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Functionalized Alkoxysilane Mediated Synthesis of gold Nanoparticles dispersible in aqueous and non-aqueous medium

2.1. INTRODUCTION

The intriguing properties (chemical, electrical, optical and electro-catalytic) of MNPs have led to an immense interest in the synthesis and study of the same (Saha et al., 2012; Rippel and Seifalian, 2011; Nouh et al., 2012; Kang et al., 2011; Singh and Nalwa, 2011; SadAbadi et al., 2012). Generally AuNPs that are produced, following different protocols, can be dispersed either in water or in organic solvents. Recently, it has been reported that specific functionality linked to NPs facilitate its dispersion in both polar and non-polar solvents (Sekiguchi et al., 2012; Martinez et al., 2013; Huang et al., 2002; Wu et al., 2013; Zhao et al., 2012; Murugan et al., 2012). Such requirement has directed to synthesize efficient nanomaterials having dispersibility both in organic and aqueous medium by simple composition variation of substituents and could be useful in developing nanodevices which has been one of the challenging requirements.

The general methodology to prepare the AuNPs is based on aqueous phase nanodispersion (Kim and Lavin, 2011; Chen et al., 2011; Niu et al., 2011; Fragoon et al., 2012). However, these aqueous sols of AuNPs are insoluble in organic solvents and flocculate gradually.

Therefore, various protocols should be implanted for preparing AuNPs in organic solvents as NPs in organic solvents can be synthesized at relatively high concentrations with better nanodispersity compared to those made in aqueous solutions (Li et al., 2013). The alkoxysilanes viz. 3-aminopropyltrimethoxysilane (3-APTMS) and 3-glycidoxypropyltrimethoxysilane (3-GPTMS) have been used for the synthesis of noble metal nanoparticles viz. gold nanoparticles- AuNPs, silver nanoparticles- AgNPs and palladium nanoparticles-PdNPs (Pandey and Chauhan, 2012). The present chapter is dedicated to the detailed study of AuNPs made using 3-APTMS and 3-GPTMS. The reagents not only affect the size of the nanoparticles but also plays major role in deciding the dispersibility of nanomaterial both in organic and aqueous media. The molar ratio of the alkoxysilanes decides the hydrophobic and hydrophilic properties of as synthesized AuNPs. Hydrophobicity in nanoparticles allocates its incursion through the cellular membrane via hydrophobic interactions and dissemination through nuclear pores (Tan et al., 2010; Naim et al., 2009). On the other hand, increase in the hydrophobicity of the nanoparticle surface leads to a decrease in nanoparticle dispersibility in aqueous solutions. Thus, the usability of nanoparticles will be extended if the nanoparticles can be designed so as to allow the same to cross the hydrophobic barrier while keeping their dispersibility in aqueous solutions. A convenient way for introducing such property is the use of functionalized alkoxysilane precursors (Pandey et al., 2003a; Pandey et al., 2001a, 2001b; Pandey et al., 1999b) where the relevant organic functionality allow control over the water wettable components during solid-state nanostructured network formation (Lee et al., 2009; Kutsch et al., 1997; Bharathi et al., 1999; Ariga et al., 2012). In addition to that hydrophilic functionality like 3-APTMS has been used as stabilizers in the sol form (Pandey and Pandey; 2013a, 2013c) whereas, hydrophobic functionality, like 3-GPTMS, allow the

reduction of metal salts (Pandey et al., 2003a; Pandey et al., 2001b). Such findings directed our attention to investigate the role of organically functionalized moieties especially 3-GPTMS and 3-APTMS in noble metal NPs synthesis (Li et al., 2013). It has been found that 3-APTMS play an important role in nanoparticles synthesis providing suitable dispersion medium for the same (Pandey and Pandey; 2013a, 2013c). The present chapter is dedicated to study in detail the interaction between 3-APTMS and 3-GPTMS during the course of AuNPs synthesis and study in detail the properties of AuNPs produced thereafter. The reaction products of 3-GPTMS and 3-APTMS may also provide suitable suspension medium due to the combination of both hydrophobic and hydrophilic components for the use of resulting nanoparticles in variety of aqueous and non-aqueous solvents. The results based on these lines are reported in this chapter.

