

Anisotropic Core-Shell Nanoparticles Using Silica Templates for Ammonia Gas Detection

A Thesis

Submitted to
Indian Institute of Science Education and Research Pune
In partial fulfillment of the requirements for the
BS-MS Dual Degree Programme

by
Vaibhav Madhav Khambalkar



Indian Institute of Science Education and Research Pune
Dr. Homi Bhabha Road,
Pashan, Pune 411008, INDIA.

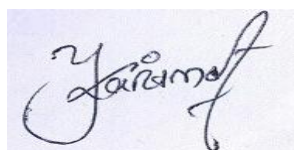
April 2018

Supervisor: Dr. Sulabha K. Kulkarni
Centre for Materials for Electronics Technology (C-MET), Pune

©Vaibhav Khambalkar 2018
All rights reserved

Certificate

This is to certify that this dissertation entitled “*Anisotropic Core-Shell Nanoparticles Using Silica Templates For Ammonia Gas Detection* “ towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education Pune represents study/work carried out by Vaibhav Madhav Khambalkar at Indian Institute of Science Education and Research and Research and Centre for Materials for Electronics Technology (C-MET) under the supervision of Dr. Sulabha K. Kulkarni, INSA Senior scientist, Department of Material science , during the academic year 2017-2018.



Vaibhav Madhav Khambalkar
20131106



(Sulabha Kulkarni)

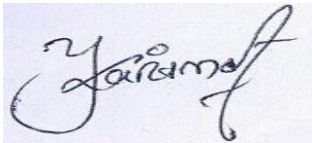
Dr. Sulabha K. Kulkarni
Professor

Committee:

Dr. Sulabha K. Kulkarni
Dr. Aparna Deshpande

Declaration

I hereby declare that the matter embodied in the report entitled “*Anisotropic Core-Shell Nanoparticles Using Silica Templates For Ammonia Gas Detection*” are the results of the work carried out by me at the Department of Physics, Indian Institute of Science Education and Research, Pune, and Centre for Materials for Electronics Technology (C-MET) under the supervision of Dr. Sulabha K. Kularni and the same has not been submitted elsewhere for any other degree.



Vaibhav Madhav Khambalkar

20131106



(Sulabha Kulkarni)

Professor

Acknowledgments

I would like to express sincere gratitude to my mentor Dr. Sulabha K. Kulkarni for her generous guidance, excellent mentorship, and constant encouragement. I consider myself fortunate 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 am also thankful to Dr. Parag Adhyapak, C-MET, Pune for his cordial support and guidance which help me in completing the project.

I express my deep sense of gratitude to Dr. Aparna Deshpande and Dr. Sunil Mukhi for entertaining my request to use the wet lab for synthesis purposes. I am indebted to my lab members Sachin, Shobha, Chinmay for their continuous support and stimulating discussions.

I am grateful to IISER Pune and C-MET Pune and its staff for providing essential tools required for the project. Finally, I thank all who directly or indirectly helped for successful completion of this project.

Table of Contents

Abstract.....	6
Chapter 1: Introduction.....	7
1.1) Anisotropic Nanoparticles.....	7
1.2) Core-Shell Nanoparticles ⁵	8
1.3) Silica-Gold Core-Shell Nanoparticles.....	8
1.4) Ammonia gas detection.....	9
1.5) Conducting Polymers and Gas sensing Principle.....	10
Chapter 2: Experimental Techniques.....	12
2.1) Synthesis of Silica Nanoparticles.....	12
2.2) Synthesis of Core-Shell (SiO ₂ @Au) Nanoparticles.....	13
2.2.1) Functionalization of nanoparticles.....	13
2.2.2) Synthesis of Gold Seeds.....	13
2.2.3) Coating Gold NPs on Silica Nanoparticles.....	14
2.3) Synthesis of Conducting Polymer.....	15
2.3.1) Synthesis of Polyaniline.....	15
2.3.2) Synthesis of Polypyrrole.....	15
2.4) Synthesis of Nano-composite.....	15
2.4.1) Preparation of Thin Film.....	15
2.5) Ammonia Sensing Technique:.....	16
Chapter 3: Characterisation of material.....	17
3.1) SEM and EDAX Results.....	17
3.2) UV-Vis Analysis.....	19
3.3) XRD Analysis.....	20
3.4) FTIR Spectra.....	20
Chapter 4: Results and Discussion.....	22
4.1) Results.....	22
4.2) Discussions.....	27
Chapter 5: Conclusions.....	30
Bibliography.....	31

Abstract

Ammonia is one of the essential components of life formation. It plays a wide role in biological processes and physiology. It widely used in chemical industries, fertilizers, a precursor to nitrogenous compound, textiles, refrigeration etc. But it is irritating, inflammable and extremely hazardous in concentrated form. Various types of ammonia sensors are available but they subject to limitations. Composites of conducting polymer and core-shell Gold-metal oxide nanoparticles prove to be the promising material for gas sensing. Gold as a bulk does not interact with gases but its nanoparticles and composites show excellent gas sensing properties.

Gas sensing properties of these materials depend on chemical composition, morphology, and method of preparation. Our attempt was to synthesize a material for the sensor, selective to only ammonia gas using Nano-composites of conducting polymer (Polyaniline, Polypyrrole) and two morphologies (spherical and rod) of anisotropic gold coated silica core-shell nanoparticles. It is found that composite of Polypyrrole and Au coated Spherical SiO₂ nanoparticles shows better sensing properties for ammonia gas as compared to other composites.

Chapter 1: Introduction

Nanotechnology deals with very small dimension materials usually in the range of 1 to 100nm. When at least one of the dimension of any material is reduced below 100nm it's mechanical, thermal, optical, magnetic and other properties changes with a change in the size of that material. Thus with the same material, one can get a range of properties. For example CdS nanoparticles have a variable colours as well as melting point according to its size in nm range.

Various types of nanomaterials like clusters, semiconductor nanomaterials, Plasmonic materials are well studied. Some special class of nanomaterials like carbon nanomaterials, porous materials, aerogels, zeolites, core-shell particles are being used in industrial scale. Core-shell particles form a novel class of nano-composite materials in which one material forms the core and another material is coated on it. Such core-shell particles are quite unique in the sense that properties of the material depend not only on the materials involved but the ratio of core to shell ratio. Such materials have found applications in sensors, drug delivery systems, enhancing luminescence of materials and so on.

This project is planned to synthesize novel anisotropic core-shell particles. Usually, spherical core-shell particles are common. Silica or polymer cores have been coated with a variety of metals/semiconductors/magnetic materials or polymers. Sometimes silica or polymers also used as shell materials on metals/semiconductors/magnetic materials. However, there are not many attempts to make anisotropic core-shell particles which may have interesting applications such as gas sensing properties.

1.1) Anisotropic Nanoparticles

Anisotropic nanoparticles are an incredible ingredient in material designing. With added anisotropy remarkable properties develop. In bottom up synthesis, anisotropy is vital for programmability; since isotropic particles lack directionality¹. Anisotropic NPs carry asymmetric axes and this break in symmetry is the origin of remarkable physical properties in metallic, semiconducting and polymeric materials¹. Small variations in growth conditions are crucial in determining anisotropy. Some chemically anisotropic rods have activated ends which can direct further chemistry or inter-particle interaction¹. Gold nanorods are such example of NPs where shape anisotropy gives rise to unique optical properties². Gold spheres have single localised SPR but two different axes of gold rod give two distinct SPR. Hence different shapes of gold like stars, flower, wires, triangles, pyramid have lots of applications in sensing³, imaging, and photothermal therapy⁴. This may apply to core-shell particles also.

1.2) Core-Shell Nanoparticles⁵

The core can be just a particle, few 100s nm thick or it can be a core with 1-10 nm thick. When thin layer or nanoparticles are coated on such particles or templates, they are called ‘Core-Shell Nanoparticles’. Some varieties of core-shell NPs are shown below. The properties of the Core-Shell Nanoparticles differ from the properties of either core or shell material. These properties depend frequently on the core to shell ratio.

Core-shell materials can be synthesised with all kind of materials viz. metal, semiconductor, insulator but dielectric materials like silica and polystyrene are more common. Silica cores are soluble in water and can be used in biological combinations. However, for hydrophobic applications polystyrene is preferred. Various combinations like dielectric-metal, dielectric-dielectric, semiconductor-metal, dielectric-biomolecule, semiconductor-dielectric, etc. are possible. It is possible to create novel structures having multi-shells and tuning optical properties from visible to infrared region of electromagnetic spectrum.

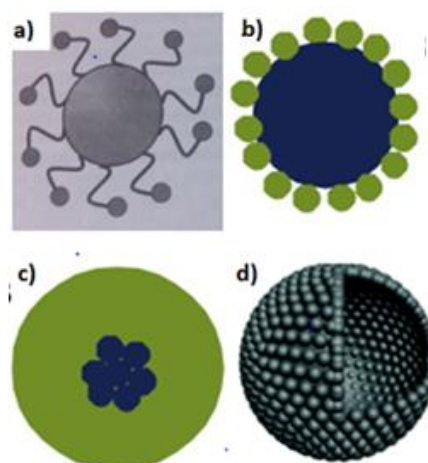
Synthesis of core-shell NPs needs highly controlled and sensitive protocol to ensure complete covering of core. Some of the methods are precipitation, polymerisation, micro-emulsion, reverse-micelle etc. These methods look simple but controlling the thickness and homogeneity of the coating is very difficult. If the reaction is not controlled properly, eventually it leads to coagulation of core particles, the formation of separate particles of shell materials or partial covering.

Varieties of core-shell particles⁵ Fig.1

a) shell NPs anchored to the core, b) smooth coating of shell on core c) Small particles encapsulated in thick core material

d) Quantum Bubble.

Image a,b,c⁶, d^[10]



1.3) Silica-Gold Core-Shell Nanoparticles

Silica is widely used material for core because of its water solubility as well as stability against coagulation. The shell can be separately grown on each particle. Also, it is chemically inert and optically transparent. Monodispersed and uniform sized Silica NPs can be synthesized with modified Stober method^{7,8}. Silica NPs coated with Cu are used for odour removal⁹.

Anisotropic gold NPs have applications in sensors, imaging, Photothermal therapy, catalysis, wave guides¹⁰ etc. Gold NPs of small size can be synthesized with Turkevich method.

One method for synthesizing Si-Au core-shell NPs is to synthesize core and shell NPs separately and then anchoring shell particles on cores. Surface modification of core can be done with a surfactant or bi-functional molecules. We used APTES (3-Aminopropyltriethoxysilane) for functionalization. This has -NH_2 group at one end and -OH group at another end. APTES forms a covalent bond with silica through -OH group while -NH_2 is available for interaction. Particles having an affinity for nitrogen can be attached to silica core through -NH_2 .

