# 7

# *3-APTMS mediated solvent induced synthesis of gold nanoparticles*

## 7.1. INTRODUCTION

Nanoparticles have been widely used for various catalytic applications, however, due to the problem of recyclability their exploitation in suspension is limited. Besides their use is also accompanied with the problem of residual metal impurities that are left in the final products (Takale et al., 2014). Nowadays, green chemistry approach towards the use of catalyst (recyclable and reusable) is favoured more and more as it is environment friendly. Among all noble metal NPs, gold nanoparticles, have received greater attention due to their unique physicochemical features (Stratakis and Garcia, 2012; Corona and Garcia, 2008).AuNPs are immobilized onto different supports like porous solids, membranes, fibres, functionalized clay(He et al., 2014; Huang et al., 2008; Dotzauer et al., 2009; Liang et al., 2011; Dotzaeur et al., 2006; Julbe et al., 2001; Petala et al., 2013; Wu et al., 2012)and various polymers. Among polymers,siloxanes are an important class of polymers that are used extensively in cosmetics, lithographic stamps and microfluidic channels, (Abbasi et al., 2001) to make biocompatible surfaces for immobilization of antibodies(Iwasaki et al., 2008) and for fabricating superhydrophobic surfaces (Artus et al., 2006).

Accordingly, the findings on the synthesis of siloxane-AuNPs hybrid have been one of the prime attentions. Efforts have been made on these lines by Goyal et al., (2010) involving the active role of octadecylsilane to form a hybrid between AuNPs and siloxane polymer (gold core-siloxane shell). Similarly Feng et al., (2009) also reported the synthesis of AuNWs using triisopropylsilane (TIPS). It has been proved through experiments that TIPS is crucial for the formation of AuNWs. Different alkylsilanes use for the fabrication of AuNPs is due to the active participation of –Si-H linkages. However, the use of alkoxysilane which is less reactive and thus easy to handle compared to alkylsilanes have not been documented for fashioning hybrid between AuNPs and siloxane. Thus, there is a need of suitable alkoxysilanes that allow the formation of stabilized AuNPs along with siloxane polymer, and 3-APTMS appears to be a perfect choice for such synthesis as discussed below.

The use of 3-APTMS for the controlled synthesis of monometallic, bimetallic and trimetallic noble metal nanoparticles involving a variety of organic reducing agents like 3-GPTMS, THF-HPO, cyclohexanone, formaldehyde, acetaldehyde, acetone and t-DMK has been discussed in previous chapters. The choice of reducing agent is very important as it has an impact on physical properties of NPs, like dispersibility in solvents, pH- and salt-tolerance etc. Also, the imine linkage, between 3-APTMS and few carbonyl moieties, have an impact on the catalytic activity as it also acts as a catalyst. In the present chapter the synthesis of AuNPs in porous matrix both in homogenous and heterogeneous systems is sought.

Recently, in a report by Mazzei et al.,(2014) which was further revisited by Schraml et al., (2015) acetone-induced polymerization of 3-APTMS in

chloroform has been observed. Using $^{1}H$, $^{13}C$ and $^{29}Si$NMR techniques they have proved that acetone reacts with the silane amino group to form an **imine** $[(CH_3)_2C{=}N(CH_2)_3Si(OCH_3)_3]$, IPTMS or N-isopropylidene-3-aminopropyltrimethoxysilane. The water that is released during the imine formation hydrolyzes the methoxysilane inducing thereby the formation of siloxane, Si-O-Si bridges. Further, the role of some organic imine, during the synthesis of AuNPs has been documented by Wu et al., (2015).However, the role of IPTMS formed from 3-APTMS and acetone as described above has not been explored during the synthesis of AuNPs, which might be useful in forming AuNPs and siloxane polymer simultaneously given the bifunctional nature of 3-APTMS. Corroborating these findings the synthesis of spherical AuNPs utilizing the interaction between 3-APTMS and acetone has been attempted under three different conditions viz. (i) all precursors ($Au^{3+}$, 3-APTMS and acetone) mixed simultaneously, **(siloxane-$Au_{sim}$)** (ii) polymer made first followed by sequential reduction of $Au^{3+}$ in homogenous suspension,**(Au-siloxane$_{homo}$)$_{seq}$** and (iii) polymer made into thin film followed by sequential reduction of $Au^{3+}$, in the heterogenous system, **(Au-siloxane$_{hetero}$)$_{seq}$**. The same reagents in aqueous medium (water) allow the formation of AuNPs**(AuNPs)$_{water}$** however, the growth of siloxane polymer is not detected in this case.

The experiments have been performed using 1 mM $Au^{3+}$ and 12 mM 3-APTMS, and 9 M acetone in all co-solvents (except when acetone is used as single solvent). Solvent dependent morphological and catalytic behavior of the AuNPs due to the formation of porous siloxane matrix in organic solvents while the absence of the same when water is used as solvent has been observed in the present study. Also, the formation of the porous siloxane matrix prompted to

synthesize and use the polymer, made from 3-APTMS and acetone, as scaffold for the synthesis of AuNPs.

## 7.2. EXPERIMENTAL

### 7.2.1. Materials and Instrumentation

All reagents were used as received. Tetrachloroauric acid hydrate was purchased from HiMedia; 3-APTMS was obtained from Aldrich Chem. Co. All other chemicals employed were of analytical grade. Aqueous solutions were prepared by using doubly distilled-deionized water (Elga water purification system). The absorption spectra of nanoparticles were recorded using a Hitachi U-2900 spectrophotometer. Transmission electron microscopy (TEM) images were recorded using Morgagni268D (Fei Electron Optics) operating at 200 kV. Scanning Electron Microscopy (SEM) studies were performed with Kratos Analytical Instrument, Shimadzu group company, Amicus, UK. Atomic force microscope (AFM) images were recorded using Nanodrive Dimension Edge 8.06 (Build RIMN 1190880), Bruker.

### 7.2.2. Synthesis of AuNPs.

The synthesis of AuNPs was carried out in different solvents viz. Water, methanol, acetone and chloroform. In a typical process, to 1mM solution of $HAuCl_4$ in either of the solvent (water, acetone and chloroform) was added 0.5M (12µl) of 3-APTMS so that its effective concentration is 12mM. The solution is then stirred continuously for over a minute, followed by the addition of acetone as mild reducing agent. The suspension is then left undisturbed for over 6-12 h at 50ºC. The appearance of wine red color indicated the formation of AuNPs in

various solvents. Stock solution of $HAuCl_4$ and 3-APTMS were prepared in acetone.

### 7.2.3. Sequential synthesis of AuNPs

3-APTMS solution in acetone using either chloroform or acetone as solvent was stirred continuously for 6-12 h at room temperature. The colorless solution turned yellow indicating the polymer synthesis. To this medium was then added the solution of $Au^{3+}$. The sequential synthesis of AuNPs over polymer can be done in two ways (i) Liquid Phase synthesis by adding the solution of $Au^{3+}$ over polymer suspension, and (ii) Solid phase synthesis by first making a film of polymer over glass surface and then suspending it in the solution of $Au^{3+}$.