2.2 EXPERIMENTAL

2.2.1 Materials and instrumentation

3-Aminopropyltrimethoxysilane, 3-Glycidoxypropyltrimethoxysilane, and o-dianisidine were obtained from Aldrich Chem. Co. Tetrachloroauric acid and silver nitrate was purchased from HiMedia; Toluene, hydrogen peroxide, ethyl acetate, dichloromethane and acetonitrile were obtained from Merck, India. All other chemicals employed were of analytical grade. Aqueous solutions were prepared by using doubly distilled-deionized water (Elga water purification system). Unless mentioned otherwise, all the experiments were performed at room temperature. The absorption spectra of nanoparticles were recorded using a Hitachi U-2900 spectrophotometer. TEM studies were performed using Morgagni 268D (Fei Electron Optics).

2.2.2 Preparation of 3-APTMS stabilized AuNPs

3-APTMS stabilized AuNPs were synthesized according to the procedure described earlier (Pandey and Chauhan, 2012). In a typical procedure, 1 mL of sol was prepared by mixing 0.08 mL solutions of 0.025 M of HAuCl_4 to 0.2 mL solutions of APTMS (1 M). Methanol was added as required to adjust the volume. The resulting yellow solution was stirred vigorously over a vortex cyclo mixer for 2 min. The solution was then subjected to reduction by adding a 0.25 mL solution of 3-GPTMS (4 M). The resulting mixture was stirred over a vortex cyclo mixer for 2 min. The mixture was left to stand in the dark for 12 h. After this, the colour of the sols turned to red indicating the formation of AuNPs. Different color of AuNPs sol was prepared by varying the concentration of both 3-APTMS and 3-GPTMS. Details are presented in Table 2.1 and reveal the characteristics of AuNPs sol as a function of the concentration of functionalized silane.

2.2.3 Peroxidase-like catalytic activity of AuNPs

The peroxidase like activity of as synthesized nanoparticles was determined spectrophotometrically by measuring the formation of oxidized product of o-dianisidine at 430nm ($\epsilon=11.3\text{mM}^{-1}\text{cm}^{-1}$) using a Hitachi U-2900 spectrophotometer. Typically, the o-dianisidine oxidation activity was measured in 0.1 M phosphate buffer (pH 7.0) in the presence of AuNPs ($20\mu\text{l mL}^{-1}$) using 60 μM o-dianisidine at 25°C. Hydrogen peroxide (1 mM) was added to start the reaction, unless otherwise specified.

2.3 RESULTS

2.3.1 Interaction between 3-APTMS and 3-GPTMS

Functional alkoxysilanes [3-APTMS and 3-GPTMS] result in the synthesis of metal nanoparticles when made to interact with metal ions following a proper protocol (Pandey and Chauhan, 2012).

Table 2.1. Concentrations of the reagents used during the synthesis of AuNPs by the action of 3-GPTMS on 3-APTMS capped Au³⁺.

Sample Name	3-GPTMS (M)	3-APTMS (M)	HAuCl ₄ (mM)
A	1.0	0.6	2.5
B	0.75	0.6	2.5
C	0.5	0.6	2.5
D	0.25	0.6	2.5
K	1.0	0.2	2.5
L	0.75	0.2	2.5
M	0.5	0.2	2.5
N	0.25	0.2	2.5
R	1.0	0.6	2.5
S	1.0	0.4	2.5
T	1.0	0.2	2.5
U	1.0	0.1	2.5

However, the detailed investigation in this regard is missing. Accordingly, the present chapter is dedicated for the detailed investigation of the above method specifically linked to: (i) study the mechanistic way of nanoparticle synthesis; (ii) investigate the usability of noble metal nanoparticles in aqueous and non-aqueous medium and (iii) study the peroxidase like activity of the same. 3-APTMS is amphiphilic in nature i.e. compatible