1.4) Ammonia gas detection

Ammonia is an important component in life formation. It plays important role in many biological and physiological processes. Ammonia is widely used in fertilizer, pharmaceuticals, refrigeration, textiles, cleaning and food packaging industry. It is a precursor of many nitrogenous compounds. Its leakage is a serious hazard. It is also released into the atmosphere by natural processes. It is inflammable and has an irritating smell. Its inhalation may lead to respiratory problems and if present in high concentration it may cause blindness and death is also possible. Hence its leakage detection is necessary.

Various types of ammonia sensors are like metal-oxide gas sensor, catalytic ammonia detector, conducting polymer based sensor, and optical ammonia detector are available. A gas sensor must have a low response time, fast recovery, stability, and selectivity. It should be easy to use and cost of fabrication should be low as well. That's why nanoparticle doped conducting polymer are gaining popularity. Properties of these sensors can be changed by using various combination of conducting polymer and dopant nanoparticles. It is reported that various combination of nanoparticles or their composites with graphene, carbon nanotubes or polymers are used in ammonia detection. However, they have limitation like sensitivity to multiple gases, expensive etc.

In this project, we synthesized two shapes of silica nanoparticles (spherical, rod) and coated them with Au nanoparticles. Later we used these NPs as a dopant and doped two polymers, polyaniline, and polypyrrole with 10% dopant concentration by the ex-citu method. Then we made a thin film of these Nano-composites and carried out sensitivity measurement. Our objective was to make a gas sensor selective to only ammonia and which has a low response time and fast recovery.

1.5) Conducting Polymers and Gas sensing Principle

As the name suggests these are the class of polymers which conducts electricity. Initially, polymers were known to have good insulating properties; but Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa discovered high conductivity in halogen doped Polyacetylene. They received the Noble prize in Chemistry in the year 2000 for their discovery.

Polymers are a long chain of a repeated unit of the molecular structure connected through covalent bonds. They contain alternate single and double bonds. This conjugated system of the single and double bond is stabilised by resonance. However, delocalisation of electron is limited by charge interaction and steric and conformational factors. Hence polymers have poor conductivity. Charge carriers are generated upon introduction of electronic impurity. This happens through charge exchange between species and dopants. Polymers can be doped with p-type or n-type; depending upon oxidation or reduction at each monomer unit respectively. Halogens or Lewis acids are best suited for p-type doping.

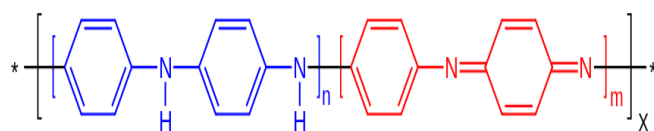


Fig.1e) Polyaniline

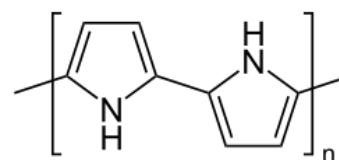
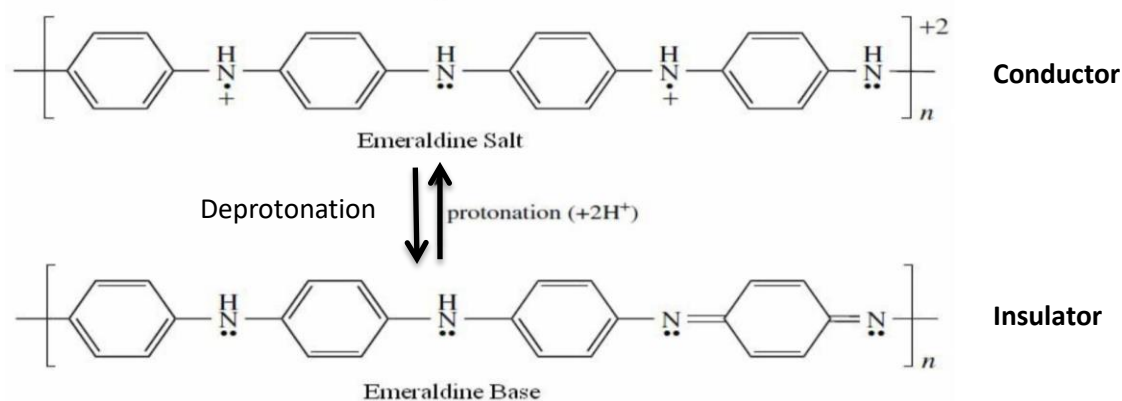
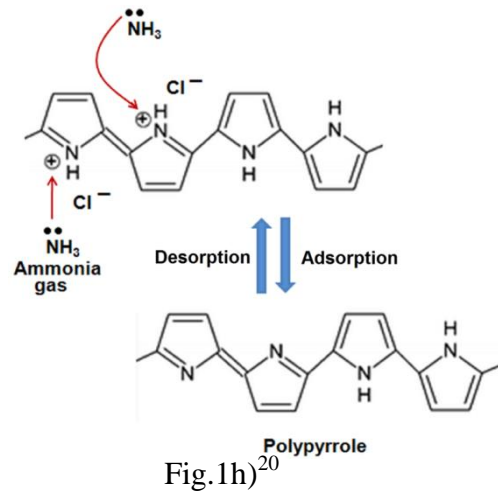
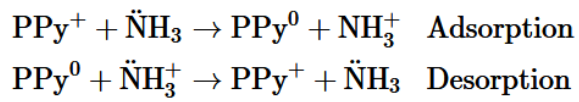


Fig.1f) Polypyrrole

Polyaniline exist in three forms: i) completely reduced ($n=1, m=0$) ii) fully oxidied ($n=0, m=1$) iii) Neutral ($n=m=0.5$): This form is called emeraldine base and if doped (protonated) called emeraldine salt, which has high electrical conductivity. This has dark green colour and will be used in ammonia gas sensor. In presence of electron donor ammonia gas PANI undergoes deprotonation. This causes de-doping which results in an increase in resistance. This process is reversible however, the degree of reversibility depends on charge exchange in conjugated chain and stability of the PANI-NH₃ complex.



Ammonia sensing by Polypyrrole (PPy) follows the same principle as PANI follows. Same is illustrated in the following figure



Our aim is to manipulate electronic properties of these two conducting polymer by doping with Core-shell nanoparticles of Silica-Gold with different morphologies and to get a material for ammonia gas sensing.

Chapter 2: Experimental Techniques

In this chapter, we discuss the synthesis of two different morphologies of Silica Nanoparticle i.e. Spherical shaped and Matchstick type rod, functionalization and gold coating of nanoparticles.

2.1) Synthesis of Silica Nanoparticles

Materials

- Absolute ethanol, Tetraethyl Orthosilicate(Sigma-Aldrich), Liquor Ammonia(25% NH₃, Fisher Scientific), Milli-Q Water
- Polyvinyl pyrrolidone(MW:28-34K g/mol, HPLC), 1-Pentanol, Trisodium citrate dihydrate(Alfa Aesar)

Procedure

Spherical Silica Nanoparticles

Spherical Silica NPs were synthesized using modified Stober method. To get monodispersed and uniform size some modifications were done. In a typical synthesis, 2.4ml ammonium hydroxide and 1.13ml Milli-Q water were added to 10ml Absolute Ethanol. Another solution is prepared by adding 0.75ml TEOS to 15ml ethanol. Both solutions were sonicated for 10 minutes and mixed together in a beaker under vigorous (900 rpm) stirring and continued stirring (300rpm) for 3 hours. The mixture will change from colorless to the white turbid solution. This mixture is centrifuged at 2000 rpm for 10 minutes, washed with water and ethanol, dried in vacuum and powder is collected. Yield will be around 250 mg.

Matchstick Shaped Silica Nanoparticles

Rodlike Silica NPs were reported previously by Kuijik¹¹. By using the PVP of different molecular weight and a varying amount of water added, new shape i.e. Matchstick shaped silica NPs were synthesized. First 1g PVP (MW=34k) was dissolved in 10ml 1-pentanol, by sonicating for 2 hours. When all PVP has been dissolved 1ml absolute ethanol, 450ul Milli-Q water and 0.1ml of 0.18M Trisodium citrate dihydrate in water was added and shaken hard to mix the content. Now, 0.2ml Liquor ammonia is added to the mixture, shaken again and 0.1ml TEOS is added. Above mixture is shaken hard, sonicated for 5 minutes and kept at rest for 12 hrs at room temperature. The mixture is centrifuged at 3500rpm for 1 hr. The supernatant was removed and washed with water and ethanol at 3500rpm for 15 minutes. Drying was carried out in vacuum and powder was collected. The yield was around 30mg.

2.2) Synthesis of Core-Shell (SiO₂@Au) Nanoparticles

General procedure involves the synthesis of gold colloids, functionalization of silica NPs with –NH₂ group and attachment of gold to functionalised silica.

2.2.1) Functionalization of nanoparticles

Different methods are discussed in the literature ref.^{12, 13, 14} were tried for functionalization; but functionalization using APTES was found to be more effective, less time consuming and gives similar results. For functionalizing both spherical NPs and Matchstick like NPs same procedure is used.

Materials

- (3-Aminopropyl)triethoxysilane(APTES, Sigma-Aldrich), Ammonium Hydroxide(10% v/v, Alfa-Aesar), Absolute ethanol

Procedure

90 mg Silica NPs are dispersed in 5ml Ethanol by sonication for 15 minutes. This mixture is transferred to a beaker while stirring at 600rpm, 260ul water, 280ul NH₄OH and 30ul APTES was added. Stirring was continued for 2 h at room temperature and 1.5 h at 70⁰ C. Centrifuge mixture on cooling and repeat the procedure one more time. Drying was carried out under vacuum.

2.2.2) Synthesis of Gold Seeds

Turkevich method^{15, 16} was used for the synthesis of gold NPs. A wide range of sizes, from 9 nm to 220 nm can be synthesized by varying concentration of Sodium citrate. We used smallest achieved sized NPs for coating Silica NPs.

Materials

- Gold(III) chloride hydrate(99% trace metal basis, Aldrich), Trisodium citrate dihydrate (Alfa-Aesar)

Procedure

50 ml Milli-Q water was boiled to 80⁰ C in a beaker under magnetic stirring. Now aqueous solution containing 0.0195 g of H₂AuCl₄.xH₂O was added to boiling water. After 5 minutes, 0.5 ml of 0.3M Na citrate was added under vigorous stirring. The yellowish solution immediately turns colorless. In few minutes, the solution turns dark blue to violet. Stirring is continued for 8 minutes and left undisturbed to cool at room temperature. This yields NPs of size around 10-15 nm.

2.2.3) Coating Gold NPs on Silica Nanoparticles

For coating gold NPs on silica nanoparticles molar ratio Au:SiO₂ equals to 2.5 was used. Same procedure is used for coating gold NPs on both Spherical and Matchstick like silica NPs.

Materials

- -NH₂ functionalised silica, 12 nm sized Gold colloids

Procedure

First powdered silica NPs were dispersed in ethanol by sonication for 30 minutes. If silica is coagulated only outer layer will get coated. 20 μmoles of silica nanoparticles were added to 50 ml gold colloid solution (50 μmoles) under vigorous stirring (900 rpm) and stirred for 3 h. Violet color of gold NPs solution changes to dark blue on attachment to Silica. The mixture was kept at rest overnight and centrifuged at 3500 rpm for 1 h.