### 7.2.4. Peroxidase mimetic ability

The catalytic activity of as synthesized AuNPs in suspension was compared by monitoring the formation of oxidized product of o-dianisidine (ODA) at 430nm ($\epsilon$=11.7$mM^{-1}$ $cm^{-1}$) spectrophotometrically using Hitachi U-2900 spectrophotometer. Typically the peroxidase mimetic ability or the ability to cause oxidation of ODA in the presence of $H_2O_2$ and catalyst is measured in water at room temperature. In brief, 40µl of $H_2O_2$ (1.6M), 40µl of ODA and 30µl of AuNPs were added to 500µl of water and mixed to make it uniform. The UV-Vis spectrum of the brown colored oxidized ODA was recorded after a time interval of 30 min.

### 7.2.5. Para nitrophenol reduction

The AuNPs made using siloxane polymer scaffold over glass slides were used as catalyst to test their ability during PNP reduction. Kinetic rate measurements for the reduction of p-nitrophenol (PNP) to p-aminophenol (PAP) were performed from a solution prepared by adding 30µl of 20 mM PNP in 5ml of water. To this was then added 9mg of powder $NaBH_4$ so that its effective concentration is

0.05M. The addition of $(Au\text{-}siloxane_{hetero})_{seq}$ (glass slides) to the PNP and $NaBH_4$ initiated the process of PNP reduction. PNP decay at 400nm was recorded after the addition of AuNPs. PNP reduction with excess $NaBH_4$ follows first order kinetics and the data was analyzed according to the first order rate law. The graph between log of the absorbance at 400nm and time was plotted, the steepest part of the curve was fitted with a line, negative slope of which gave the apparent rate constant $K_{app}$.

### 7.2.6. Electrochemical measurements

Electrochemical measurements were carried out in an electrochemical cell equipped with a three electrode configuration having working volume of 3ml (0.1M phosphate buffer, pH=7 with 0.5MKCl as electrolyte) using Electrochemical Workstation Model CHI660B, CH Instruments Inc., TX, USA. Glassy Carbon Electrode (GCE) as working electrode, Ag/AgCl as reference electrode and platinum as counter electrode were used in all electrochemical measurements. Effect of scan rate on cyclic voltammogram of potassium ferricyanide was recorded and analyzed at various scan rates from 0.01 to $0.7Vs^{-1}$.

## 7.3. Results

### 7.3.1. Effect of solvent during AuNPs synthesis

3-APTMS, when mixed with acetone in aprotic solvents, forms an imine $[(CH_3)_2C{=}N(CH_2)_3Si(OCH_3)_3]$, IPTMS or N-isopropylidene-3-aminopropyltrimethoxysilane. The water molecules that are released during the imine formation hydrolyze the methoxysilane moieties of 3-APTMS, inducing the formation of siloxane, Si-O-Si bridges upon condensation (Mazzei et al., 2014; Schraml et al., 2015). In chapter fifth the role of 3-APTMS and acetone during the synthesis of AuNPs in methanolic medium has been described. The

effect of solvent during AuNPs synthesis through 3-APTMS and acetone and the formation of "siloxane–AuNPs" hybrid as a function of solvent has been discussed in the present chapter. The hybrid materials made of siloxane polymer and AuNPs is obtained in case of aprotic organic solvents like chloroform and acetone (acetone used both as solvent and mild reducing agent). On the opposite, only discrete and spherical AuNPs are obtained when using protic solvents like, water and methanol.

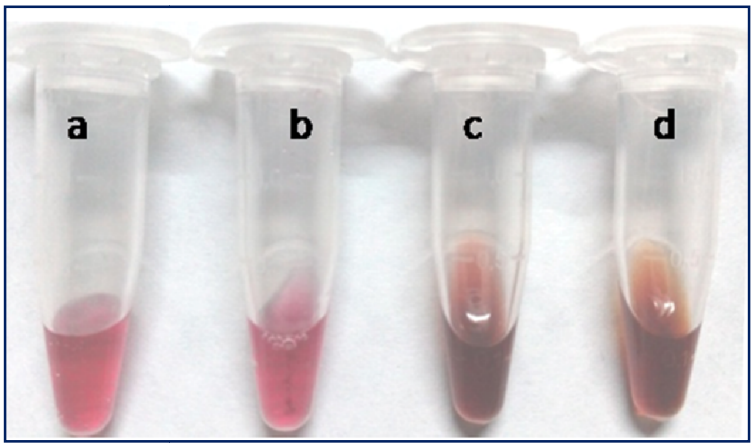



Figure 7.1. Pictorial representation of AuNPs made using 3-APTMS and acetone in (a) water, (b) methanol, (c) acetone and (d) chloroform.

### 7.3.2. Structural Characterization

The picture and corresponding UV-Vis spectra of AuNPs prepared in different solvents using 3-APTMS and acetone are given in Fig.7.1 and Fig.7.2 respectively. SEM images of the AuNPs made in water and acetone given in Fig.7.3 display the difference in structure of the two. The porous structure obtained in the case of organic solvents (chloroform and acetone), when made simultaneously, has been further validated by the SEM images given in Fig. 7.4. Wire-like structures in case of (siloxane-$Au_{sim}$) made in chloroform solvent can

be seen from AFM and SEM images as depicted in Fig.7.5. TEM images of AuNPs and "siloxane-gold" are shown in Fig. 7.6.

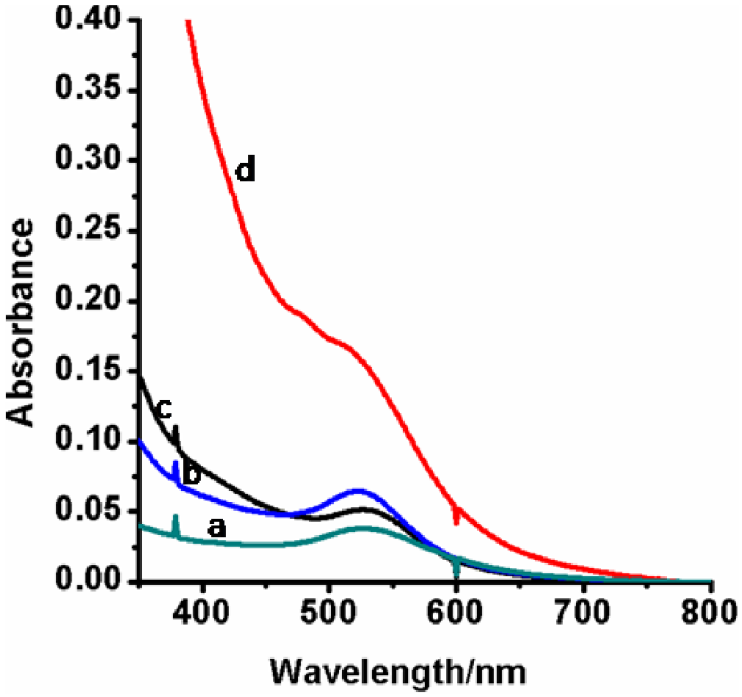



Figure 7.2. UV-Vis spectra of AuNPs made using 3-APTMS and acetone in (a) water, (b) methanol, (c) acetone and (d) chloroform.