with most of the solvents including water. On the other hand 3-GPTMS forms a separate layer with water or is hydrophobic in nature. The functional group in 3-APTMS is a primary amine group whereas 3-GPTMS contains highly reactive epoxy group. At first instant the chemistry of 3-APTMS and 3-GPTMS interaction in methanolic medium is monitored to understand the mechanistic behavior. For this fixed concentration of 3-APTMS is added to 3-GPTMS and vice-versa in the absence and presence of Au^{3+} as shown in Fig. 2.1(A&B) and Fig. 2.2(A&B) respectively. Fig. 2.1 shows the UV-Vis spectra for the interaction between 3-GPTMS and 3-APTMS; (A) constant concentrations of 3-GPTMS followed by addition of increasing concentration of 3-APTMS; (B) constant concentrations of 3-APTMS followed by addition of increasing concentration of 3-GPTMS. Such interaction of 3-GPTMS to 3-APTMS is confirmed due to appearance of new peak at ~ 280 nm which is evaluated from the reaction product as shown in Fig. 2.1. The next phase of investigation is to understand the role of HAuCl_4 on the interaction dynamics of 3-APTMS and 3-GPTMS if any. For this, the reaction system as shown in Fig. 2.1 is again recorded in the presence of HAuCl_4 and the finding is recorded in Fig. 2.2(A&B). It is observed that peak at ~ 280 nm is facilitated in the presence of Au^{3+} when 3-GPTMS is added to 3-APTMS.

2.3.2 Structural Characterization

The role of nitrogen containing compound as base catalyst has been demonstrated and reviewed (Wight and Davis, 2002). Such finding reveals that 3-APTMS treated metal ions move close to methoxy derivative of 3-GPTMS resulting into the formation of amine derivative through NH-group. In absence of 3-APTMS the synthesis of metal nanoparticles

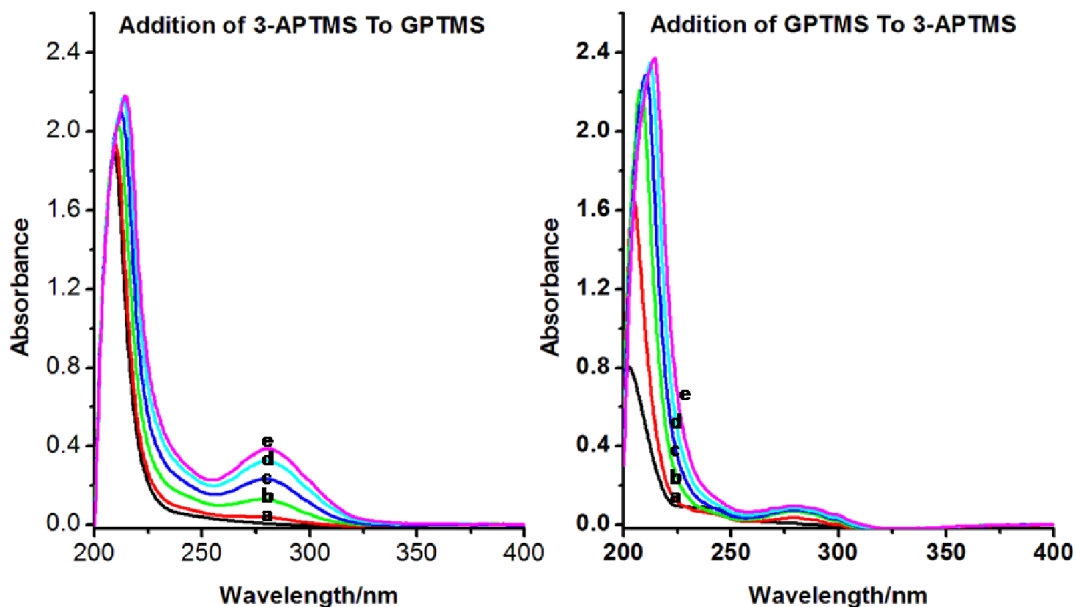


Figure 2.1. UV-Vis spectra recorded for the interaction between 3-GPTMS and 3-APTMS; (Left) systems containing constant concentrations of 3-GPTMS(24 mM, black line) followed by addition of varying concentration between 8–18 mM of 3-APTMS (a)–(e); (Right) systems containing constant concentrations of 3-APTMS (27 mM, black line) followed by addition of varying concentration between 9–20 mM of 3-GPTMS (a)–(e).

is not observed. 3-APTMS not only promote such interaction but also act as a potent stabilizing reagent for the resulting nanoparticles. The concentration of 3-APTMS and 3-GPTMS control the size of the AuNPs that are produced. An increase in concentration of 3-APTMS at constant 3-GPTMS concentration results in an increasing trend in AuNPs size whereas an increase in concentration of 3-GPTMS at constant 3-APTMS concentration causes a decrease in the AuNPs size. The as prepared nanoparticles under two different compositions of 3-APTMS/GPTMS are characterized by TEM as shown in Figure 2.3.