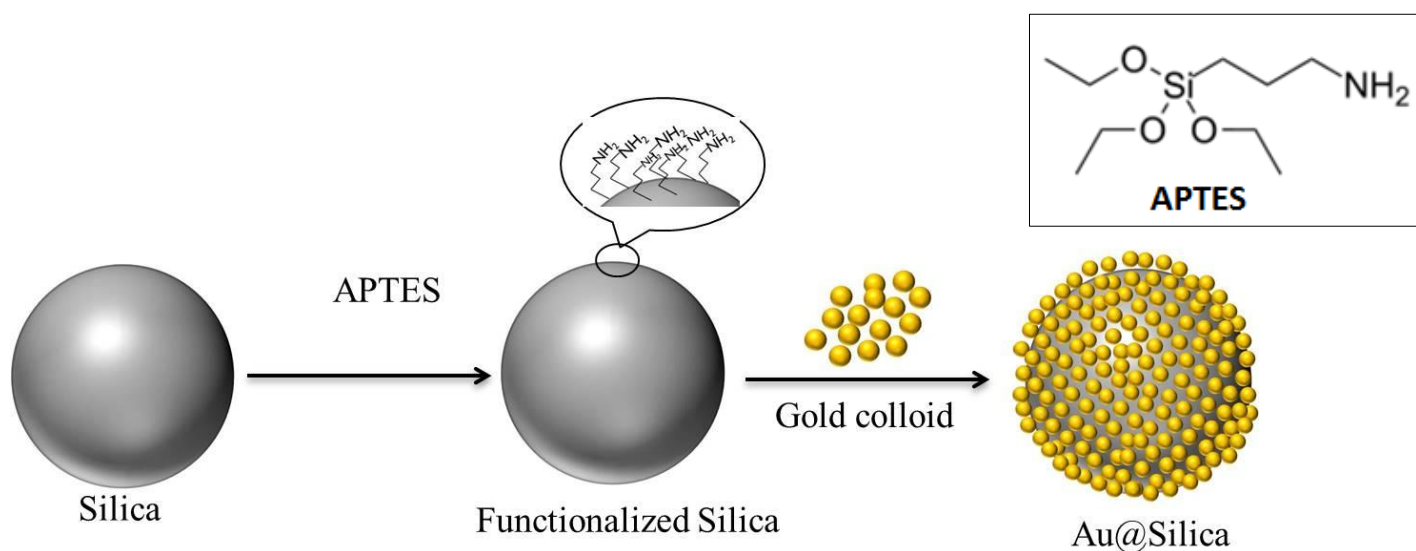


Figure 1 Schematic for the synthesis of SiO₂-Au core-shell NP^[12]

Synthesis of core-shell NPs requires highly controlled and sensitive synthesis protocol to ensure complete covering of core. Methods of synthesis appear simple but it is difficult to control the thickness and homogeneity of the coating. If the reaction is not controlled properly, eventually it leads to aggregation of core particles, the formation of separate particles of shell materials or incomplete coverage

2.3) Synthesis of Conducting Polymer

2.3.1) Synthesis of Polyaniline

Materials

- Ammonium persulphate, 1M HCl, Aniline

Procedure

For the synthesis of polyaniline Ammonium persulphate(122.36mg) was dissolved in 2.13ml of 1M HCl precooled at 1⁰C. Next Aniline (212.8μl) is dissolved in 3.2ml of 1M HCl which has been precooled to 1⁰C. The above solutions were kept in an ice bath with continuous stirring. Ammonium persulphate solution was added to aniline solution with constant stirring over a period of 5 minutes. Above solution is kept in ice bath having a temperature below 5⁰C with stirring for 1.5 hours. Next, the mixture is centrifuged at 600rpm for 20 minutes and the product is dried at 50⁰C. The yield obtained is 45mg.

2.3.2) Synthesis of Polypyrrole

Procedure

Pyrrole monomer (0.02M) was added drop-wise to aqueous solution of FeCl₃ (0.06M). The solution was stirred for 3 hrs. It was then washed with water and ethanol to remove traces of unreacted pyrrole. Then the precipitate was dried in vacuum at 50⁰C for 1 hour.

2.4) Synthesis of Nano-composite

Nanocomposites were synthesised by an ex-citu method with 10% (w/w) doping. Hence 45 mg of polymer was dissolved in 5 ml ethanol and 5 mg Au-SiO₂ core-shell NPs were dispersed in 5 ml ethanol. These two mixtures were mixed together and sonicated for 15 minutes. Later the mixture is centrifuged at 6000rpm for 8 minutes and the precipitate was dried in vacuum at 50⁰C for 4 hours.

2.4.1) Preparation of Thin Film

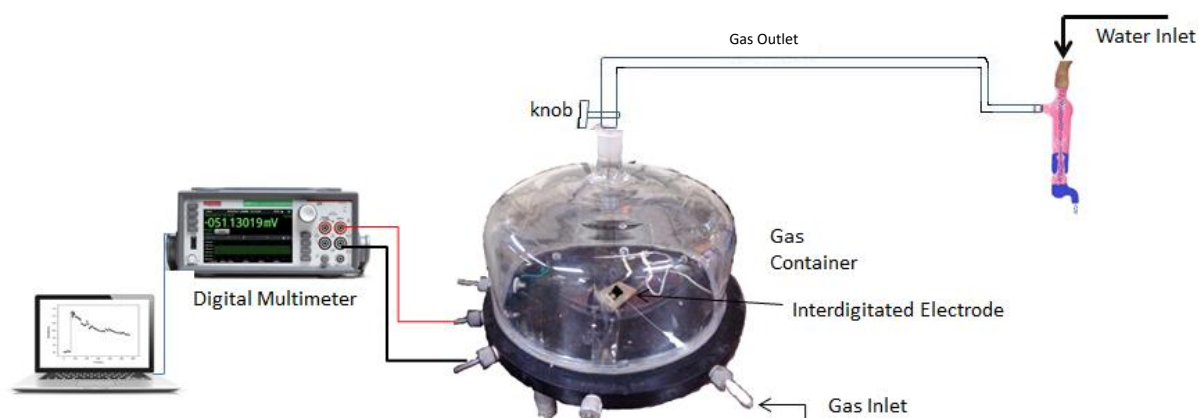
Thin film for gas sensing is prepared by drop casting method. So take 5 mg of sample in a crucible, add 2-3 drops of Ethanol and grind it for 3-4 minutes to make a fine slurry. With the help of micro-pipette spread the slurry uniformly on IDE (Interdigitated electrode). Add more ethanol if slurry gets dried. Sintering is done at 120⁰ C for 30 minutes. Collect an excess sample from the crucible.

2.5) Ammonia Sensing Technique:

Gas sensing characteristics of Au-SiO₂ core shell NPs + conducting polymer thin film were measured in a static system. The setup consists an airtight glass dome with multiple outlets to connect IDE to Keithly multimeter, to connect heater, thermocouple and to inject and to remove gas. Gas was injected using a syringe though a thin metallic pipe connected to the base of the dome. Target gas was taken from a bottle of aqueous ammonia in ml (in gaseous form) and converted to ppm using vapour pressure calculations and volume of glass chamber. The gas is removed from the chamber using hydraulic suction. Hydraulic suction ensures the removal of gas and does not disturb the interaction between thin film and gas molecule. A thin film of nanop-composite was made on 10mm*10mm aluminium interdigitated electrode. Copper contacts were used.

The electrical resistance of the thin film sensors in the air (R_a) and in the presence of gas (R_g) was measured with respect to time to evaluate the gas response (S). The gas response (S) is calculated using the following equation¹⁸:

$$S = \frac{R_g - R_a}{R_a} \times 100 \%$$



Experimental Setup for ammonia gas detection

Chapter 3: Characterisation of material

3.1) FESEM and EDAX Results

To confirm the morphologies and composition scanning electron microscopy and EDAX were done. The sample was prepared by drop casting highly dispersed silica in ethanol, on ultrasonically cleaned silica wafers. The almost transparent solution was used for drop casting.

Fig.3a) Spherical silica Nanoparticles

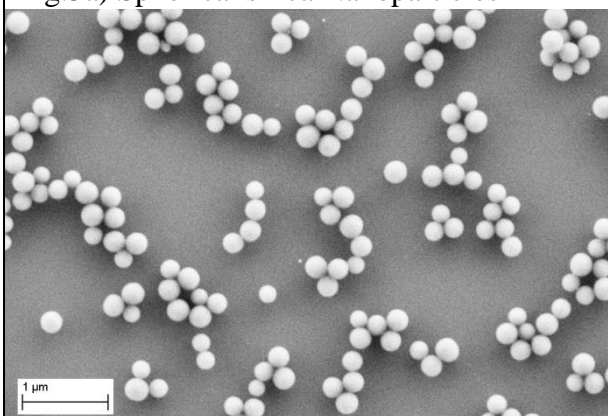


Fig.3c) Gold coated Spherical silica NPs

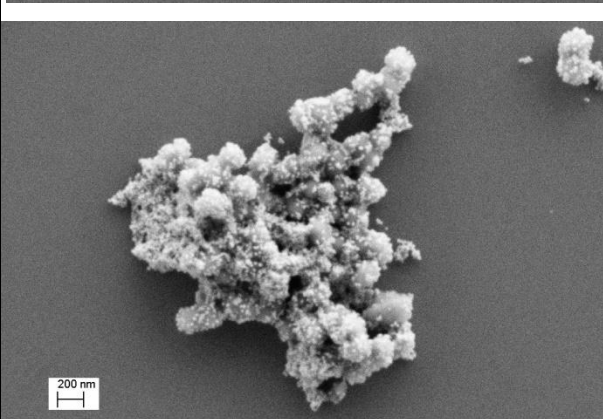
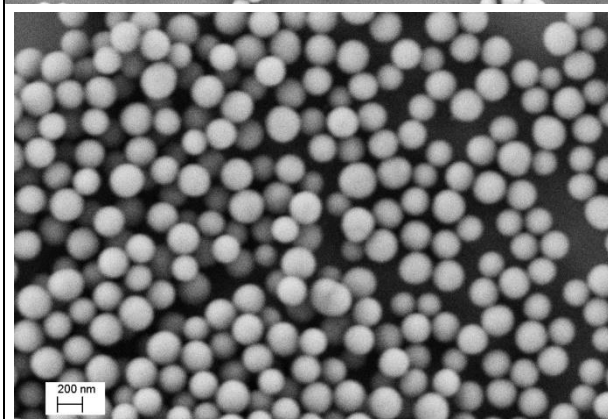
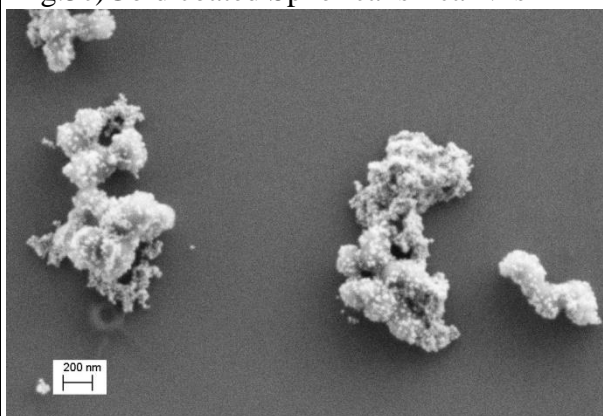


