in radians) and Θ_B is the Bragg angle

For the nanoparticles with size ~ 2 nm, the broadening is very large and the XRD pattern corresponds to the one of amorphous material.

Electrons and neutrons can also be used for obtaining the diffraction pattern. Two atoms with similar atomic scattering factor (f) or similar atomic number (Z) are difficult to distinguish using X-RD. Neutron diffraction can overcome the limitation as the intensity no longer depends on the atomic number in neutron diffraction. Neutrons are diffracted by the atomic nuclei and Light elements like Hydrogen (H) can also be detected. The main advantage of the neuron diffraction is that it can be employed to study the magnetic structure of the material as neutron has magnetic moment.

2.6.5 Field emission transmission electron microscopy (FETEM)

In transmission electron microscopy, the electrons transmit through the specimen to give an image. TEM uses a high energy electron beam for getting the image. TEM provides better resolution (~ 0.5 nm) when compared to SEM. Although the initial formation of electrons, then their acceleration and collimation works as same as in SEM, the difference comes when obtaining the image. From the initial generation of electrons to interaction with the sample, everything happens in vacuum (10^{-3} - 10^{-4} Pa). Other advantage of the TEM is that one can also obtain diffraction pattern of the specimen, thus obtaining information about its crystal structure.

The limitation of TEM include preparation of thin samples. As we know that for getting the image electrons penetrate though the sample, thus sample cannot be very thick.

For the TEM analysis, JEOL JEM 2200 FS transmission electron microscope was used. The samples were prepared on a square mesh copper grid using drop casting technique. The prepared grids were vacuum dried.

Chapter 3

Result and discussions

This chapter includes the results obtained from various characterizations of the synthesized particles followed by a brief discussion on the results obtained.

3.1 Silica nanoparticles

Silica nanoparticles were synthesized using the described Stober method in chapter 2. Obtaining monodisperse silica nanoparticles can sometimes get tricky. Dropwise and slow addition of tetra ethyl ortho silicate (TEOS) is very important. Monodisperse particles of diameter ~ 250 nm were obtained after few attempts. The synthesized silica nanoparticles were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM) and field emission transmission electron microscopy (FETEM).

3.1.1 SEM analysis

For checking the mono-dispersity of the synthesized silica nanoparticles, SEM analysis were done. For the analysis, the sample was drop casted onto clean cover slip. The sample prepared was vacuum dried. As discussed earlier that scanning electron microscope has limitation for insulating samples, thus a gold film ~5 nm was spray coated onto the sample. Monodisperse silica nanoparticles with diameter ~250 nm were obtained. High quality particles were synthesized.

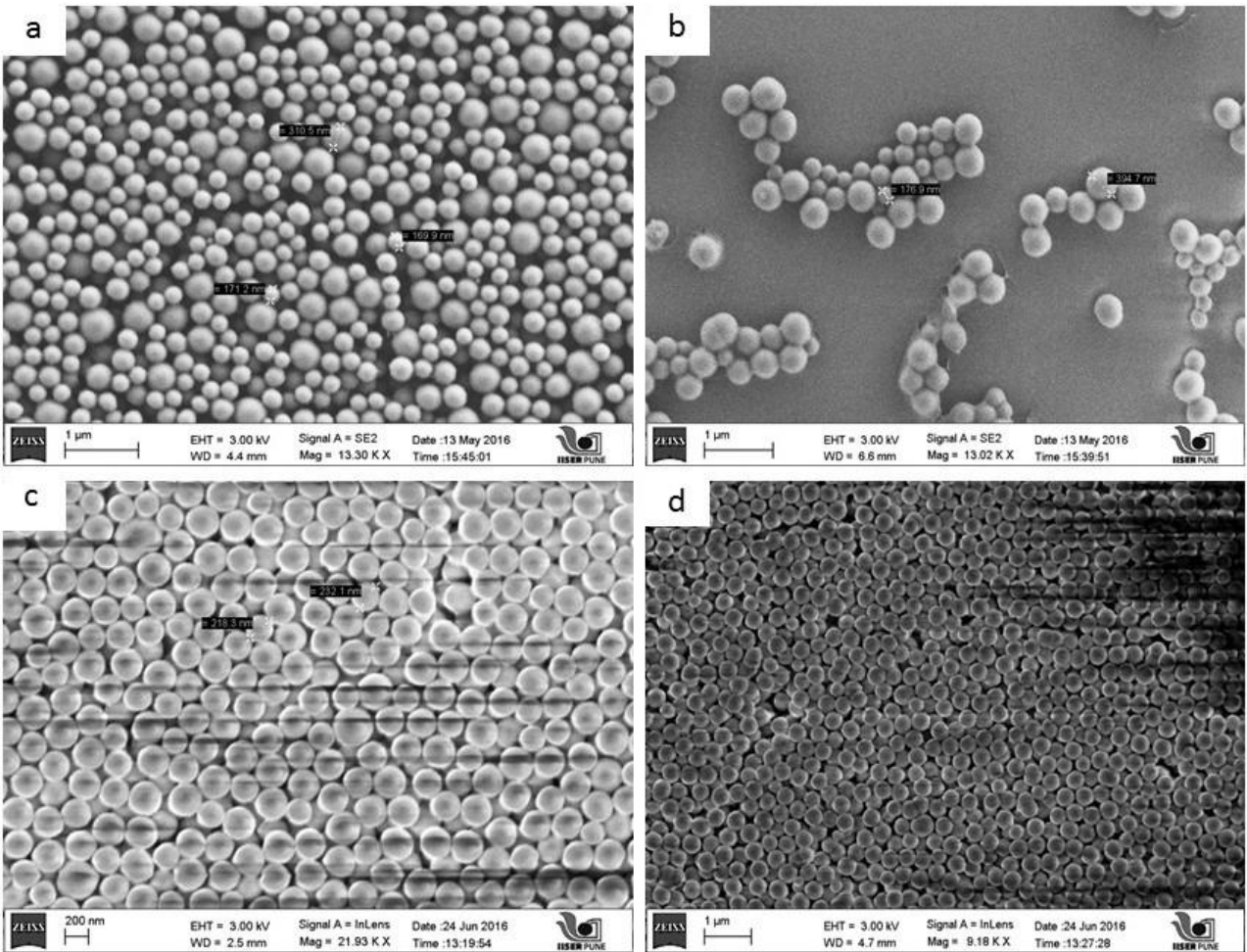


Figure 3.1: FESEM of the silica nanoparticles a) and b) correspond to silica nanoparticles obtained with non-uniform size distribution c) and d) correspond to mono disperse silica nano particles

3.1.2 UV-Vis analysis

Liquid state UV-Vis analysis of the synthesized silica nanoparticles were done. Dilute sample of silica nanoparticles in ethanol was prepared for the analysis. The absorption spectrum didn't show any absorption peak in the visible region.