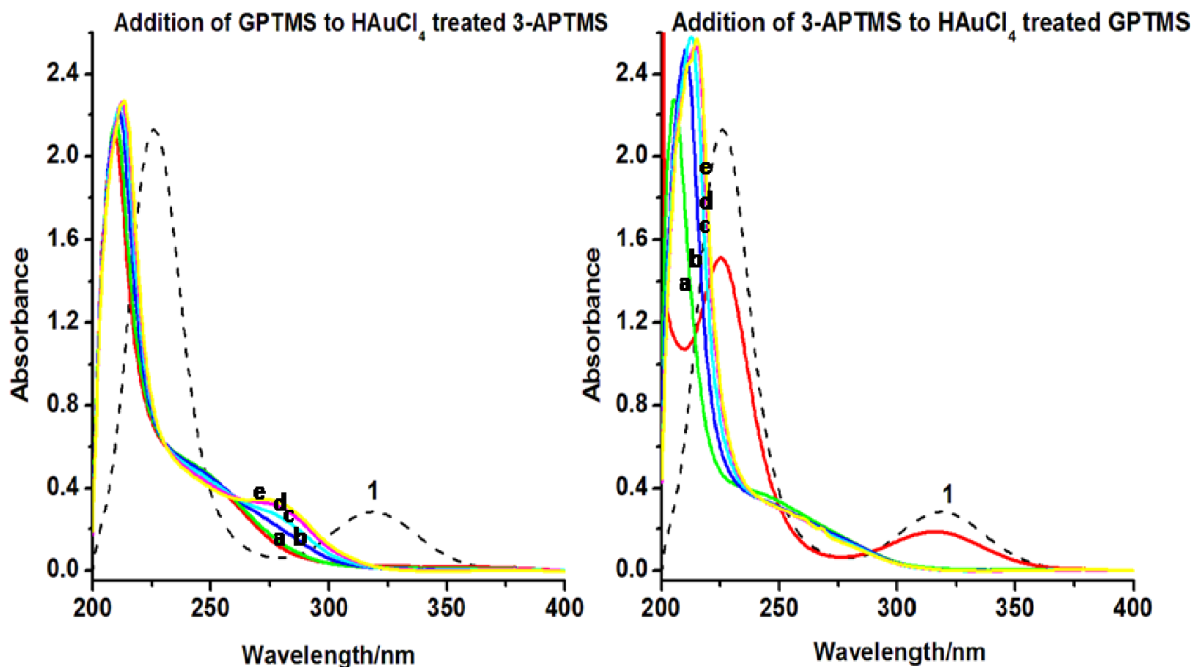


Figure 2.2. UV-Vis spectra recorded for interaction between 3-GPTMS and 3-APTMS in the presence of tetrachloroauric acid (HAuCl_4). Curve-1 (for both Figures) shows the absorption spectra of methanolic solution of HAuCl_4 (0.125 mM); (Left) systems containing methanolic solutions of 3-APTMS (27 mM) treated HAuCl_4 (red line) followed by addition of varying concentration of 3-GPTMS between 9–20 mM (a)–(e). (Right) systems containing methanolic solutions of HAuCl_4 (0.125 mM, red line) and 3-GPTMS (24 mM) followed by addition of varying concentration between 8–18 mM methanolic solution of 3-APTMS (a)–(e);