Fig.3b)EDAX of Spherical Silica NPs

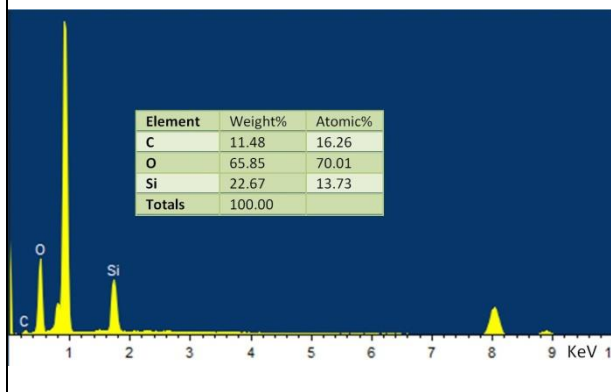


Fig.3d)EDAX of Spherical Au@Silica

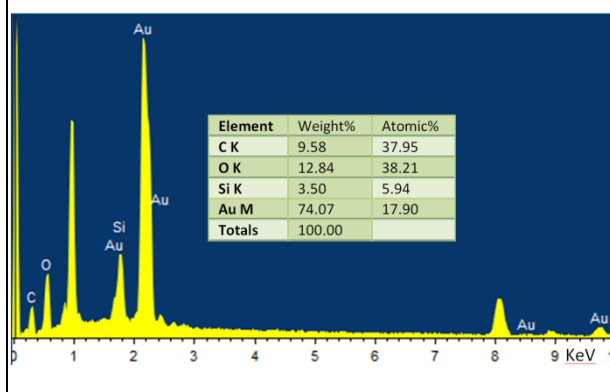


Fig.(3a) is SEM image of spherical silica NPs. It is found that highly monodispersed and particles of uniform size around 200nm were synthesized. In fig.3c) it is observed that most surface of silica spheres is coated with gold NPs.

Doing EDAX on silica wafers is not good idea because; rays from the wafer may get added to silica composition. So we used copper substrate to get EDAX spectrum. Fig.3b),3d) shows the composition of spherical silica and gold coated silica NPs. 17.9 atomic % of gold is observed on silica spheres.

Fig.3e) Matchstick like Silica NPs

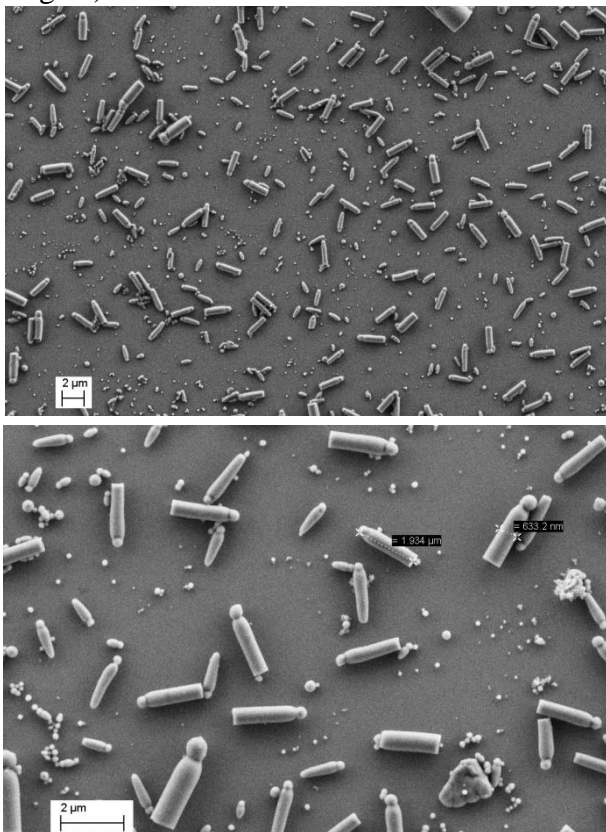


Fig.3g) Gold coated matchstick like silica

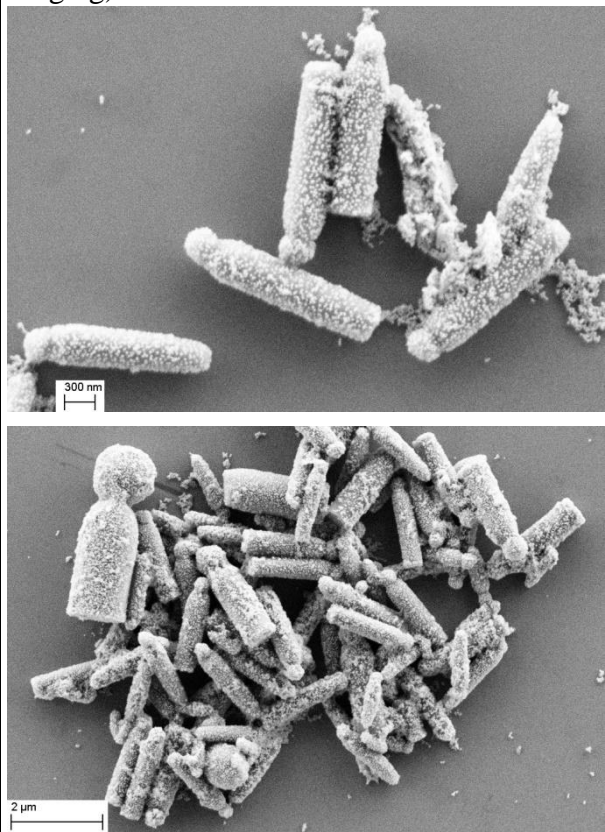


Fig.3f) EDAX of M-type Silica Rod

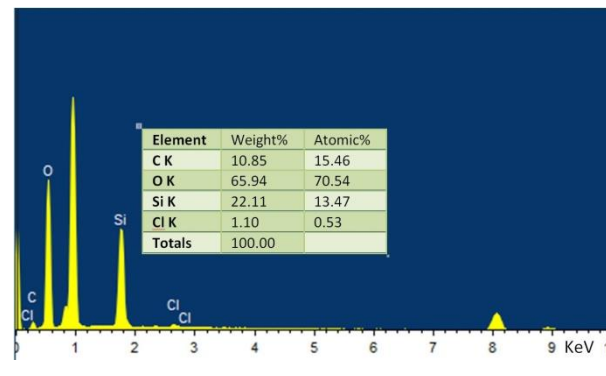
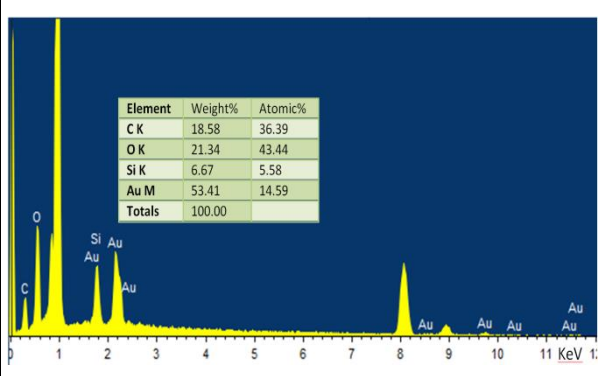


Fig.3h) EDAX of Au@M-type Silica Rod



Through SEM result matchstick like silica rods was confirmed (fig3e). It has a cylindrical base and a spherical particle attached at one end. It has a length around 2 μ m and cross section around 300nm. Most of the NPs had uniform size but few NPs of smaller size and oval shape were observed. EDAX (fig.3f) confirms the composition as 13.47 atomic % of silicon and 70.54 atomic% of oxygen. Silicon to oxygen ratio is 0.19 which almost equal to that of spherical silica which is 0.20.

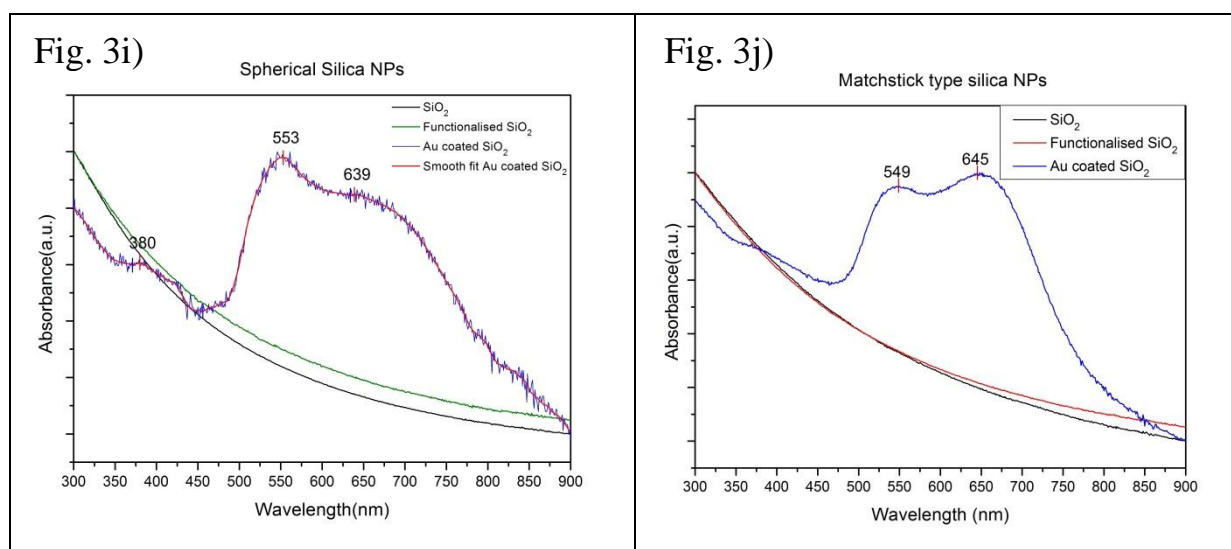
Morphology of gold coated matchstick like silica NPs are shown in (fig.3g). It can be clearly seen than gold particle has been attached to $-NH_2$ functionalised silica NPs. A complete shell is not formed as we were expecting but most of the surface is covered with gold NPs. EDAX result (fig.3h) shows 14.59 atomic% of gold. In both cases we didn't find spectrum for nitrogen; which suggest that all of the $-NH_2$ functionlised end had gold colloid attached to it.