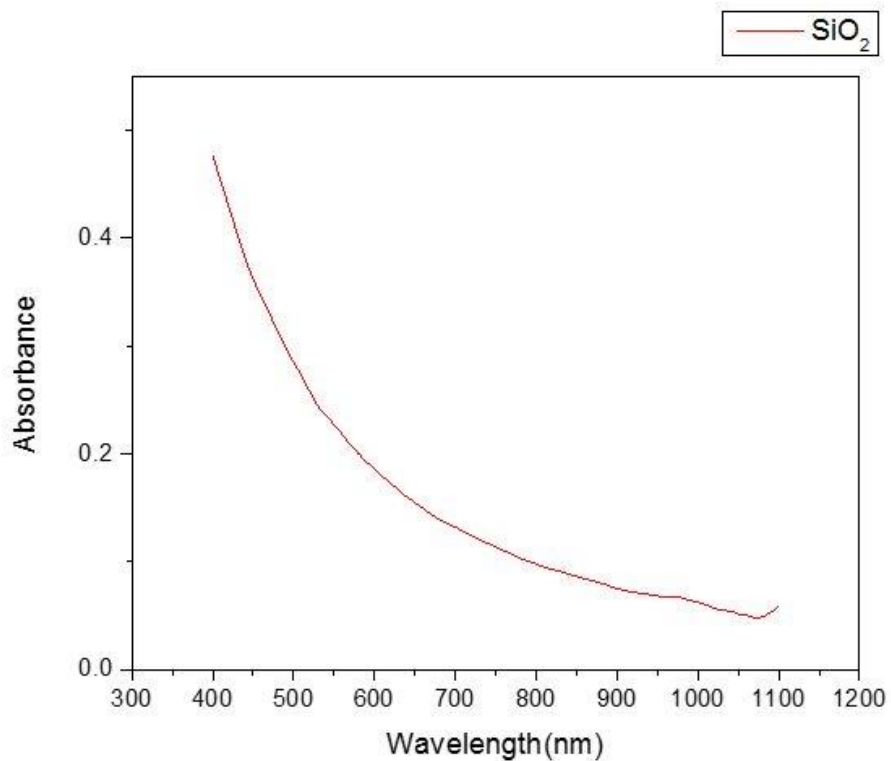


Figure 3.2: Absorption spectrum of the silica nanoparticles

3.1.3 X-ray diffraction

X-ray diffraction of the synthesized silica nanoparticles was done. A concentrated sample of silica nanoparticles was prepared on a cover slip, followed by vacuum drying. A 2 hour long scan was done to get XRD spectrum. A broad peak ($\Theta = 23^\circ$) and absence of any diffraction peaks in the XRD pattern confirmed that the prepared silica nanoparticles are amorphous.

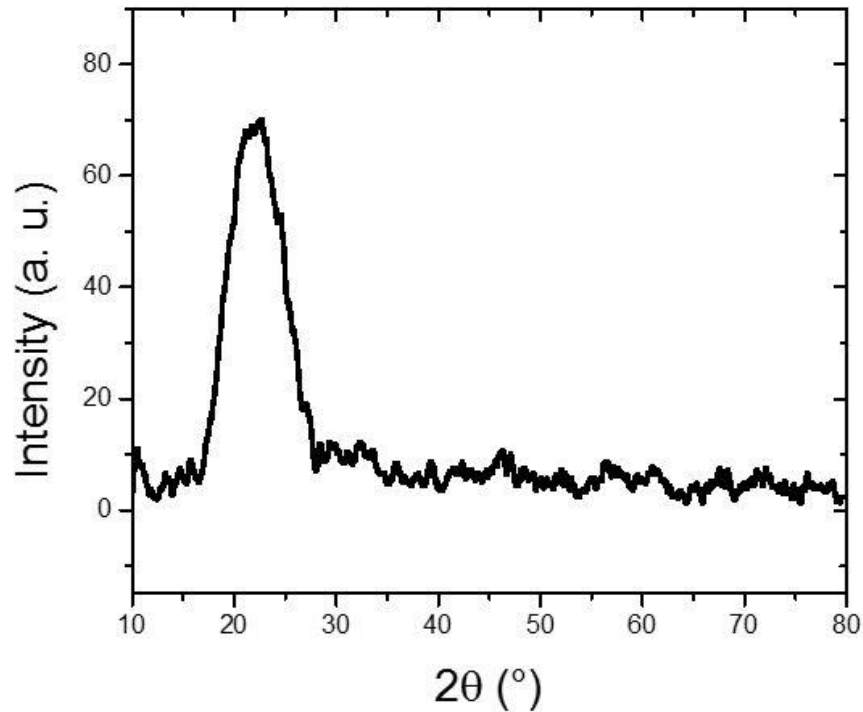


Figure 3.3: XRD pattern of the synthesized silica nanoparticles

3.2 Core-shell nanoparticles

3.2.1 SEM analysis

For the morphological analysis of the prepared core-shell nanoparticles, scanning electron microscopy was done. A good quality core shell nanoparticles were obtained after several attempts and modifications to the already published method. Silica nanoparticles with the proper growth of nanowires were observed. Gold nanowires growing radially from silica nanoparticles were observed. Silica nanoparticles having diameter $\sim 250\text{nm}$ along with the gold nanowires having length of $\sim 200\text{ nm}$, formed the core shell nanoparticles.