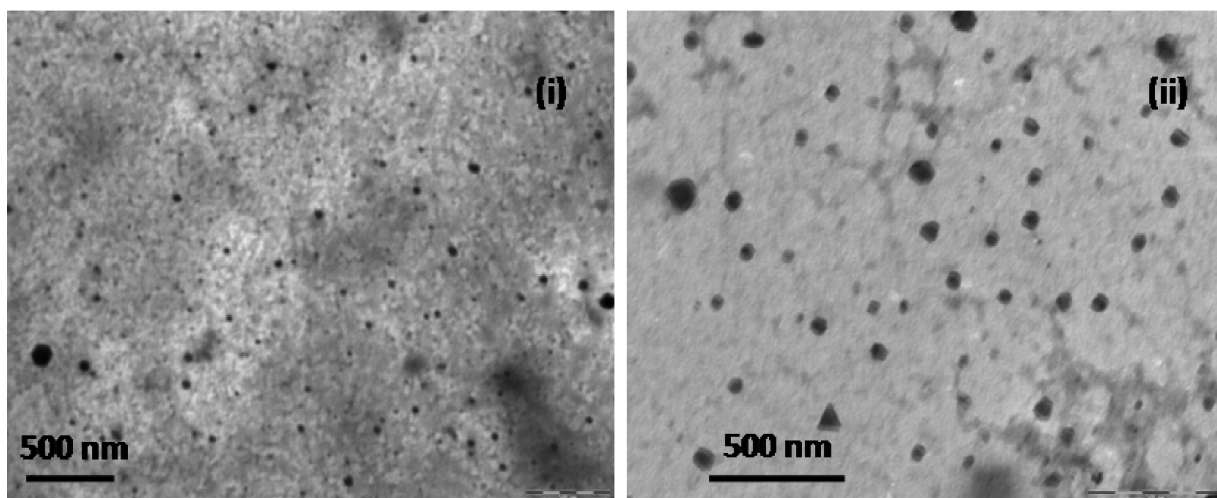


Figure 2.3. TEM images of two different sizes AuNPred (i), AuNPpurple (ii).

The TEM images illustrate the homogenous distribution of nanoparticles with the average size of 15 nm and 35 nm. The finding demonstrates the role of proposed functional alkoxysilanes that control the size of AuNPs and validate the novelty of the present process in nanoparticles synthesis.

2.3.3 Dispersibility of AuNPs sol in aqueous and organic medium

The dispersibility of AuNPs both in aqueous and organic solvents is subsequently investigated based on the absorption spectra and visual photographs. For this, two common solvents having polarity at extreme ends i.e., Toluene and Water have been chosen. The dispersibility is studied through visual photographs of AuNPs and their respective UV-Visible spectra in toluene and water made at different composition of 3-APTMS/3-GPTMS. Fig.2.4 depicts a photograph of three different AuNPs (A, B and C) formed as a result of increasing the concentration of 3-GPTMS whilst keeping the concentrations of HAuCl_4 and 3-APTMS constant. The variation in color of the photograph justifies the alkoxysilanes mediated formation of AuNPs showing different size. The comparative dispersibility as a function of alkoxysilane composition is shown in Table 2.2. The dispersion ability of the AuNPs has been further examined keeping the limiting concentrations of 3-APTMS with variable concentrations of 3-GPTMS as shown in Fig. 2.5. The results indicate better dispersibility of AuNPs (K, L and M) in toluene. However, when the molar concentration of 3-GPTMS is lower the dispersion shifts towards water. The comparative dispersibility as a function of proposed alkoxysilane concentrations is recorded in Table 2.3. The finding also justifies that at controlled limited 3-APTMS concentration AuNPs are dispersible in both toluene and water to similar extent.