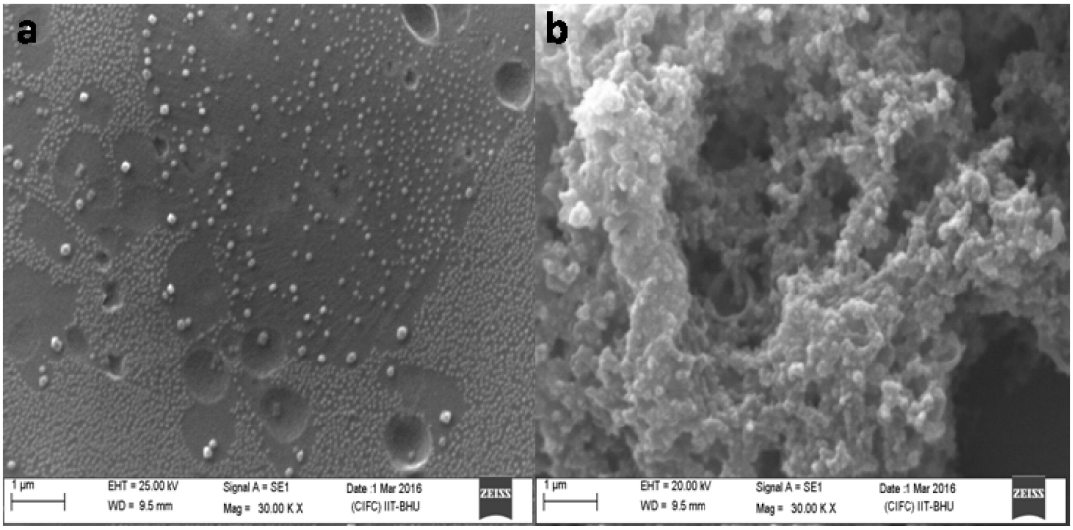



Figure 7.3. SEM images of AuNPs made in water (a) and acetone (b).

To get further insight into the hybrid structure and strengthen claim for hybrid formation HAADF-STEM-EDS elemental mapping for the constituent element was performed for the AuNPs made using 3-APTMS and acetone as shown in Fig.7.7- Fig.7.9.

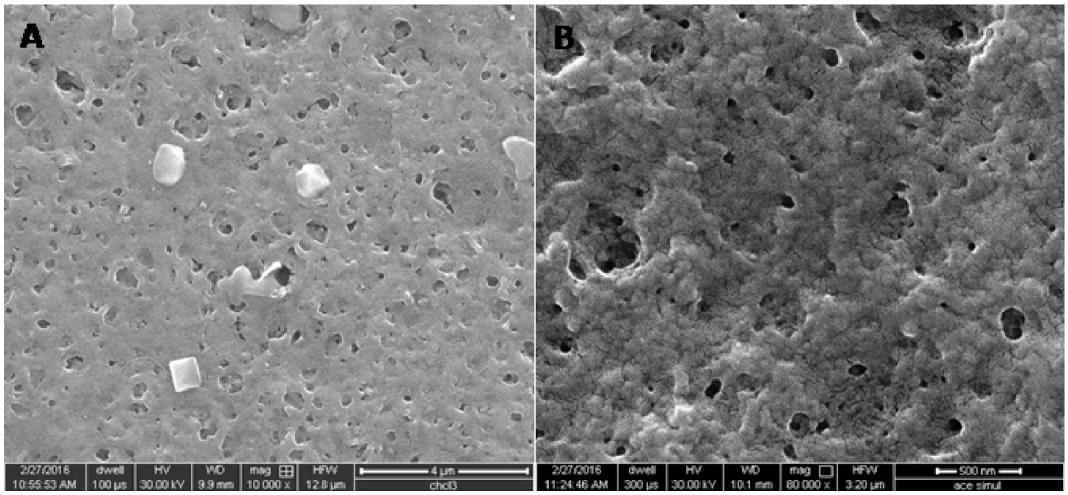



Figure 7.4. SEM images of " Siloxane-AuNPs" hybrid made using (A) chloroform and (B) acetone. The images clearly display the porosity in hybrid structures.

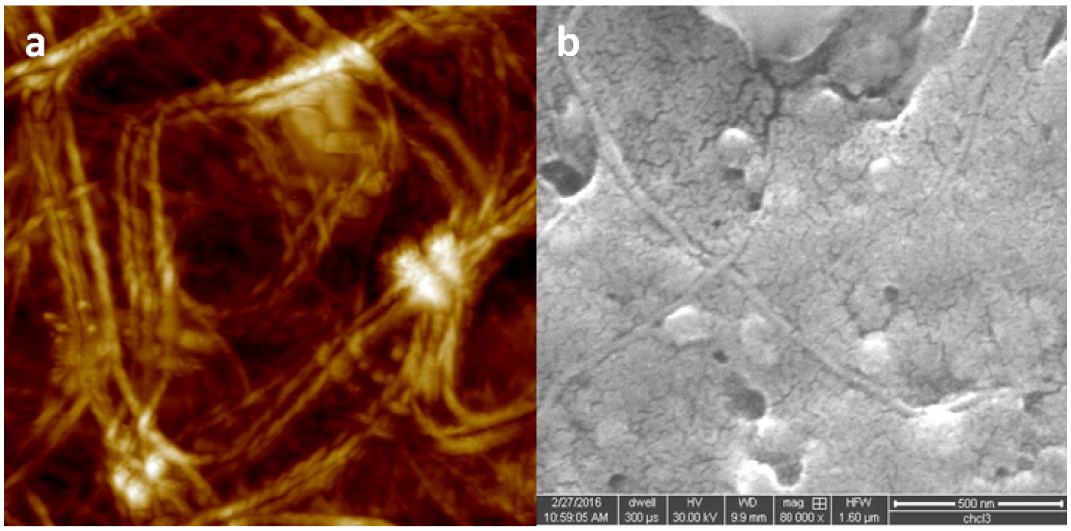



Figure 7.5 AFM (a) and SEM (b) images of AuNPs made in chloroform showing organized wire-like structures.