3.2) UV-Vis Analysis

UV-Vis spectra for all samples are obtained by dispersing powdered samples in water. Very dilute solutions were used. In both type silica NPs (spherical and matchstick like) no peaks were found. The absorbance of functionalised silica followed the same trend; but for gold coated silica two peaks were observed, which indicates that silica NPs are coated with gold.

In case of Au coated Spherical silica peaks at 553nm and 639nm corresponds transverse and longitudinal Plasmon resonance of gold respectively. The intensity of transverse peak is more than that of longitudinal which implies that most of NPs are spherical but some can be slightly elongated or oval shaped. The third peak at 380nm can be due to silver impurity.

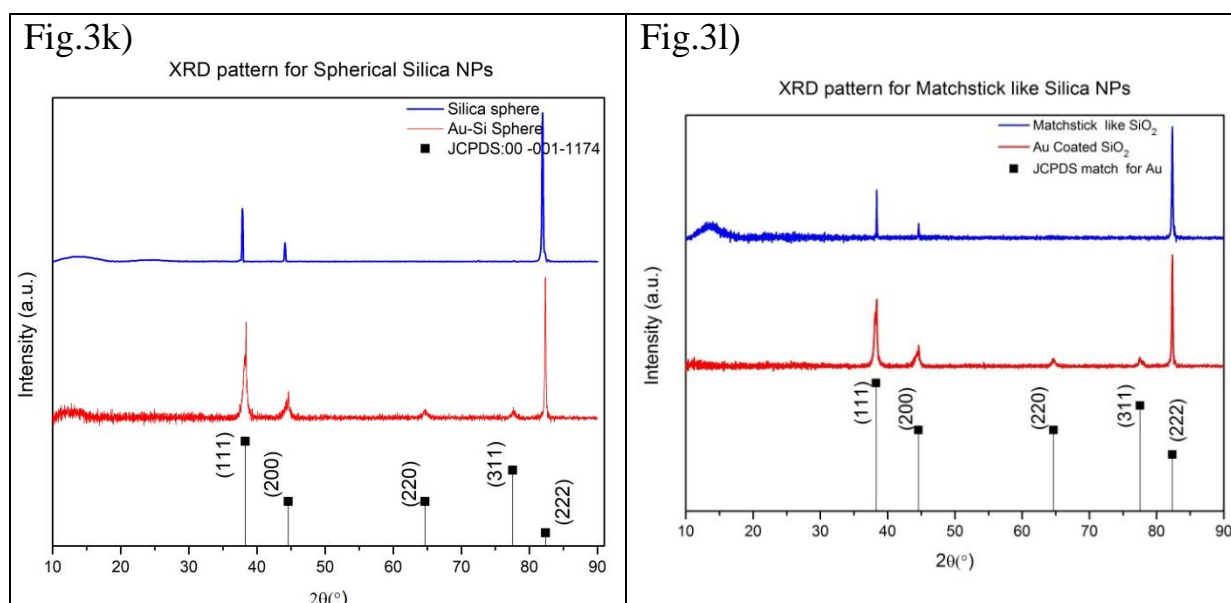
In case of Au coated matchstick like silica NPs two peaks at 549 nm and 645nm were observed. This is typical spectra for rod shaped NPs. The intensity of the longitudinal peak at 645nm is more than the transverse peak at 549 nm.



3.3) XRD Analysis

Samples were prepared on a glass slide by drop casting samples dispersed in water and dried under vacuum. Silica NPs are amorphous in nature. So there should not be any peak in XRD pattern. In XRD pattern obtained for spherical silica NPs two sharp peaks, one at 2θ equals to 38.3° and other at 82.3° were observed. These peaks correspond to gold impurities. However, EDAX has not confirmed the presence of gold; so these impurities are assumed to be very small in amount. Same is the case with matchstick like silica NPs.

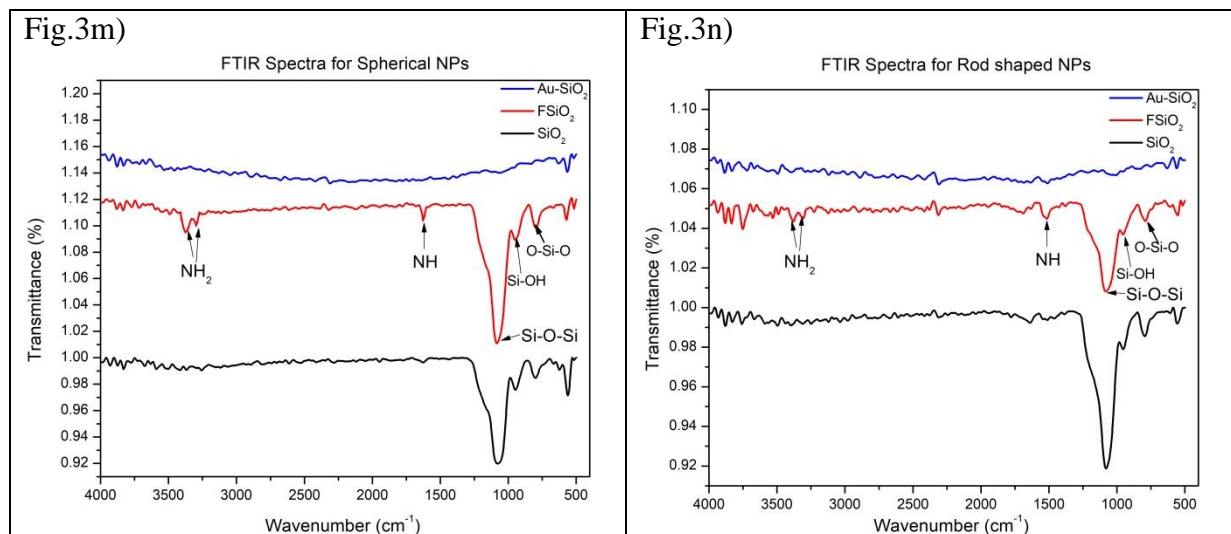
On Au coating silica get covered with gold and peaks for FCC gold were obtained (JCPDS No: 00-001-1174). Peaks and corresponding plane are shown below.



3.4) FTIR Spectra

FTIR spectral analysis was done to verify functionalization of Silica NPs. We recorded FTIR spectra of Silica NPs, $-\text{NH}_2$ functionalized Silica NPs and Au-coated Core shell NPs for both spherical and matchstick-like Rod shaped NPs. Both spectra are moreover same as material and methodology of functionalization and Au coating is same. Silica NPs shows peaks at 1082 cm^{-1} , 947 cm^{-1} , 747 cm^{-1} which correspond to Si-O-Si asymmetric stretch, Si-OH asymmetric stretch and bending, O-Si-O stretch respectively¹⁹. In case of functionalised Silica 3 additional peaks were observed. Peaks at 3370 cm^{-1} , 3290 cm^{-1} belong to asymmetric, symmetric stretch of $-\text{NH}_2$ respectively. These two peaks correspond to a primary amine. The third peak at 1626 cm^{-1} belongs to asymmetric deformation of the amino group. Hence functionalization by $-\text{NH}_2$ group using APTES was confirmed.

On coating these functionalised NPs with Au NPs all peaks disappear. This indicates that Silica NPs were coated with Au NPs.



Summary

SEM images confirm formation as well as a gold coating on silica sphere and matchstick like rod. EDAX analysis shows elemental composition. UV-Vis spectra give one intense transverse peak and one comparatively low intense longitudinal peak for gold coated silica spheres. In case of matchstick like gold coated silica two peaks with longitudinal more intense than transverse. XRD confirms amorphous nature of silica and shows five sharp peaks for gold coated silica. FTIR confirms functionalization of Silica NPs with -NH₂ and also the formation of an anchored shell around Silica NPs.

Chapter 4: Results and Discussion

4.1) Results

By using a combination of two polymers (Polyaniline, Polypyrrole) and two morphologies (Sphere, Matchstick shaped rod) of Au-coated silica particles we got four materials for sensing purposes. First of all, we checked the sensitivity of PANI and its Nano-composite for four gases, namely Ethanol, Acetone, NO_x and NH₃ gas at Room temperature. Out of these four materials, no one shows sensitivity for Ethanol, Acetone, NO_x. This can conclude from Fig.4a-4f. Here sensitivity is checked in terms of resistivity for 100ppm of gas. For comparison purposes, we readjusted time scale such that gas is injected at 60 seconds. This is true for Fig.4g and 4i) as well. Now we will focus on ammonia case.

We checked if Au coated silica NPs have any sensitivity or not. Au@SiO₂ sphere (Fig.4a) shows increase in resistance when ammonia gas is inserted. Response and sensitivity is good but resistance curve get steady after few minutes. It does not drop to initial; indicating that it lacks recovery. Reverse case is observed in case of Au@SiO₂ Rod (Fig.4b). Here resistance decreases when in contact with ammonia; but again resistance get steady. These both materials cannot be considered good for sensor as they have very low resistance (3Ω) and there is less scope of its increasing or decreasing, also they do not get recovered quickly and completely.

PANI sample (Fig.4c) shows sensitivity for ammonia. Resistance increases significantly when ammonia (100ppm) is injected, but it does not lower down when gas is removed. That means PANI shows sensitivity for ammonia gas, but it is irreversible. Addition of Au NPs to it does not make any difference (Fig.4e). When we add Spherical Au-coated Silica NPs (Fig.4i) sensitivity, response time and recovery improves slightly. It can be seen from Fig 4b) that even after 10 minutes only half of the materials were recovered. This recovery process slows down further. Since it lacks recovery it is not possible to use as a sensor. Nano-composite of PANI and Au-Silica rod (Fig.4g) also has recovery problem. This was even slower than that of Spherical NPs case. Now, will look at Polypyrrole (PPy) based material.