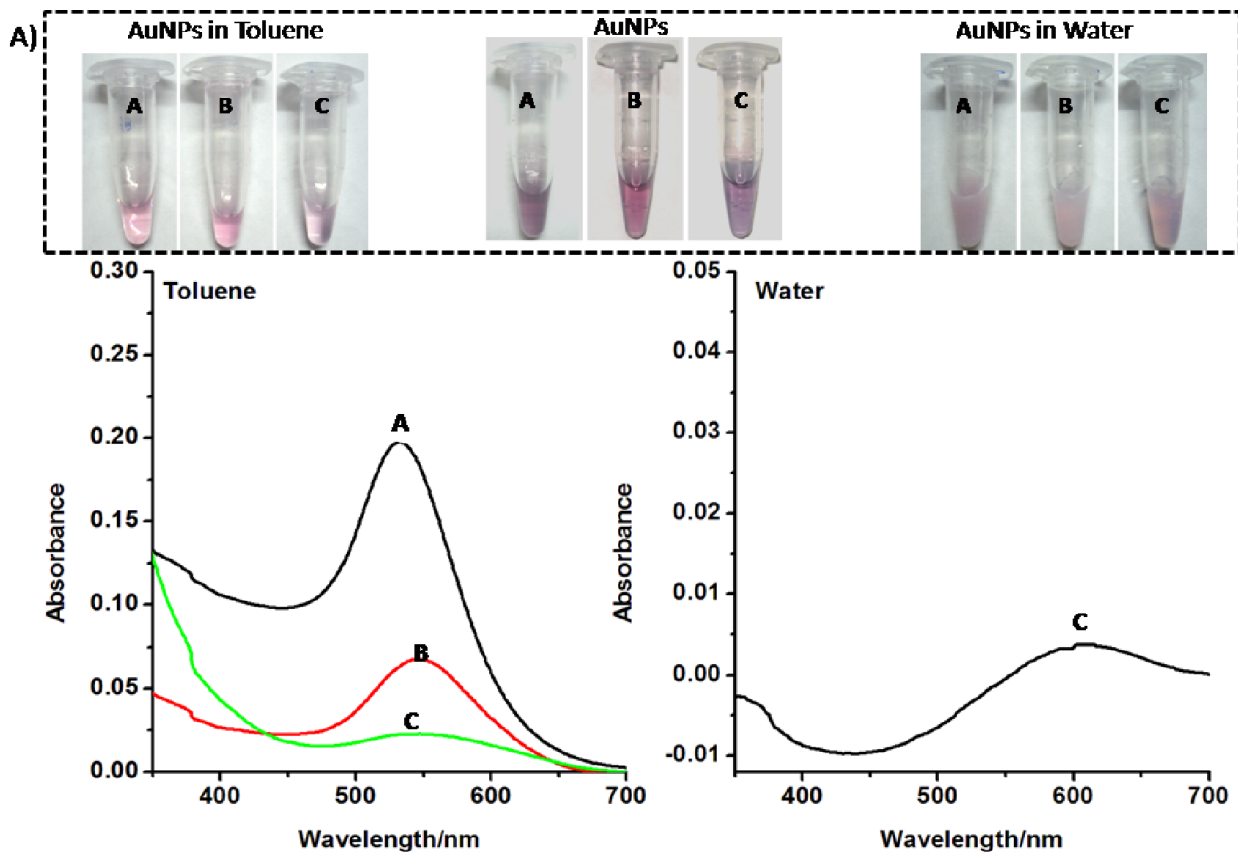


Figure 2.4. The visual photographs of AuNPs made by using constant concentration of 3-APTMS (0.6M) and varying concentrations of 3-GPTMS (A) 1.0 M, (B) 0.75 M, and (C) 0.5 M and their dispersibility in toluene and water. The lower portion shows the UV-Vis spectra of the corresponding sols in toluene and water.

Table 2.2. Dispersibility of nanoparticles having constant concentrations of 3-APTMS (3 M) and varying concentrations of 3-GPTMS.

Sample Name	3-APTMS Conc. (M)	3-GPTMS Conc. (M)	Dispersibility Toluene	Water
A	0.6	1.0	+++	--
B	0.6	0.75	++	--
C	0.6	0.5	+	-
D	0.6	0.25	+	+