The present study further describes the role of siloxane polymer during AuNPs synthesis. The formation of siloxane polymer during the synthesis of AuNPs in

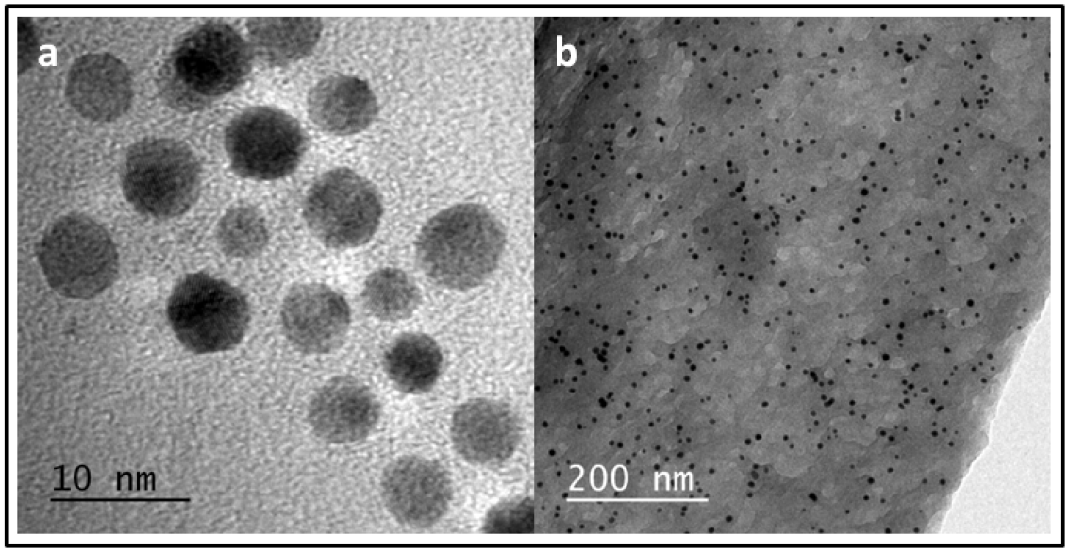



Figure 7.6. TEM images of AuNPs made in water (a) and acetone (b).

chloroform and acetone is clear from the SEM and AFM images. From the pictorial representation of AuNPs made in different solvents as shown in Fig. 7.1 a clear cut difference in the color of the AuNPs made in different solvents is visible which might be due to the polymer formed from 3-APTMS and acetone. So, the formation of polymer utilizing the same reagents was monitored in different solvents without the addition of $Au^{3+}$. Both chloroform and acetone showed yellow colored polymer solution while the same was absent in water. To this yellow colored solution was then added $Au^{3+}$solution and left undisturbed for few hours. Both chloroform and acetone resulted in a ruby red color with peak around 520nm in UV-Vis spectra indicating AuNPs synthesis. Fig. 7.10gives the UV-Vis spectra of siloxane polymer and AuNPs made over preformed polymer $(Au\text{-}siloxane_{homo})_{seq}$. As the AuNPs are made over preformed polymer sequentially in suspension it is labelled as $(Au\text{-}siloxane_{homo})_{seq}$.

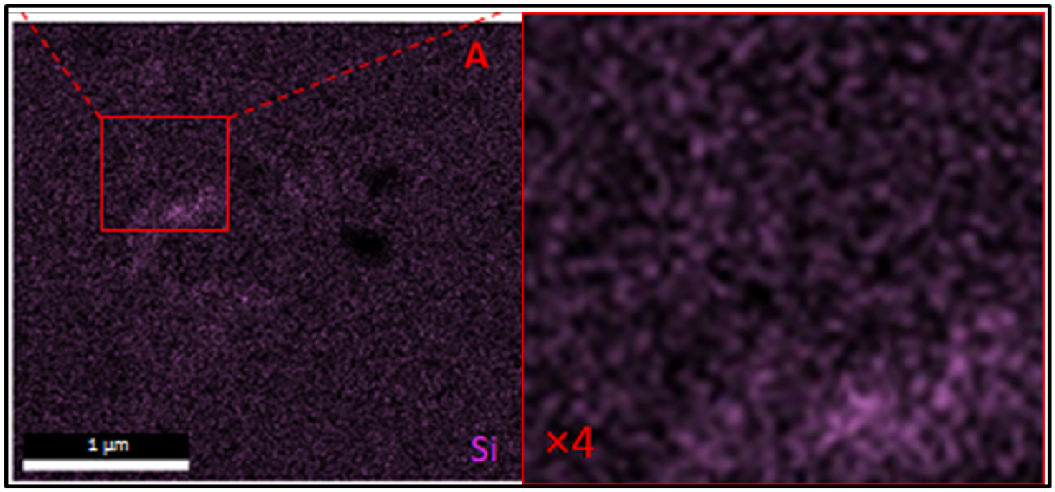



Figure7.7.HAADF-STEM-EDS images showing Si mapping images for AuNPs made using 3-APTMS and acetone (both as solvent and mild reducing agent).

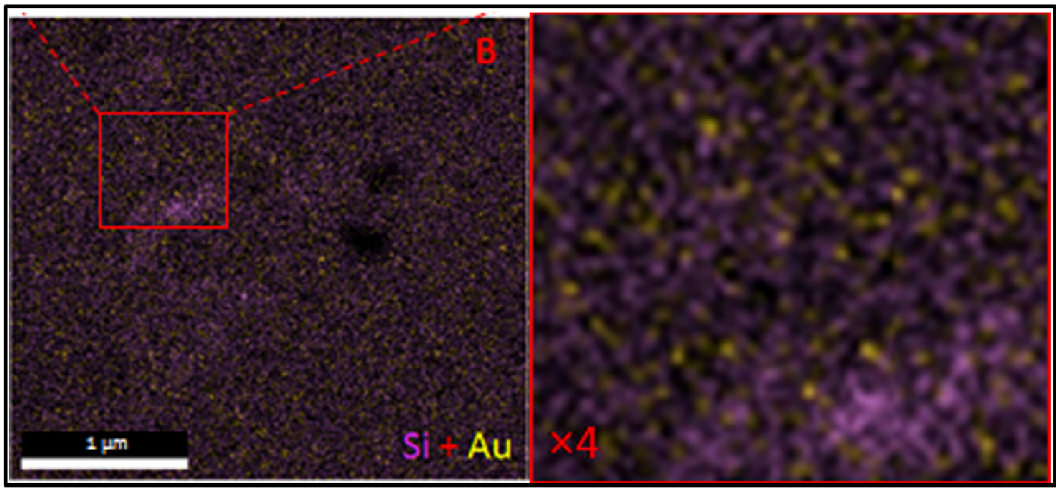



Figure7.8.HAADF-STEM-EDS images showing (Si + Au) mapping images for AuNPs made using 3-APTMS and acetone (both as solvent and mild reducing agent).

---

After having synthesized $(\text{Au-siloxane}_{\text{homo}})_{\text{seq}}$ in suspension the possibility of using a film of siloxane polymer for the synthesis of AuNPs over solid surface is observed. The siloxane polymer was deposited as thin film over glass slides and dipped into the 1mM $Au^{3+}$ solution. After a few hours a layer of AuNPs was formed over the siloxane polymer.