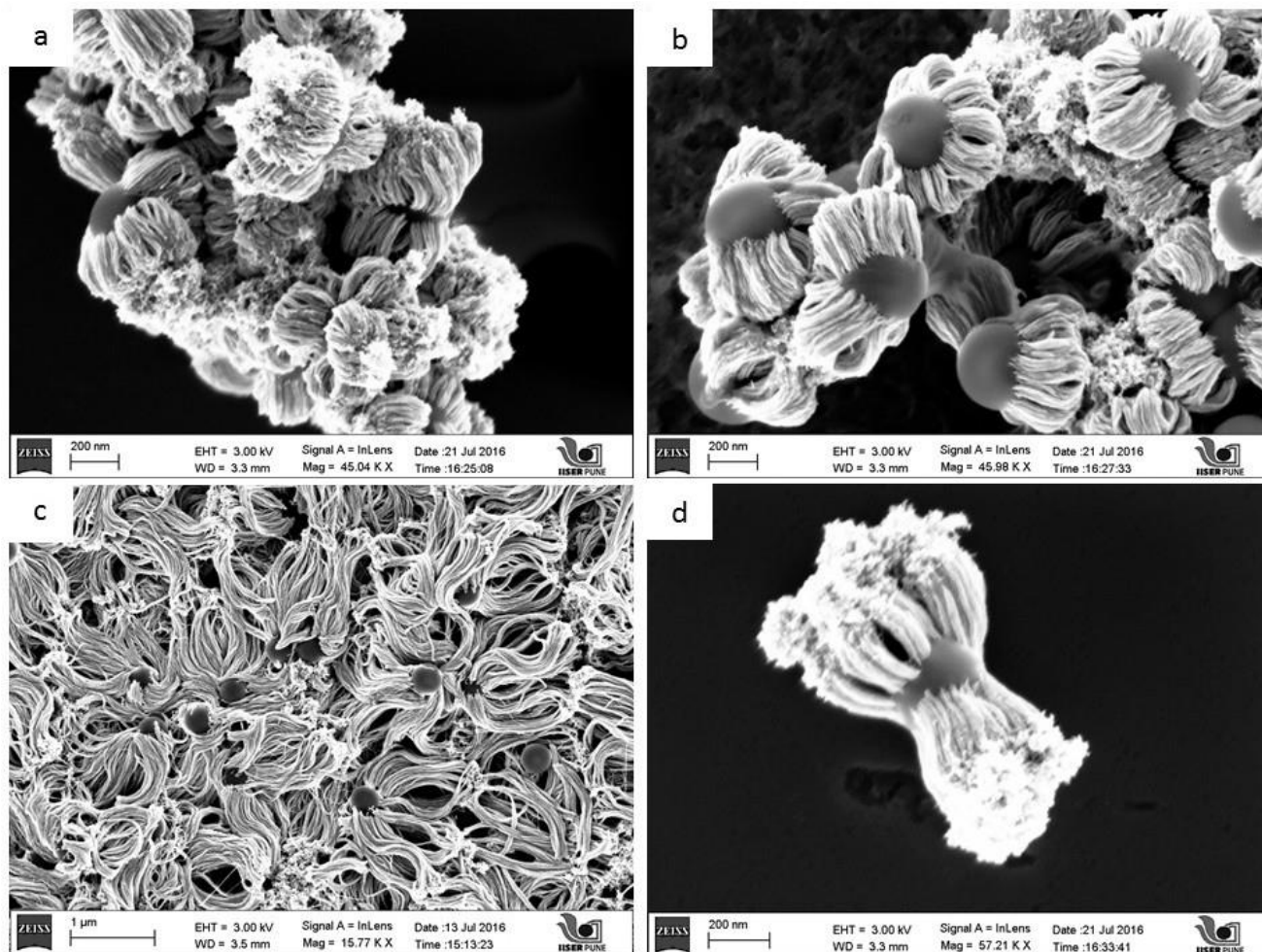


Figure 3.4: FESEM images of the core-shell nanoparticles

The core shell nanoparticles were also observed from an angle. The silicon wafer having core shell nanoparticles was mounted onto an inclined stage for viewing and getting the FESEM images. The images confirmed that the gold nanowires were actually originating from silica nanoparticles. The FESEM images are shown in figure 3.5.