Sensitivity in terms of resistance for individual components of Composites for four gases namely Ammonia, Acetone, Ethanol, NOx

Fig.4a)

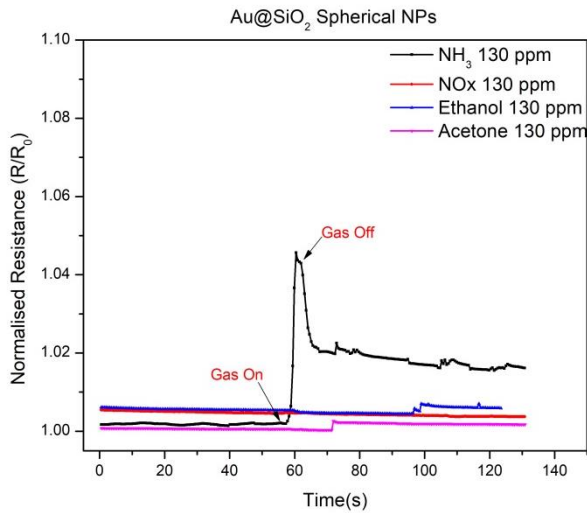


Fig.4b)

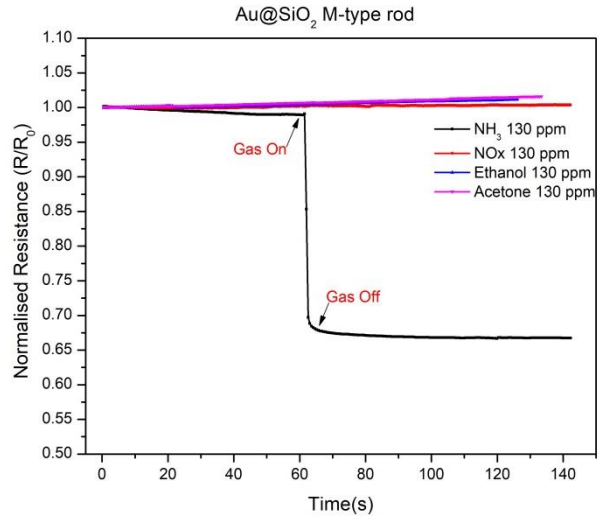


Fig.4c)

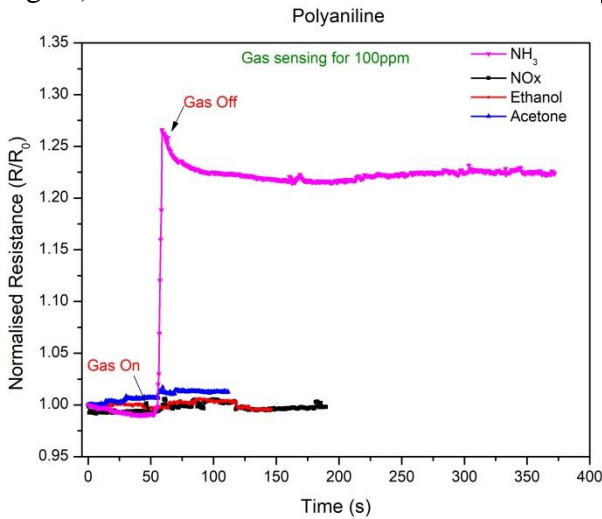


Fig.4d)

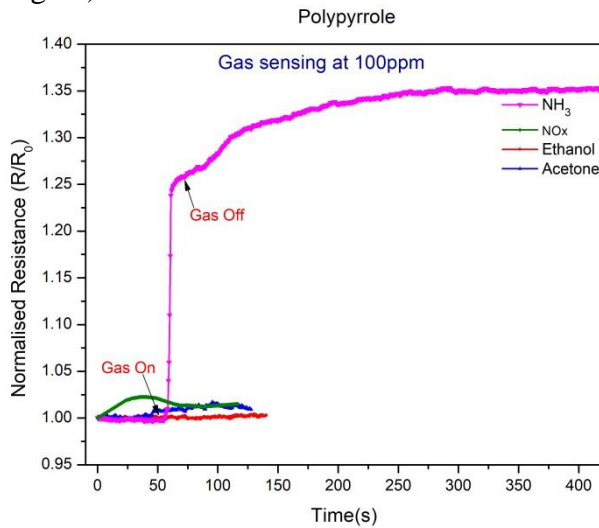


Fig.4e)

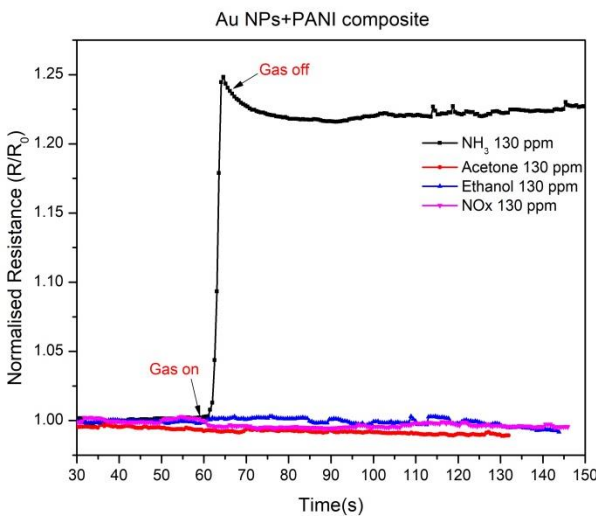
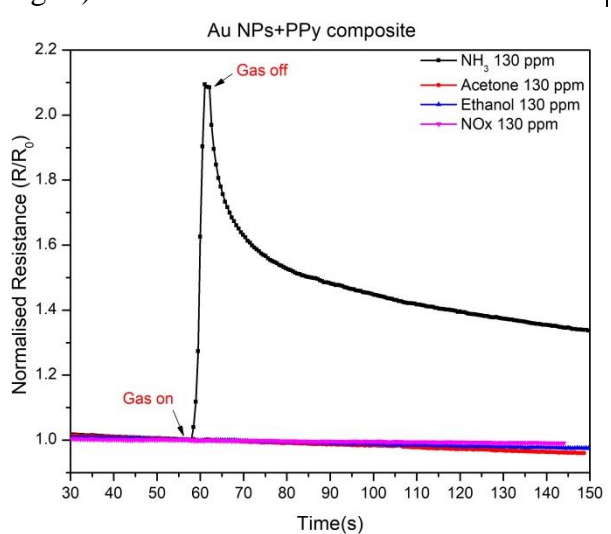


Fig.4f)



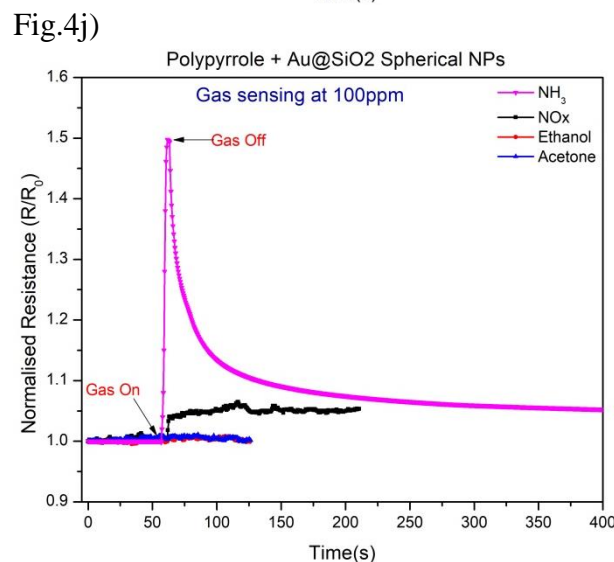
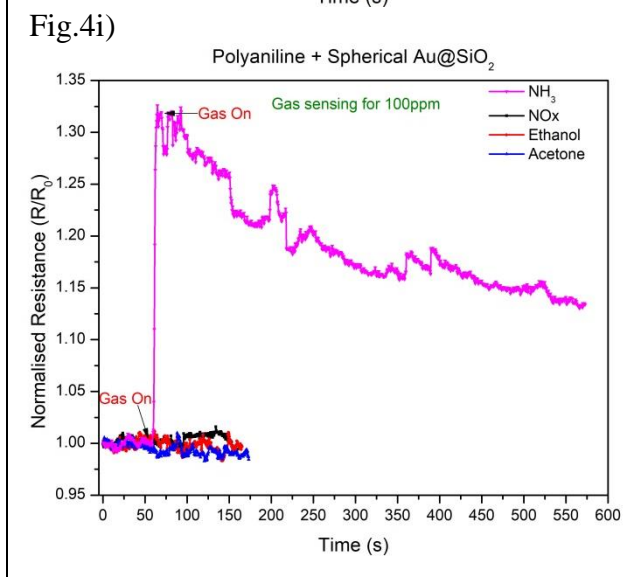
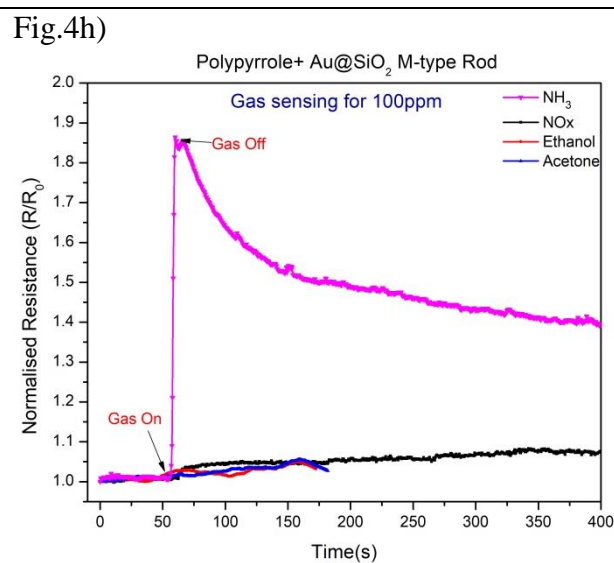
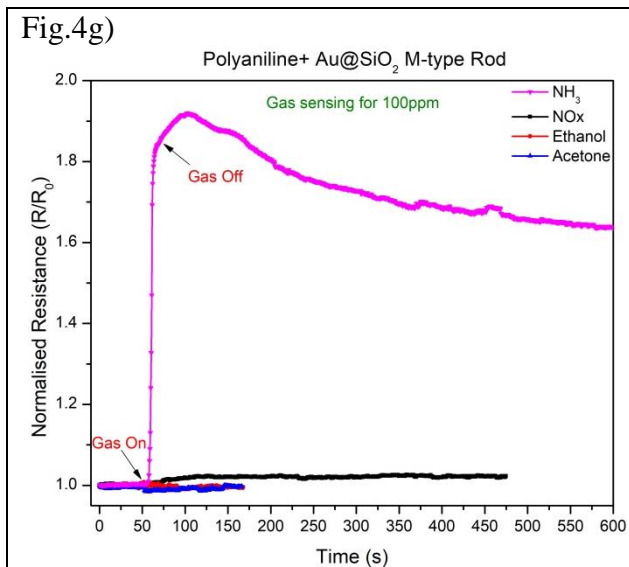


Fig.4d) for PPy sensor clearly shows response similar to PANI case. Here PPy shows a quick response to ammonia gas, resistance increase rapidly; but this too lacks in recovery. Resistance is almost constant upto 10 minutes and decreases very slowly. Even after 15 minutes, resistance has not come to the initial stage. Addition of Au NPs to polypyrrole helps in improving recovery, but only 50% recovery is achieved (Fig.4f). On adding Au-silica NPs (10%(w/w)) Fig4h), Fig.4j) PPy shows quick response and much faster recovery than any of previous cases i.e. PANI Composites. Sensitivity measurements till now were done at room temperature and for 100ppm gas. Since Composite of PPy and Au-Silica NPs, both Spherical and matchstick shaped rod were selective to only ammonia and have a quick response and fast recovery they suit as good sensing material. So, detailed measurements of these two samples are needed to check which one is best.