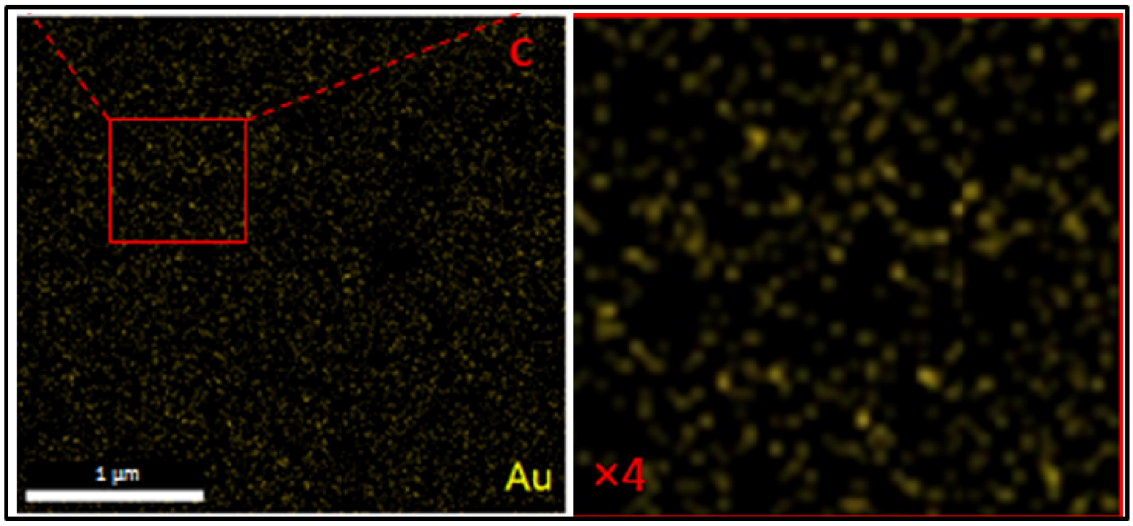



Figure 7.9. HAADF-STEM-EDS images showing AuNPs made using 3-APTMS and acetone (both as solvent and mild reducing agent): A) Si mapping; B) Si+Au mapping ; and C) Au mapping. (Enlargements of the same part of each image)

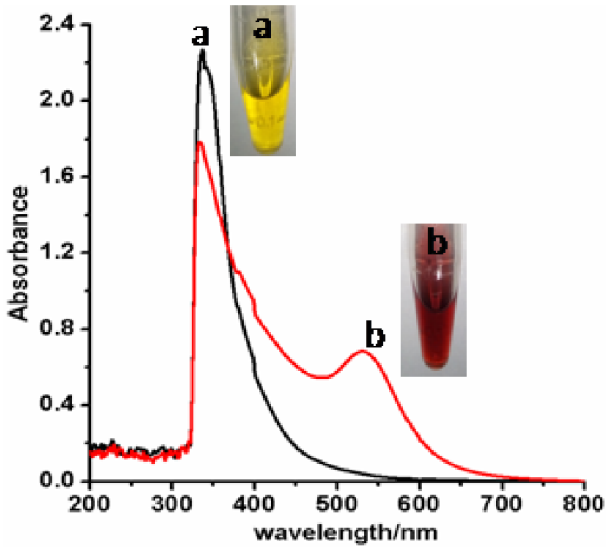



Figure7.10. UV-Vis spectra of siloxane polymer (a) and "$(\text{Au-siloxane}_{\text{homo}})_{\text{seq}}$" NPs (b).

---

As the AuNPs are grown over preformed solid film of polymer it is labelled as $(\text{Au-siloxane}_{\text{hetero}})_{\text{seq}}$. Fig. 7.11 gives the SEM image of the siloxane polymer and AuNPs $(\text{Au-siloxane}_{\text{hetero}})_{\text{seq}}$ grown over preformed polymer over solid surface.

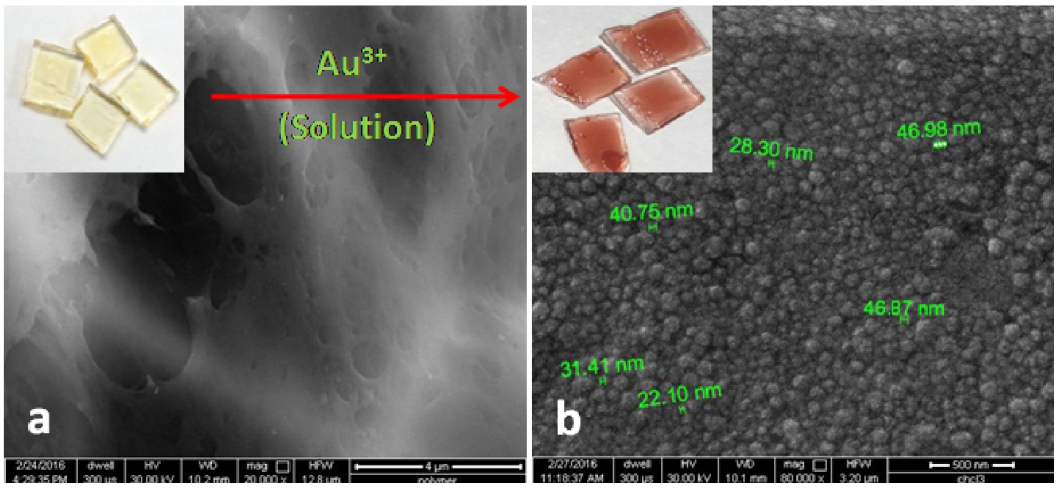



Figure7.11**.** SEM images of siloxane polymer (a) and "Au@siloxanehetero" NPs (b).

---

### 7.3.3. Electrochemical Behaviour of Siloxane-Au polymer modified electrode

"Siloxane-Au" polymer made through both sequentially [(Au-siloxane$_{homo}$)$_{seq}$] and simultaneously [siloxane-Au$_{sim}$] route can be coated on glassy carbon electrode. The electrochemical response of such modified electrodes was examined using a redox probe in solution (i.e. ferricyanide). In the case of simultaneously made AuNPs (siloxane-Au$_{sim}$) a very interesting property was observed. The electrochemical response of the probe increased with successive cycles at the same scan rate, as a result of accumulation of $Fe(CN)_6^{3-}$ in the pores of the film as shown in Fig.7.12. On the opposite, such behaviour was not observed in sequentially made (Au-siloxane$_{homo}$)$_{seq}$ as the pores become covered due to the sequential synthesis of [AuNPs] as shown in Fig.7.13. Fig.7.14 shows the cyclic voltammogram of the potassium ferricyanide in 0.1M phosphate buffer pH 7.0 containing 0.5MKCl at the scan rate of 10 $mVs^{-1}$ between -0.2 to +0.6V versus Ag/AgCl for (A) blank electrode and (B) (Au-siloxane$_{homo}$)$_{seq}$ modified electrode respectively. The dependence of peak current as a function of scan rate and

(scanrate)$^{1/2}$ is shown in Fig.7.15justifying the faster charge dynamics for (Au-siloxane$_{homo}$)$_{seq}$ as compared to that of blank electrode.