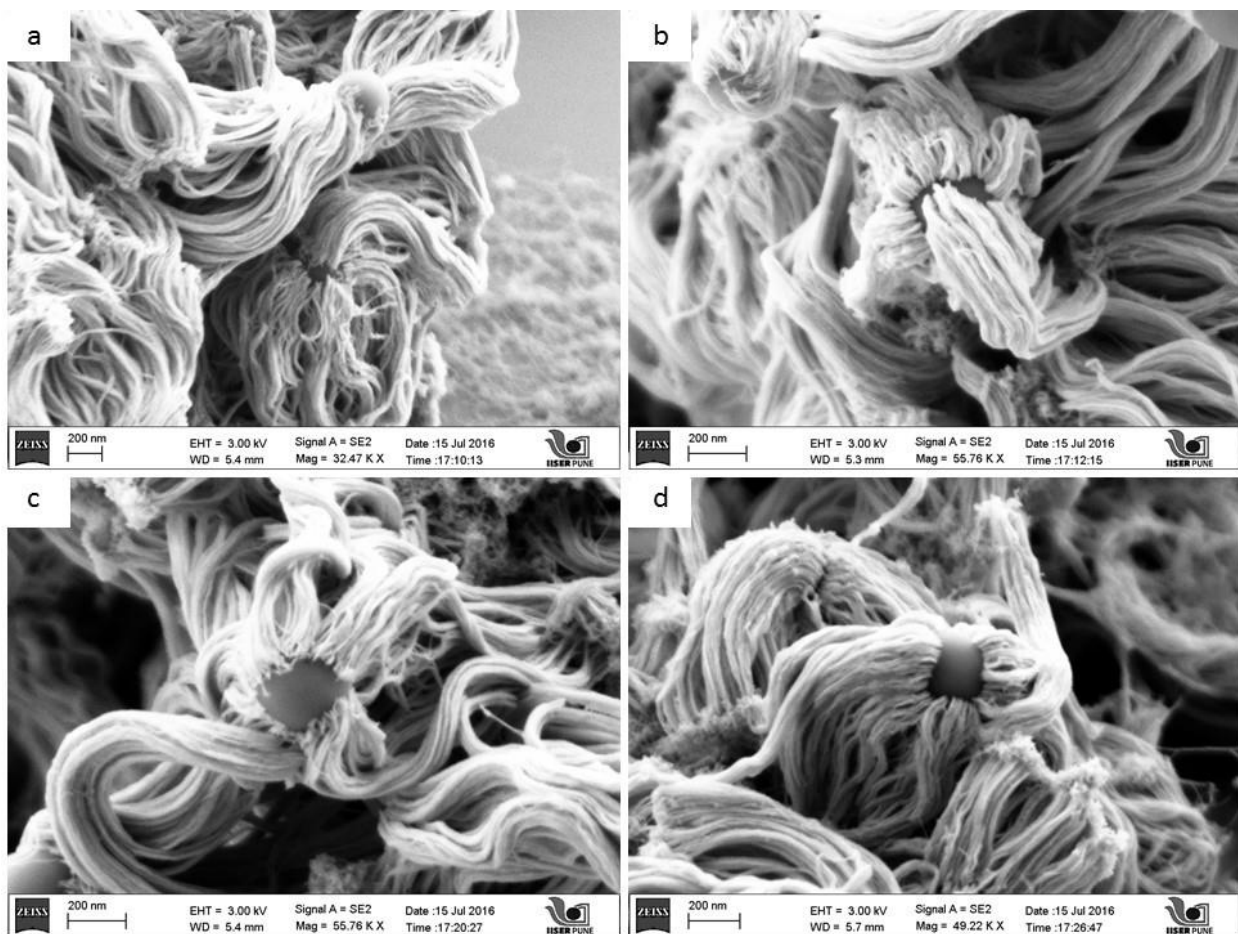


Figure 3.5: FESEM images of the core shell nanoparticles obtained from an inclined plane

3.2.2 FTIR analysis

FTIR spectrum of the core shell nanoparticles was taken and compared with the FTIR spectrums of silica nanoparticles and functionalized silica nanoparticles. Silica nanoparticles FTIR spectrum showed the peaks corresponding to Si-O-C and O-Si-O vibrations. Upon functionalization with APTES, two extra peaks were observed corresponding to $-NH$ and $-NH_2$ groups. Thus confirming that the silica nanoparticles were indeed functionalized successfully. FTIR spectrum of gold silica core shell nanoparticles contained few peaks corresponding to $-NH$ group signifying that few particles were still $-NH$ terminated.

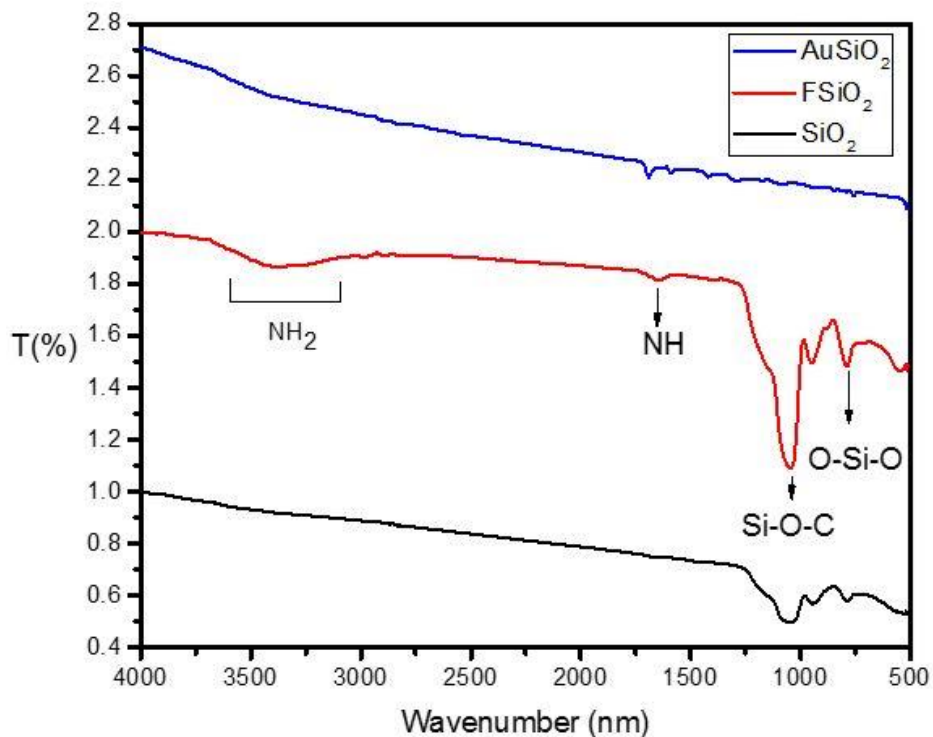


Figure 3.5: FTIR spectrum of the a) SiO₂ (Black) b) Functionalized Silica nanoparticles (Red) and c) Core-shell nanoparticles (Blue)

3.2.3 UV analysis

Solution phase absorption analysis of the silica gold core shell nanoparticles were done. The absorption spectrum was compared with the absorption spectrum of silica nanoparticles and functionalized silica nanoparticles. The absorption spectrum of silica nanoparticles as explained in section 3.1.2 didn't show any absorption peak in visible region. Functionalized silica nanoparticles also followed the same trend. For silica-gold core-shell nanoparticles, two peaks were observed. One peak around 550 nm corresponding to transverse surface plasmon resonance and around 999nm correspond to longitudinal surface plasmon resonance. And the same is true for anisotropic nanomaterials, which have two resonance modes.^[20]