Fig.4k)

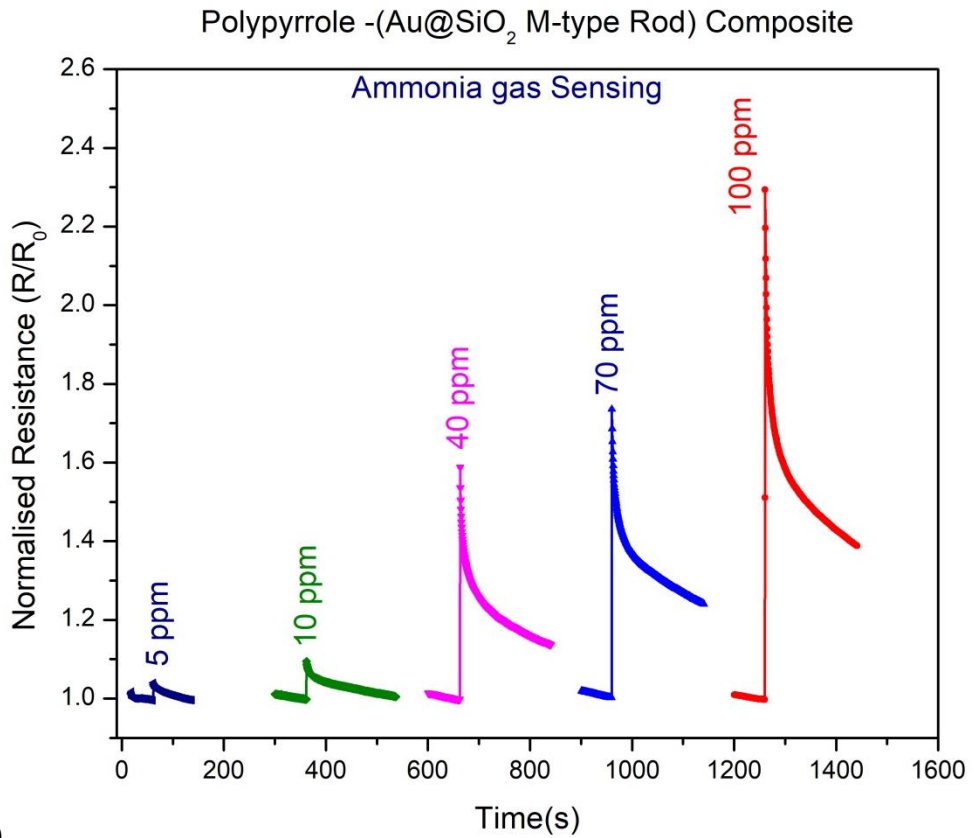
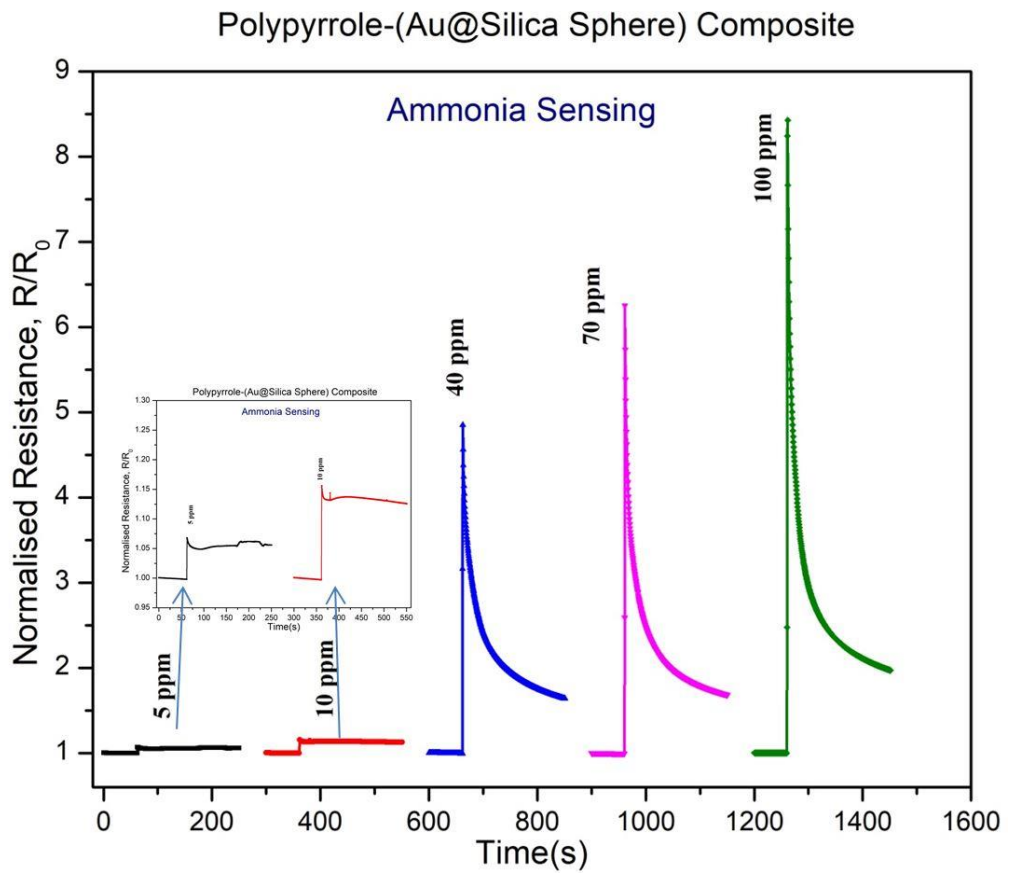
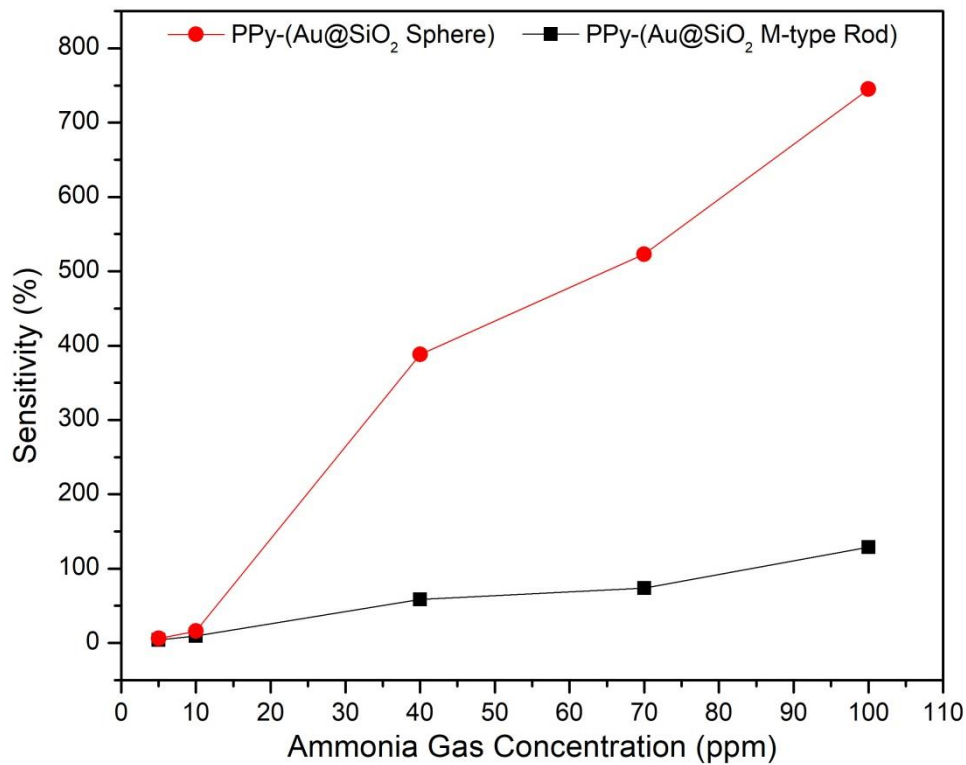


Fig.4l)



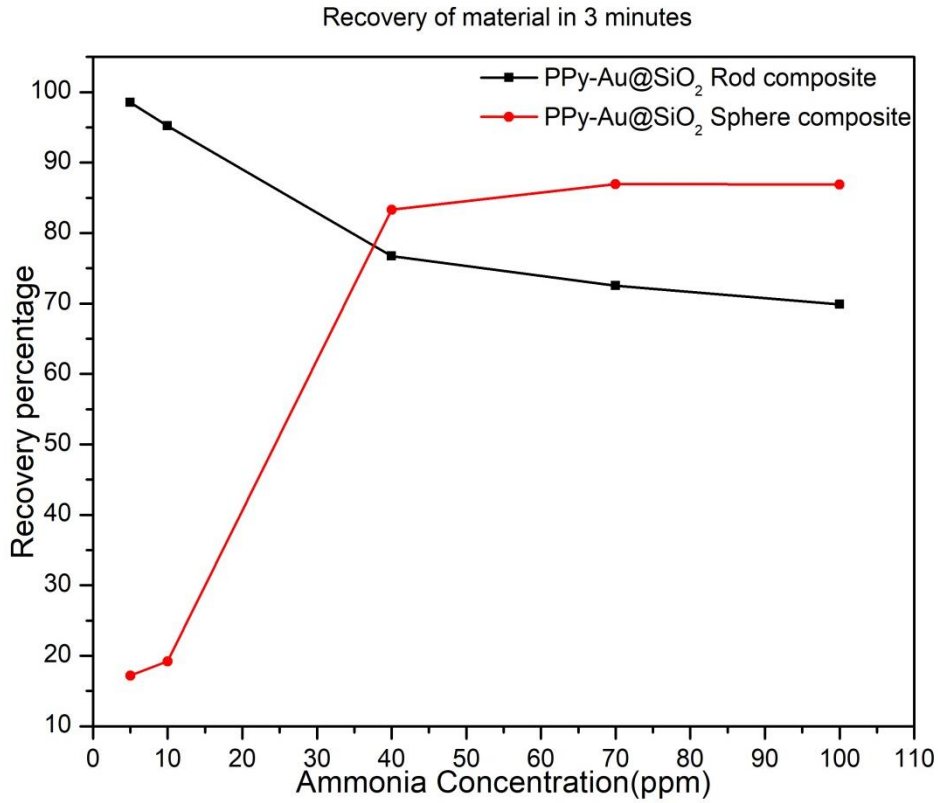
Further measurements were carried out for different concentration of ammonia i.e. 5ppm, 10ppm, 40ppm, 70ppm, 100ppm. Ammonia is injected at 60 seconds and each plot in Fig.4k) and Fig.4l) shows resistance change for 4 minutes. Both the material shows a quick response to ammonia gas. Response time in both cases is less than 10 seconds. We calculated sensitivity for these two cases and plotted w.r.t. concentration of ammonia (Fig.4m). PPy-Spherical Au-Silica composite has more sensitivity upto 740% which is much more than that of Matchstick shaped rod (140%). To check recovery of material we looked at how much material is recovered in 3 minutes when gas removal is initiated. Fig.4n) shows that at higher concentration of ammonia (>40ppm) Spherical NPs get recovered 80-85% in 3 minutes. While in case of the rod it gets recovered upto 70%. This trend is reversed for low gas concentration. For low concentration PPy-Au@SiO₂ rod composite shows faster recovery than that of PPy-Au@SiO₂ sphere composite. Both the composite have high sensitivity as well as fast recovery. But since PPy-Au@SiO₂ sphere composite have 7 times higher sensitivity than rod, we can conclude that Composite of PPy and Spherical Au@SiO₂ core-shell NPs is best suitable for ammonia gas sensing. It fulfils properties like quick response, fast recovery, reversibility, greater sensitivity and easy for fabrication and use.