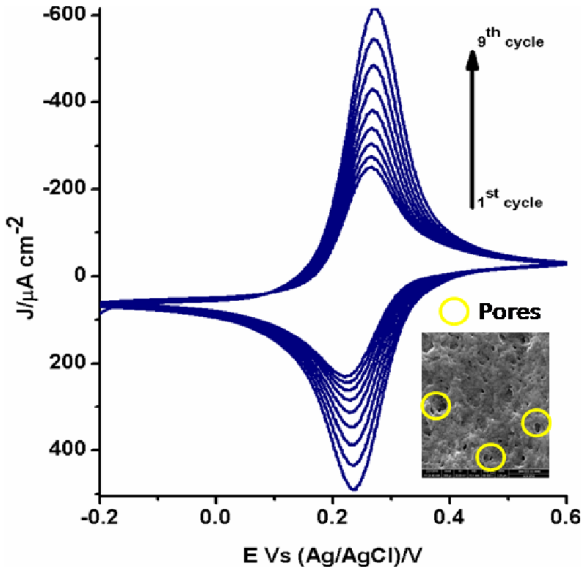



Figure 7.12. Cyclic voltammogramme of "siloxane-Au$_{sim}$" NPs showing increasing current trend at a scan rate of 10mV s$^{-1}$.

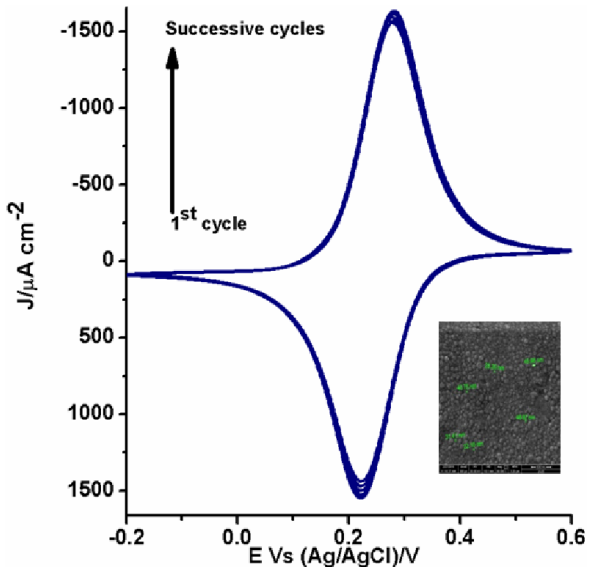



Figure 7.13. Cyclic voltammogramme of "Au@siloxane$_{homo}$" NPs showing constant current with successive cycles at a scan rate of 10mVs$^{-1}$.

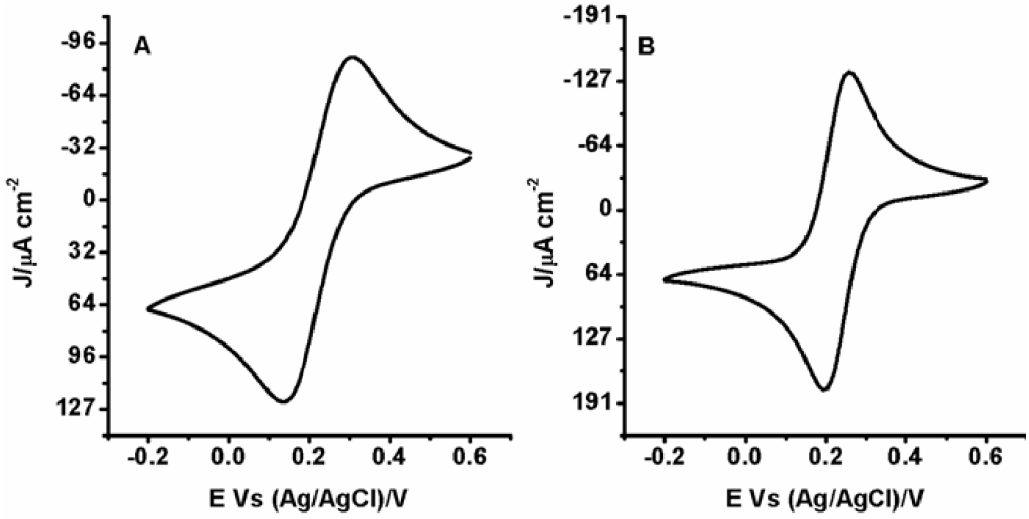



Figure7.14.Cyclic voltammogramme of $(FeCN_6)^{3-/4-}$ in 0.1M phosphate buffer (pH=7) containing 0.5M KCl in blank (A) and modified electrode (B) at a scan rate of $10mVs^{-1}$.

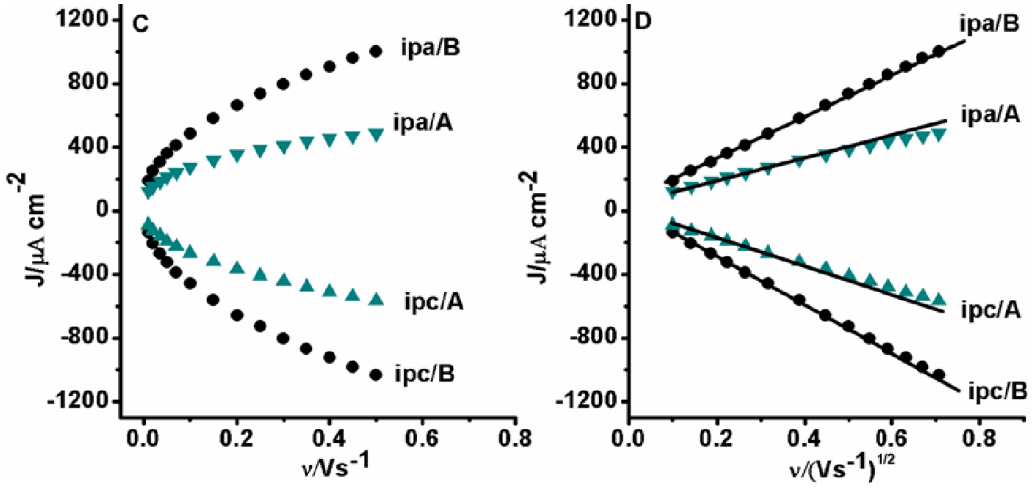



Figure 7.15. Plot of anodic (ipa) and cathodic (ipc) current density vs scan rate in blank (A) and modified electrode (B) (Left, C). Plot of anodic (ipa) and cathodic current density (ipc) vs square root of scan rate in blank (A) and over modified electrode (B) (Right, D).

---

### 7.3.4. PNP reduction using $(\text{Au-siloxane}_{\text{hetero}})_{\text{seq}}$ hybrid as catalyst

The $(\text{Au-siloxane}_{\text{hetero}})_{\text{seq}}$ synthesized over glass surface was used as catalyst for the reduction of PNP into PAP in the presence of excess $NaBH_4$. In the presence of excess $NaBH_4$ and sufficient amount of catalyst, the reaction follows pseudo-

first order and its rate can be determined only by monitoring the degradation of PNP. The peak at around 400 nm in the UV-Vis spectra upon addition of $NaBH_4$ to PNP solution is due to the formation of nitrophenolate ion (yellow colored solution). Upon the addition of the catalyst to this medium, the yellow color fades away forming a colorless solution of p-aminophenol (PAP) as shown in Fig. 7.16. This decrease in the concentration of PNP is monitored spectrophotometrically. The UV-Vis spectra for the reduction of PNP to PAP have been given in Fig. 7.17.