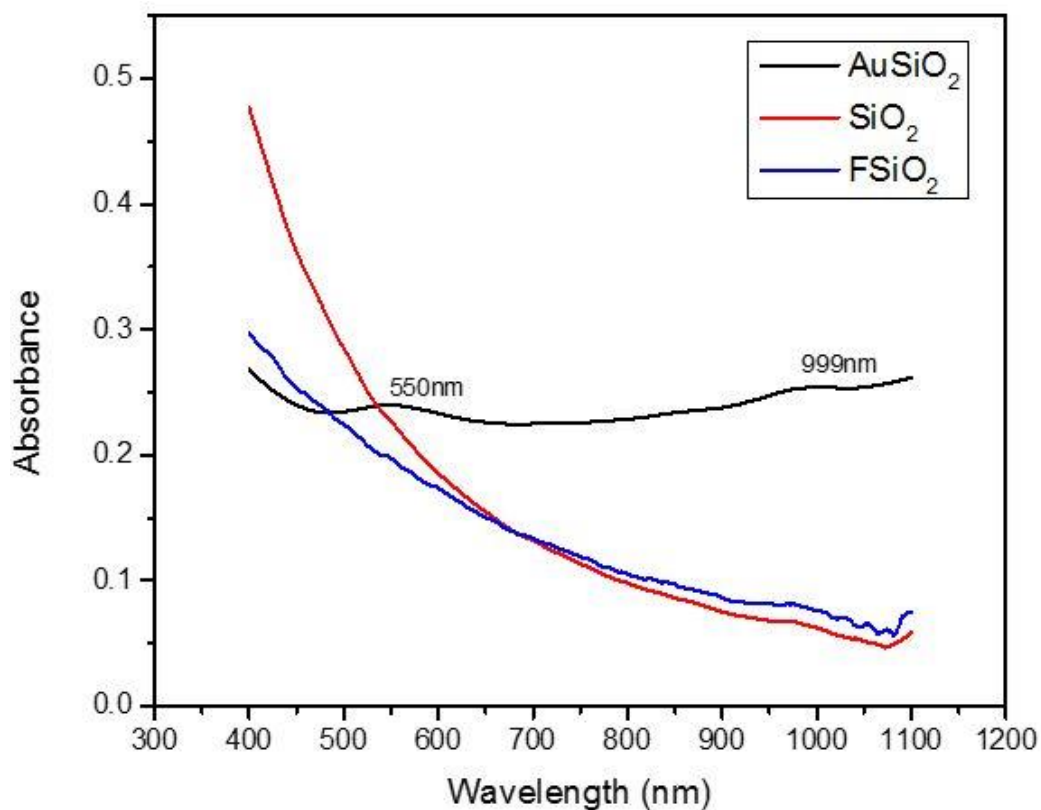


Figure 3.6: Absorption spectrum of a) SiO₂ nanoparticles (Red) b) Functionalized Silica nanoparticles (Blue) and c) Silica gold core-shell nanoparticles (Black)

3.2.4 TEM analysis

For higher resolution, transmission electron microscopy of the core shell nanoparticles was done. Samples were prepared on a very tiny and thin copper grid. A very dilute sample of the core shell nanoparticles was used for drop casting. High resolution images of the particles were obtained. The core shell nanoparticles with core (silica) size ~ 250 nm and shell (gold nanowires) size ~300 nm were observed.

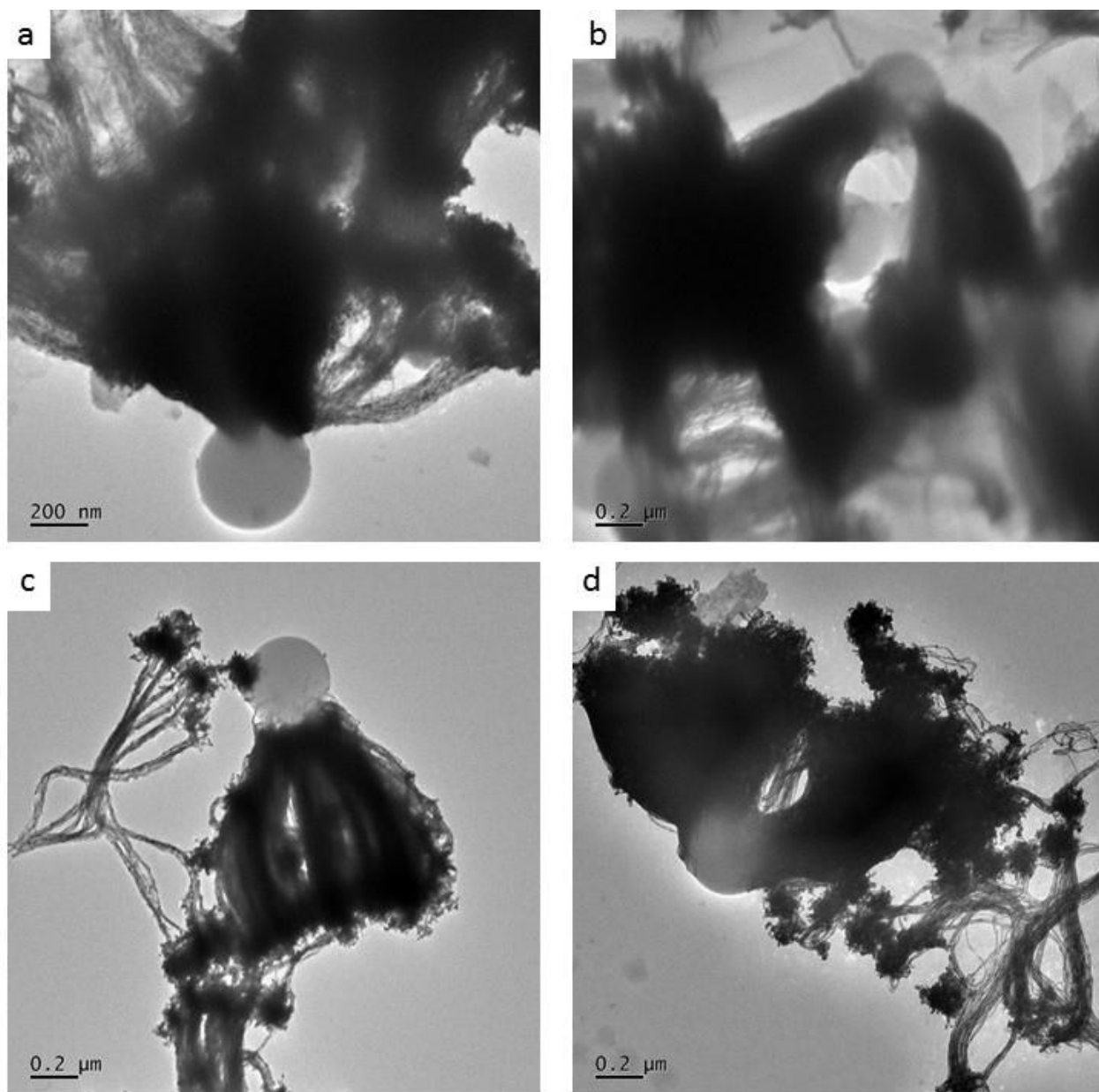


Figure 3.7. : FETEM images of the core shell nanoparticles

3.3 Gold nanowires

Gold nano wires were synthesized using simple wet chemical synthesis procedure as described in chapter 2. Auophilic interactions play an important role in nanowire formation. The addition of Oleylamine, leads to complex formation between Oleylamine and gold, thus developing a polymeric chain. Addition of TIPS (tri-isopropylsilane) reduces gold, giving us Oleylamine capped nanowires. Oleylamine doesn't allow gold nanowires to aggregate.^[21]