Fig.4m)



In Fig.4k), Fig.4l), Fig.4n) for low concentration of ammonia i.e. 5ppm and 10ppm it looks like that rod based composite is better; but it is not so. At high concentration response is very high in case of spherical NPs; so the plot for 5ppm and 10ppm looks flat. Actually, they are not, see inlet of (Fig.4l). With respect to recovery % plot shows fast recovery at low conc. In case of the rod based composite. This can be an experimental error as injecting such low gas with a syringe may have human error.

Fig.4n)



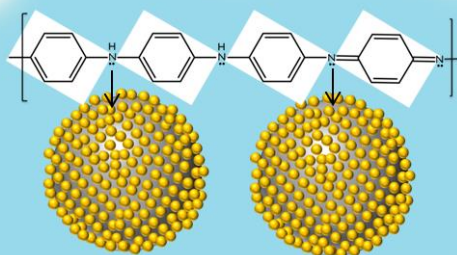
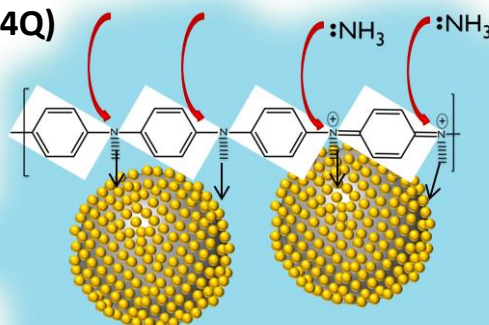
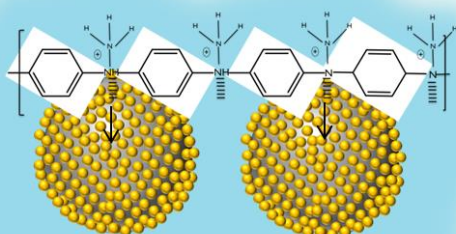
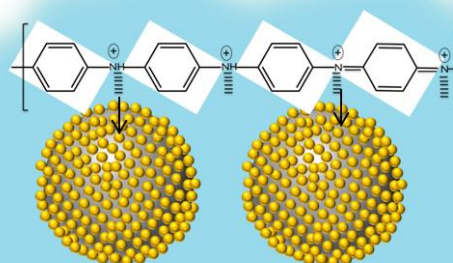
4.2) Discussions

We synthesized two morphologies of SiO₂ nanoparticles. Spherical Silica was synthesized using modified Stober's method and a new shape of silica was prepared using a method similar to Kuijik. These NPs has matchstick like shape. It has a cylindrical rod like base and spherical NP at one end. This morphology was not reported earlier. These two shapes were functionalized with -NH₂ and freshly prepared spherical Au NPs were attached to these particles. Uniform Au shell on Silica NPs has been used earlier. Our attempt was to coat SiO₂ NPs partially as depicted in Fig.1b so that these NPs would have properties of Au NPs, SiO₂ NPs, and some new properties. Hence Au coated silica has hotspot/ dot like Au NPs on the surface.

Nano-composites (NC) of these core shell NPs and conducting polymer (Polyaniline, Polypyrrole) were used as sensing material for ammonia gas. Both materials show an increase in resistance in presence of electron donating ammonia gas. It is reported that reaction between ammonia and PANI composite is reversible and hence it forms a base for so many PANI based sensor. However, reversibility depends on the method of preparation. In our case, PANI based NC shows sensitivity for ammonia but the process of decreasing resistance to initial resistance was very slow (in few hours) and also it does not get recovered fully. Whether dopant is Spherical core-shell NPs or Matchstick like rod, it makes no significant difference.

When we use NC of Polypyrrole and SiO₂ response time, as well as recovery time, improves significantly. For NC of Spherical Au-SiO₂ recovery time falls rapidly. Almost 85% of material get recovered in 3 minutes and remaining takes 10-15 minutes. As the concentration of ammonia increases, sensitivity also increases. Resistance falls rapidly to a certain level (till 80% of recovery) when gas is removed, later it slows down. Hence for ammonia concentration below 10ppm recovery time large. NC of PPy + Matchstick shaped Au-SiO₂ rod lags behind in sensing properties than that of spherical NPs; this may be due to higher surface to volume ratio of spherical NPs. Spherical NPs were 250nm in diameter while rod had a length of 1200nm and width of 240nm.

Thus Polypyrrole + Au-SiO₂ (spherical) NC is very effective for ammonia gas sensing for concentration upto 10ppm, below 10ppm recovery is a bit slow but still, it can sense effectively ammonia upto 5ppm. This NC does not show sensitivity for Ethanol, Acetone, NOx. Thus the presence of these gases does not affect/reduce the ammonia sensitivity of NC.

Fig. 4P)**Fig. 4Q)****Fig. 4R)****Fig. 4S)**

Schematic for Ammonia Gas sensing mechanism

The mechanism for ammonia sensing in PANI composite is same as mentioned by Vished^[18]. Here, a Au-N coordinate bond is formed between Nitrogen atom of PANI and Au NPs on Silica base. Thus the PANI Nitrogen atom becomes electron deficient (Fig.4P). When exposed to ammonia gas which is electron donor, Lewis acid-base binding happens between NH₃ molecules and electron deficient N of PANI (Fig.4Q). Now there is formation of transition complex PANI-NH₃ which reduce the conjugation in PANI and results in increase in resistance (Fig.4R). When gas is evacuated NH₃ gets unbounded and the material recovers (Fig.4S). Similar case is with Polypyrrole where N atom is part of the pentagonal ring. Depending upon how structure of Polymer and Au NPs present on Silica base favours formation and breaking of dative/coordinate bonds resistance/Sensitivity changes. It also depends on degree of protonation in Polymer used. We got lesser sensitivity for Spherical Au@SiO₂-Ppy composite than Rod based composite. This may be due to leaching of Au NPs from silica base.

Chapter 5: Conclusions

Two morphologies of Silica nanoparticles were successfully synthesized, functionalised and coated with gold nanoparticles. The characterisation was done using FE-SEM, EDAX, UV-Vis spectroscopy and XRD. Nano-composites of the NPs with both Polyaniline and Polypyrrole were tested for gas sensing. Out of these NC, spherical Au@SiO₂ + Polypyrrole is selective for ammonia gas and has an excellent response as well as recovery time. It achieves sensitivity up to 740% for 100ppm of gas and can sense NH₃ as low as 5ppm. This low cost material can be used in an alarm system for ammonia gas leak in industry, agriculture, or laboratory.

Bibliography

1. Burrows, N. D. et al. Anisotropic Nanoparticles, and Anisotropic Surface Chemistry. *J. Phys. Chem. Lett.* **7**, 632–641 (2016).
2. Link, S. & El-Sayed, M. A. Spectral Properties and Relaxation Dynamics of Surface Plasmon Electronic Oscillations in. *J. Phys. Chem. B* **103**, 8410–8426 (1999).
3. Chen, D. et al. Effects of morphologies on acetone-sensing properties of tungsten trioxide nanocrystals. *Sensors Actuators, B Chem.* **153**, 373–381 (2011).
4. Huang, X., El-sayed, I. H., Qian, W. & El-sayed, M. A. Cancer Cell Imaging and Photothermal Therapy in the Near-Infrared Region by Using Gold Nanorods Cancer Cell Imaging and Photothermal Therapy in the Near-Infrared Region by Using Gold Nanorods. 2115–2120 (2006). doi:10.1021/ja057254a
5. Kulkarni, S. K. *Nanotechnology : Principles and Practices.*
6. Hayes, R., Ahmed, A., Edge, T. & Zhang, H. Core-shell particles: Preparation, fundamentals, and applications in high performance liquid chromatography. *J. Chromatogr. A* **1357**, 36–52 (2014).
7. W. Stober, A. Fink, E. B. Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range I. *J. Colloid Interface Sci.* **26**, 62–69 (1968).
8. Rao, K. S., El-Hami, K., Kodaki, T., Matsushige, K. & Makino, K. A novel method for synthesis of silica nanoparticles. *J. Colloid Interface Sci.* **289**, 125–131 (2005).
9. Singh, A. et al. Copper coated silica nanoparticles for odor removal. *Langmuir* **26**, 15837–15844 (2010).
10. Li, N., Zhao, P. & Astruc, D. Anisotropic gold nanoparticles: Synthesis, properties, applications, and toxicity. *Angew. Chemie - Int. Ed.* **53**, 1756–1789 (2014).
11. Kuijk, A., Van Blaaderen, A. & Imhof, A. Synthesis of monodisperse, rodlike silica colloids with tunable aspect ratio. *J. Am. Chem. Soc.* **133**, 2346–2349 (2011).
12. Choma, J., Jamiola, D., Nyga, P. & Jaroniec, M. Synthesis of rod-like silica-gold core-shell structures. *Colloids Surfaces A Physicochem. Eng. Asp.* **393**, 37–41 (2012).
13. English, M. D. & Waclawik, E. R. A novel method for the synthesis of monodisperse gold-coated silica nanoparticles. *J. Nanoparticle Res.* **14**, (2012).
14. Saini, A. et al. Synthesis and SERS Application of SiO₂@Au Nanoparticles. *Plasmonics* **10**, 791–796 (2015).
15. Turkevich, J. & Stevenson, P. C. a Study of the Nucleation and Growth Processes IN the Synthesis of. **55**, (1951).
16. Kimling, J. et al. Turkevich Method for Gold Nanoparticle Synthesis Revisited.pdf. *J. Phys. Chem. B* **110**, 15700–15707 (2006).
17. Ahn, J. P., Kim, J. H., Park, J. K. & Huh, M. Y. Microstructure and gas-sensing properties of thick film sensor using nanophase SnO₂ powder. *Sensors Actuators, B Chem.* **99**, 18–24 (2004).
18. Kumar, V. et al. Ultrasensitive Gold Nanostar-Polyaniline Composite for Ammonia Gas Sensing. *Langmuir* **31**, 13247–13256 (2015).
19. Feifel, S. C. & Lisdat, F. Silica nanoparticles for the layer-by-layer assembly of fully electro-active cytochrome c multilayers. *J. Nanobiotechnology* **9**, 59 (2011).
20. Dilip Patil, www.chemarc.com Synthesis, Properties, Applications Of Polyaniline Especially In Surface Coatings