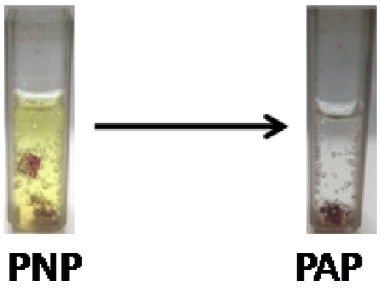



Figure7.16. Picture presenting change of color from yellow (PNP) to colorless (PAP) in the presence of excess $NaBH_4$ and "$Au@siloxane_{hetero}$" solid catalyst.

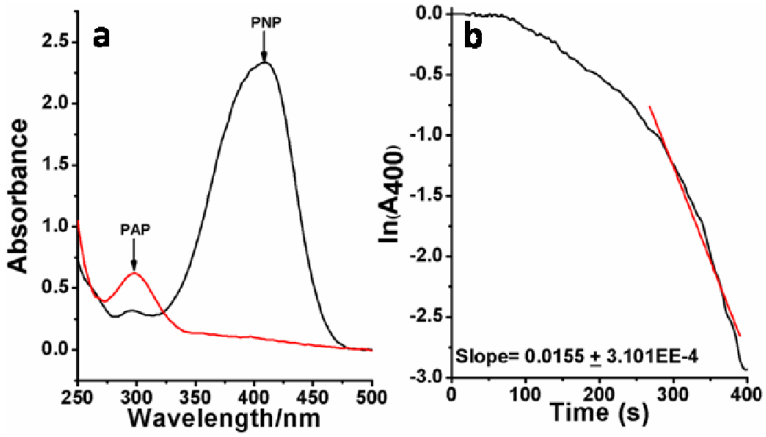



Figure7.17. Typical UV-Vis spectra for reduction of PNP over catalyst of interest with an excess amount of $NaBH_4$ (a). Plot of $lnA_{400}$vs time for the reduction of PNP using "$Au@siloxane_{hetero}$" NPs (b).

### 7.3.5. Effect of porosity on catalytic behaviour

In order to monitor the effect of pores on catalytic activity a comparative peroxidase mimetic behavior of three kinds of AuNPs viz. $(Siloxane\text{-}Au_{sim})_{ace}$, $(Siloxane\text{-}Au_{sim})_{wat}$ and $(Au\text{-}siloxane_{homo})_{seq}$ was monitored and compared as shown in Fig. 7.18. It can be concluded from the figure that the porous structure is more catalytic $[(Siloxane\text{-}Au_{sim})_{ace}]$ compared to the non-porous structure of $[(Siloxane\text{-}Au_{sim})_{wat}$ and $(Au\text{-}siloxane_{homo})_{seq}]$. The reason for porosity in the former case and non porosity in later case has been discussed in detail above. Thus, it was concluded that porous structure has positive effect on the catalytic property of AuNPs. The experiment was conducted by carrying out the oxidation of peroxidase substrate o-dianisidine in the presence $H_2O_2$ using the as mentioned hybrid structures as catalyst.

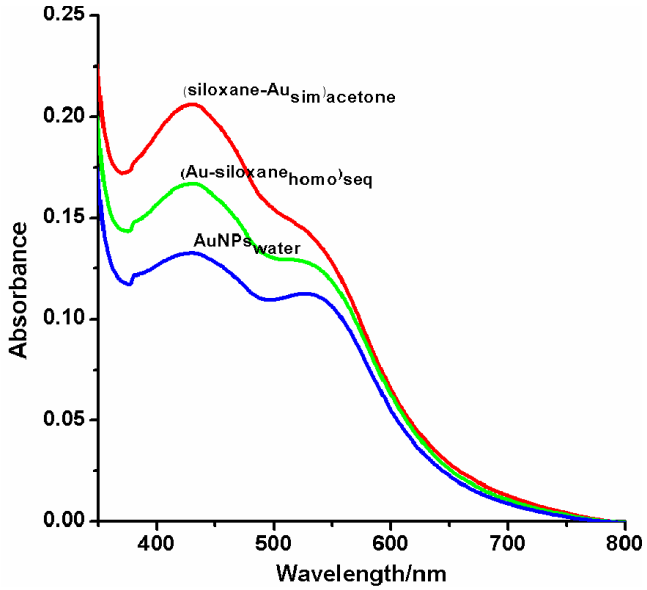



Figure7.18. UV-Vis spectra for the competitive ability of different AuNPs towards peroxidase mimetic ability.

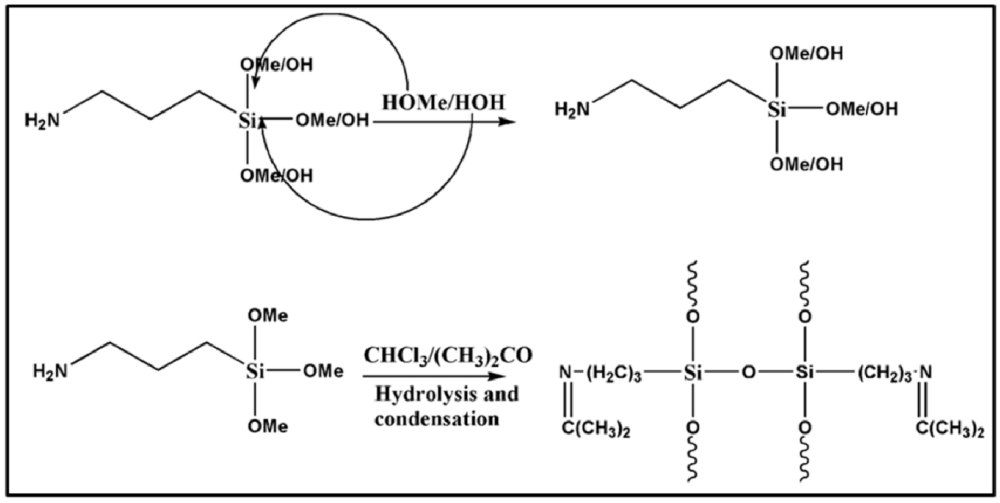
## 7.4. DISCUSSION

### 7.4.1. Choice of 3-APTMS and acetone for solvent induced AuNPs synthesis

In previous chapters 3-APTMS mediated synthesis of AuNPs utilizing variety of organic reducing agents has been documented. In order to observe the impact of solvent on 3-APTMS mediated AuNPs solvent compatible reducing agent "acetone" has been selected and the results are discussed as follows. 3-APTMS is amphiphilic in nature and among all the reducing agent used in last chapter acetone is dispersible in almost all the solvents. This explains the choice of 3-APTMS and acetone to monitor the solvent effect.