3.3.1 SEM analysis

Scanning electron microscopy of the synthesized nanowires is done for the morphological analysis. Samples were prepared on a cleaned silicon wafer by drop casting followed by vacuum drying. The diameter of the gold nano wires was found out to be 8-10 nm with length in micrometer. The aspect ratio of the gold nano wires could not be calculated because the actual length of the nanowires could not be measured due to intertwining. With the limitation on the resolving power of SEM, it was difficult to distinguish between single wire and their cluster. Overall, high quality gold nanowires were produced.

On drying the gold nanowire sample on a substrate, they self-assembled into parallel 2D bundles because of hydrophobic interaction between the alkyl groups of Oleylamine. Time dependence of the growth of nanowires was also studied with the formation of gold nanoparticles in the beginning.

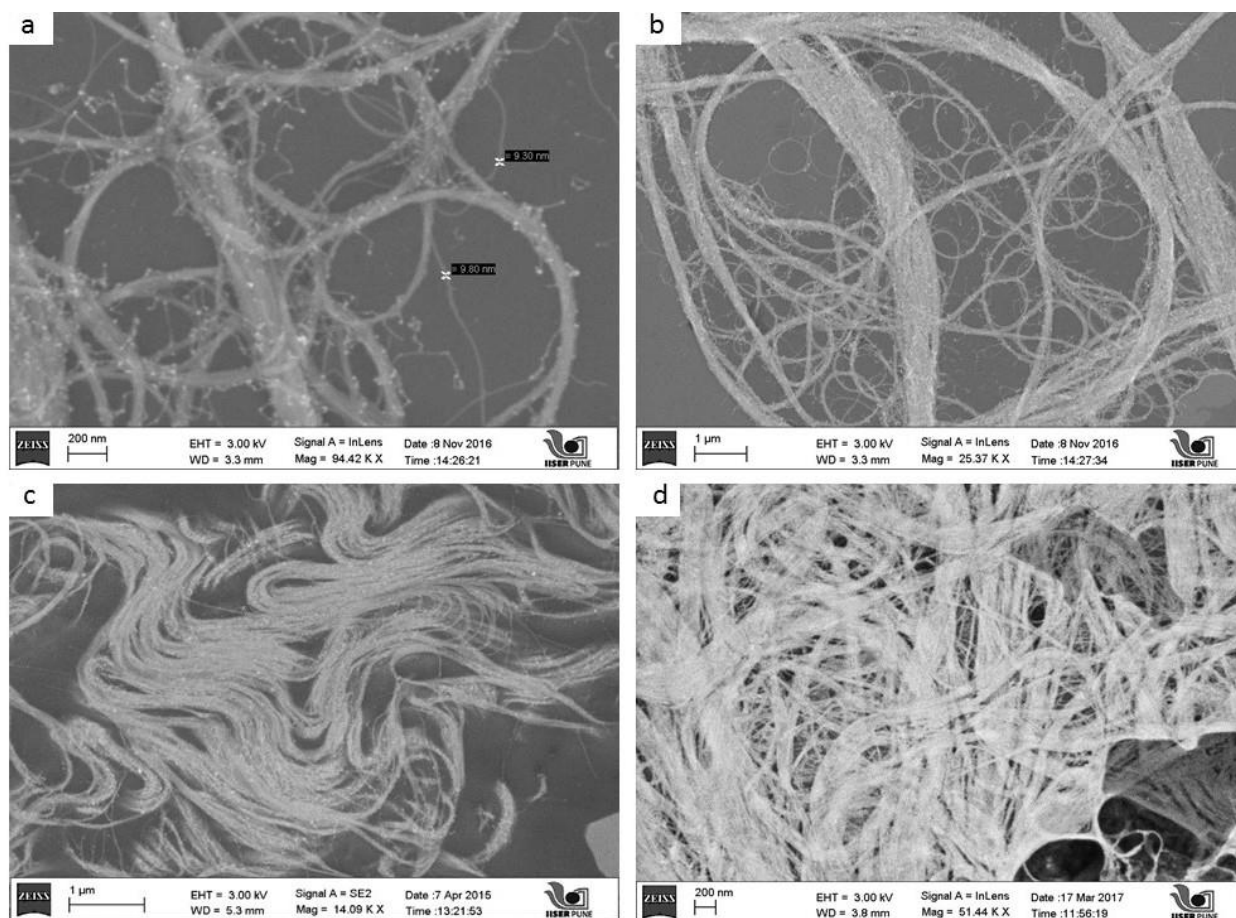
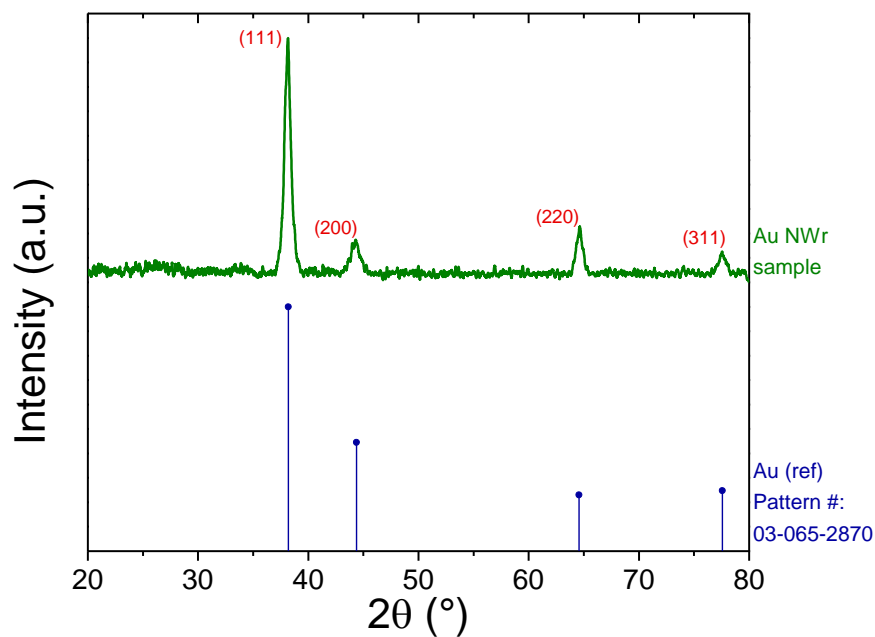


Figure 3.8: FESEM images of the Gold nanowires (AuNws)

3.3.2 XRD Analysis

For the XRD analysis, a concentrated sample of gold nanowires (AuNws) was prepared on a cleaned cover slip. 2 hour long scan was done for getting the XRD pattern. As we know that gold crystallize in face centered cubic (FCC) lattice, X ray diffraction pattern also confirmed the face centered cubic structure of gold nanowires. Peaks corresponding to the miller indices (111), (200), (220) and (311) were observed and we know that for the crystal in FCC lattice the miller indices should either all odd or all even. Peaks also showed agreement with Au diffraction standard.



s

Figure 3.9: XRD pattern of the gold nanowires (AuNws)

3.3.3 UV-Vis analysis

Absorption spectrum of the gold nanowires was obtained in liquid phase with a peak around ~527 nm, corresponding to transverse surface plasmon resonance peak (TSPR) as discussed in section 1.4.

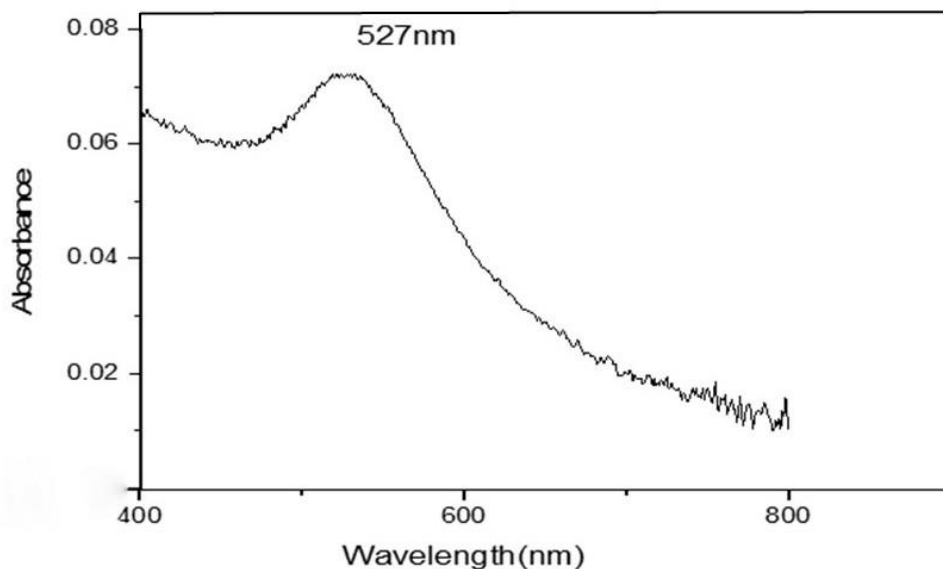


Figure 3.10: Absorption spectrum of gold nanowires (AuNws)

3.4 Nanocomposites

Polyaniline in its emeraldine form was synthesized. Green color solution was obtained. Obtaining a good film of PANI with a nanomaterial is a challenging task. Blending silica gold core shell with the polymer is also challenging as the gold nanowires detach from the silica nanoparticles upon prolonged sonication. Polymer solution was sonicated separately for getting a homogeneous solution.

3.4.1 SEM analysis

FESEM images of the polyaniline thin films obtained on a glass slide by dip coating were obtained.

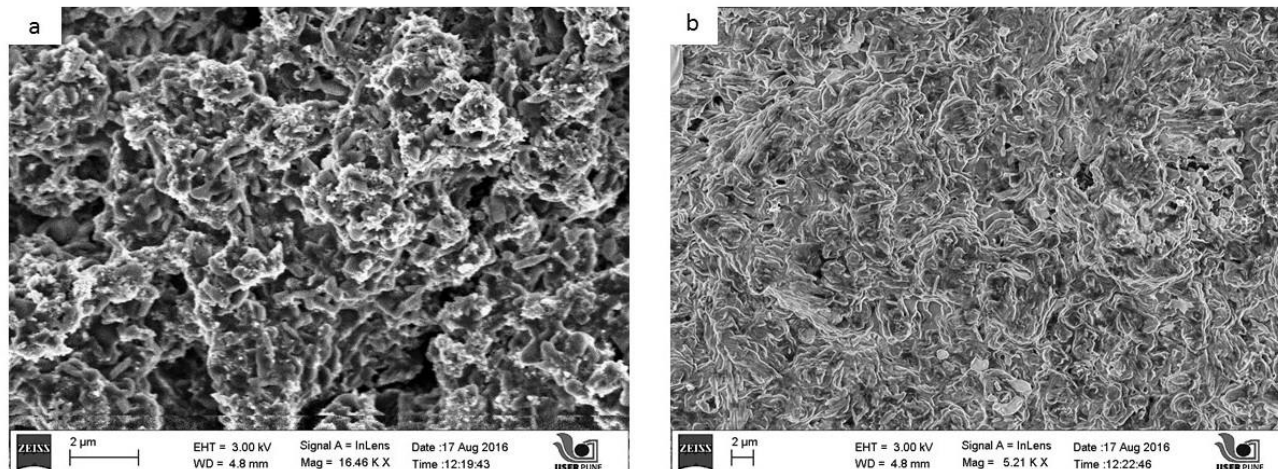


Figure 3.11: FESEM images of the PANI thin Films

3.5 Concluding remarks

Silica gold core-shell nanoparticles and gold nanowires were synthesized and studied. Various characterization techniques were employed to study and characterize them. FESEM, FTIR and UV-Vis analysis successfully confirmed the growth of gold nanowires on silica nanoparticles. Growth and structure of gold nanowires was also studied separately, confirming the crystalline nature of the gold nanowires. Later the nanocomposites containing a conducting polymer (polyaniline and PEDOT:PSS) and nanomaterials (silica gold core shell nanoparticles and gold nanowires) were synthesized. The work on potential application of the nanocomposite in gas sensing is still going on and the results will be included in the final presentation.