### 7.4.2. Structural analysis of different types of nanomaterials

From the picture of AuNPs (Fig.7.1) and SEM images (Fig.7.3) of AuNPs the difference in the color and structure of AuNPs fabricated in aqueous and organic solvents can be clearly seen. All prepared samples when monitored spectrophotometrically display peak at around 520nm, which is characteristic of AuNPs as given in Fig.7.2. From SEM images as shown in Fig.7.3, polymeric structure in case of organic solvents can be seen clearly whereas no such structures were seen when water was used as synthesis medium. The hybrid materials made of siloxane polymer and AuNPs is obtained in case of aprotic organic solvents like chloroform and acetone (acetone used both as solvent and mild reducing agent). On the opposite, discrete and spherical $AuNPs_{water}$ are obtained when protic solvents like, water and methanol are used. In case of water and methanol oxygen with the lone pair itself participates in reaction with trimethoxysilyl group whereas in case of solvents like acetone and chloroform, in absence of any other lone pair source intermolecular reaction (condensation) between two 3-APTMS molecule prevails. Scheme 7.1 depicts the fate of 3-APTMS in different solvents.




Scheme 7.1. Effect of solvent on the chemistry of 3-APTMS

---

SEM images clearly indicate the formation of polymeric structures in the presence of acetone while only discrete spherical particles can be seen in case of water used as co-solvent. Former is labelled as **(siloxane-$Au_{sim}$)** and later as **$(AuNPs)_{water}$**. Both chloroform and acetone result in the synthesis of hybrid structure between siloxane and AuNPs (Fig.7.4) but chloroform as a solvent gives more organized structures as can be seen from the AFM and SEM images given in Fig. 7.5. The more organized structure in this case might be the result of slow hydrolysis and condensation as the solvent is non polar and the release of water from the synthesis of IPTMS imine is also very slow due to decreased acetone concentration compared to the case using acetone itself as solvent. The spherical AuNPs can be seen either attached to polymeric structure or free in case of water used as co-solvent. TEM images of AuNPs made in water and acetone as shown in Fig. 7.6 again indicate discrete spherical structure for AuNPs made in water solvent and polymeric structure (formed by 3-APTMS) with studded AuNPs in chloroform solvent. The contrast between dark gold nanoparticles and the lighter siloxane polymer is very clear from the image.

Characterization data clearly indicate polymer formation during AuNPs synthesis in acetone and chloroform. The claim of AuNPs-siloxane hybrid is further strengthened by the HAADF-STEM-EDS elemental mapping that show silicon matrix interspersed with AuNPs as shown in Fig.7.7-Fig.7.9. So, the synthesis of AuNPs over preformed polymer (formed by mixing 3-APTMS with acetone in organic solvent) was attempted. Sequentially made AuNPs when made in suspension are labeled as **$(\text{Au-siloxane}_{\text{homo}})_{\text{seq}}$** and when made over a solid surface as **$(\text{Au-siloxane}_{\text{hetero}})_{\text{seq}}$**. The UV-Vis spectra for sequentially made AuNPs in suspension display the peak around 520nm concominant with the appearance of striking ruby red color on the formation of AuNPs (Fig 7.10). Similarly film making property of siloxane polymer has been exploited for carrying out AuNPs synthesis over solid surface. Pieces of glass slides coated with the film of polymer and dipped in acetonic solution of $Au^{3+}$ results in a layer of AuNPs over film. The SEM images for polymer and AuNPs made over polymer are given in Fig. 7.11. The reversible nature of the imine linkage in IPTMS is the driving force for the conversion of $Au^{3+}$ to AuNPs. Imine bond formed is of covalent nature that can be formed and cleaved in response to some stimuli reversibly (Rowan et al., 2002). Imine role for the synthesis of AuNPs is established. For instance, amine stabilized AuNPs have been synthesized by exploiting the reversible formation and dissociation of the imine linkage by Wu et.al., (2015). Sol-gel-derived silica thin films on solid supports such as electrodes for instance are widespread and the silica matrix has been used of various modifiers, including metal nanoparticles, with applications notably in electrocatalysis and biosensors (Walcarius et al., 2005; Etienne and Walcarius., 2005; Wand and wang., 2004; Chen et al., 2006; Rozhanchuk et al., 2009). The protons present in the solution of $HAuCl_4$drive the reversible imine reaction to cause the AuNPs synthesis over solid surface.

### 7.4.3. Effect of porosity on electrochemical behaviour

The electrochemical behaviour of $[Fe(CN)_6]^{3-/4-}$ observed in the presence of GCE modified with "siloxane-Au" and "Au@siloxane$_{homo}$" hybrids as discussed in the result section with former displaying an increasing peak current with successive cycles at same scan rate and later a constant current with successive cycles (Fig. 7.12 and Fig. 7.13). The trend observed in the case of "siloxane-gold" is due to the porous nature of the hybrid as shown in the SEM images. As a result of accumulation of $Fe(CN)_6^{3-/4-}$ in the pores of the film the peak current increases with successive cycles at same scan rate. This accumulation is most probably due to favourable electrostatic interactions between the negatively-charged $Fe(CN)_6^{3-/4-}$ probe and the positively-charged siloxane matrix [the amino groups on the material are protonated at pH (7) and the presence of conducting AuNPs in the matrix ensures effective charge transfer processes].

In case of "Au@siloxane" NPs the pores become covered due to the sequential synthesis of [AuNPs] over preformed polymer and hence the stability of the system (no variation in peak current with successive cycles at same scan rate).Extended linearity on the dependence of peak current versus scan rate reveals the contribution of AuNPs on facilitated charge transport and clearly demonstrates the significance of AuNPs in electroanalytical chemistry as shown in Fig. 7.15.

### 7.4.4. Reduction of PNP using (Au-siloxane$_{hetero}$)$_{seq}$

(Au-siloxane$_{hetero}$)$_{seq}$ system has been used as catalyst for causing the reduction of PNP in the presence of excess $NaBH_4$. Fig. 7.16 gives the change in yellow color of PNP to colorless PAP on complete reduction. Fig. 7.17 shows the decrease in the absorbance value of PNP at ~400nm with time that has been used to calculate the

rate constant value. It can be seen, the reaction completed in 400s with a rate constant value of 0.0155+3.101E-4. As the catalytic system is made over solid surface it has been used several times with good operational stability, justifying its interest for heterogenous catalysis.

## 7.5. CONCLUSION

In summary, 3-APTMS and acetone have been used for the synthesis of AuNPs in solvents of different polarity. The AuNPs have been characterized by UV-Vis spectroscopy, SEM, AFM and TEM techniques. The characterization data reveal the formation of hybrid between siloxane and AuNPs in case of organic solvents while discrete AuNPs in case of water solvent. The siloxane polymer formed from 3-APTMS and acetone has been used for the synthesis of AuNPs over siloxane both in suspension and over solid surface utilizing the reversible imine linkage.