Chapter 4

Summary and future directions

Nanoscience and nanotechnology has totally transformed the today's world. With the materials showing different properties in nano form as compared to their bulk form. These properties if properly harnessed can act as a boon for whole mankind. These properties mainly arise from electron confinement and increase in surface area to volume ratio. As these properties mainly depend on size of the nanomaterial and morphology, thus developing methods for obtaining desired size and morphology is a essential task.

In this work, nanomaterials (silica nanoparticles, silica gold core-shell nanoparticles and gold nanowires) and conducting polymer polyaniline were synthesized using chemical methods. Silica nanoparticles were synthesized using a sol-gel method. Gold nanowires were synthesized using a single step chemical method. Synthesis of silica gold core-shell nanoparticles was a multistep process including surface modification of silica nanoparticles, synthesis and attachment of gold seeds onto surface modified silica nanoparticles and later the growth of gold nanowires on the gold seed attached silica nanoparticles. Certain changes in the concentrations of the materials involved in the synthesis along with changes in reaction time were to be done to get the desired product. The whole reaction was optimized to get the best core shell nanoparticles. A detailed characterization of all the materials synthesized was done. The optical property of the noble metals eg. Gold (Au) in our case was also discussed briefly. Surface plasmon resonance which is the collective oscillation of the free surface electrons was explained in context with gold nanomaterials. Gold nanowire being an anisotropic material possess two resonant absorption peaks namely transverse surface plasmon resonance peak and longitudinal surface plasmon resonance peak.

The synthesized nanomaterials were blended with conducting polymers to create nanocomposites. Conducting polymers polyaniline and PEDOT:PSS were used because of ease of their synthesis. Nanocomposites were obtained as a thin film on a glass slide and characterization of these films was still in progress.

The aim and future direction of the project is to find out a good-practical application of the synthesized nanomaterials. Many applications are being considered like as gold nanowires as SERS substrate, pressure sensor based on gold nanowires and gas sensor based on silica-gold core shell nanoparticles – polyaniline/PEDOT:PSS nanocomposites. At present, gas sensing ability of the nanocomposites is under study and good results are expected. Future work includes the synthesis of nanocomposites with different morphology of nanomaterial and better sensitivity for the gas to be studied.

Bibliography

- [1] S. K. Kulkarni, *Nanotechnology: Principles and Practices*, Capital Publishing Company, New Delhi (2011).
- [2] H. S. Nalwa, *Hand Book of Surfaces and Interfaces of Materials*, Vol. 3: Nanostructured Materials, Micelles and Colloids (2001).
- [3] S. J. Oldenberg, R. D. Averitt, S. L. Westcott, and N. J. Halas., Nanoengineering of optical resonances, *Chem Phys. Lett.*, **288**, 243-247 (1998).
- [4] H. Kim, M. Achermann, L. P. Balet, J. A. Hollingsworth, and V. I. Klimov, Synthesis and characterization of Co/CdSe core/shell nanocomposites: Bifunctional magnetic-optical nanocrystals, *J. Am. Chem. Soc.*, **127**, 544-546 (2005).
- [5] N. Toshima and T. Yonezawa, Bimetallic nanoparticles-novel materials for chemical and physical applications, *New J. Chem.*, 1179-1202 (1998).
- [6] K. H. See, M. E. Mullins, Mills, and O. P., Heiden, P. A., A reactive core-shell nanoparticle approach to prepare hybrid nanocomposites: effects of processing variables, *Nanotechnology*, **16**, 1950-1959 (2005).
- [7] T. Li, J. Moon, A. A. Morrone, J. J. Mecholsky, D. R. Talhman, and J. H. Adair, Preparation of Ag/SiO₂ nanosize composites by a reverse micelle and solgel technique, *Langmuir*, **15**, 4328-4334 (1999).
- [8] J. L. West, and N. J. Halas, Engineered nanomaterials for biophotonics applications: Improving sensing, imaging and therapeutics, *Annu. Rev. Biomed Eng.*, **5**, 285-292 (2003).
- [9] S. Kalele, S. W. Gosavi, J. Urban, and S. K. Kulkarni, Nanoshell Particles: Synthesis, Properties and Applications, *Current Science*, 91, 8, 1038 (2006).
- [10] H. Shirakawa, Edwin J. Louis, Alan G. MacDiarmid, Chwan K. Chiang and Alan J. Heeger *J. Chem. Soc., Chem. Commun.*, 578-580 (1977).
- [11] https://www.nobelprize.org/nobel_prizes/chemistry/laureates/2000/popular.html
- [12] Z. A. Boeva, and V.G. Sergeyev, *Polymer Science, Ser. C*, Vol. 56, No. 1, pp. 144–153 (2014).

- [13] T. K. Das and S. Prusty, Review on Conducting Polymers and Their Applications, *Polymer-Plastics Technology and Engineering*, 51:14, 1487-1500 (2012).
- [14] G. Greczynski et al, *Journal of Electron Spectroscopy and Related Phenomena*, Photoelectron spectroscopy of thin films of PEDOT–PSS conjugated polymer blend: a mini-review and some new results, 121, 1–17 (2001).
- [15] L. Groenendaal et al, Poly(3,4-ethylenedioxythiophene) and Derivatives, *Adv. Mater.*, 12, 7 (2000).
- [16] J. Huang, R. Fan, S. Connor, and P. Yang, One-step patterning of aligned nanowire arrays by programmed dip coating, *Angew. Chem. Int. Ed. Engl.*, 46, 14, 2414–7 (2007).
- [17] G. Mie, *Ann. Phys.*, 330, 377–445 (1908).
- [18] R. Gans, *Ann. Phys.*, 342, 881–900 (1912).
- [19] W. Stöber, A. Fink, and E. Bohn, *J. Colloid Interface Sci.* 26 62–69 (1968).
- [20] E. Farrokhtakin et al, *Journal of Colloid and Interface Science*, 449, 87–91 (2015).
- [21] H. Feng, Y. Yang, et al, *Chem. Commun.*, 1984-1986 (2009).
- [22] J. Stejskal, R. G. Gilbert, Polyaniline. Preparation of a Conducting Polymer Pure Appl. Chem., 74, 857–867 (2002).