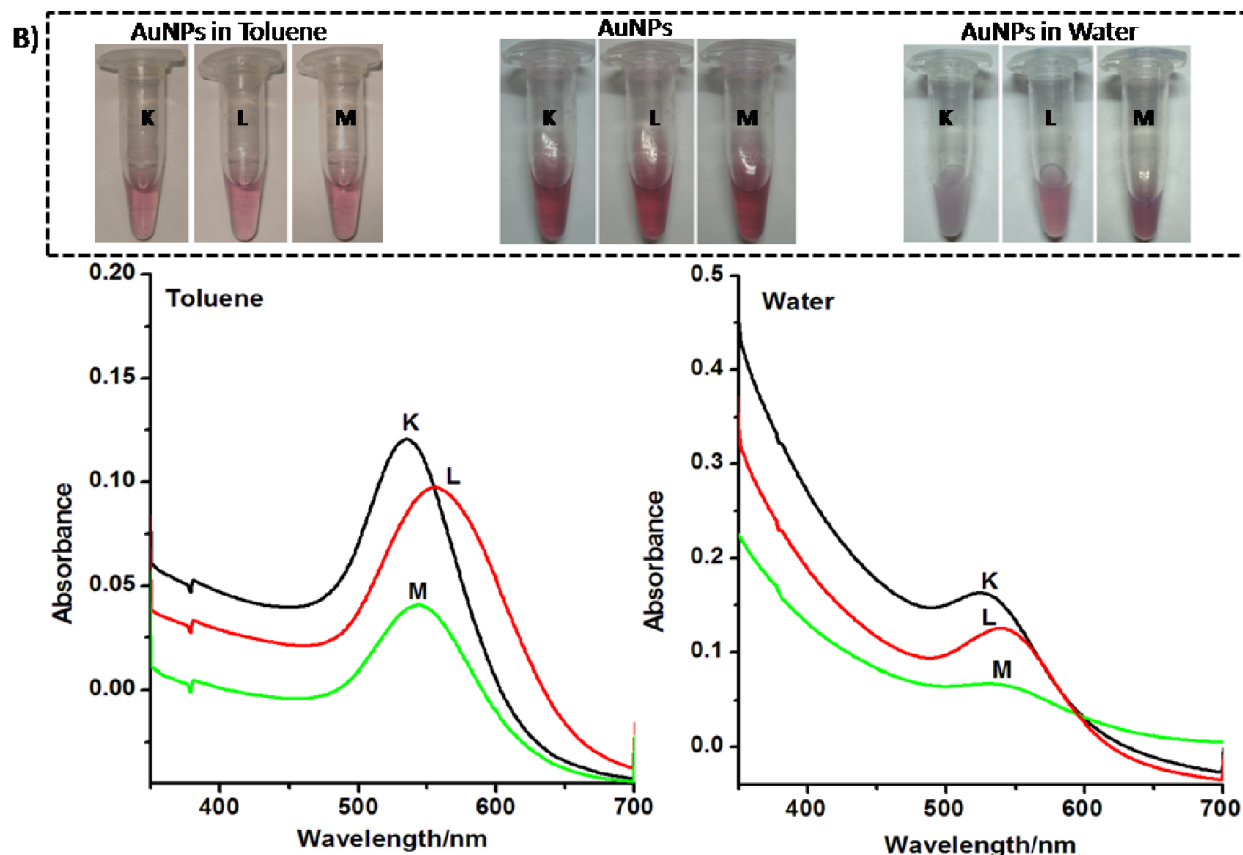


Figure 2.5. The visual photographs of AuNPs made by using constant concentration of 3-APTMS (0.2 M) and varying concentrations of 3-GPTMS (K) 1.0 M, (L) 0.75 M, and (M) 0.5 M and their dispersibility in toluene and water. The lower portion shows the UV-Vis spectra of the corresponding sols in toluene and water.

Table 2.3. Dispersibility of nanoparticles having constant concentrations (limiting) of 3-APTMS (1 M) in presence of varying concentrations of 3-GPTMS.

Sample Name	3-APTMS Conc. (M)	3-GPTMS Conc. (M)	Dispersibility	
			Toluene	Water
K	0.2	1.0	++	+
L	0.2	0.75	++	+
M	0.2	0.5	++	+
N	0.2	0.25	+	++

Further, in order to have deeper insight on dispersibility limits, four different compositions of 3-APTMS and 3-GPTMS are taken (Table 2.4) and examined the optical behavior of

these AuNPs (R, S and T) as shown in Fig. 2.6. There is significant change in absorption spectra of AuNPs (R, S and T) with better dispersibility in water for T which tends to be converted into a plateau for S and R. On the other hand the same in toluene show good dispersibility suggesting that an increase in molar ratio of 3-GPTMS to 3-APTMS to the order of 4:3 results into better dispersibility in toluene as compared to that when molar ratio is 1:1. To examine the compatibility of AuNPs in other organic solvent, the absorption spectra as function of AuNPs concentrations has been monitored in toluene, ethylacetate (Fig. 2.7) and dichloromethane, acetonitrile (Fig. 2.8). There is dependence of λ_{\max} on the refractive index and polarity index of these solvent as shown in Fig. 2.9 and Fig. 2.10, respectively. These findings justify potential applications of the AuNPs in variety of non-aqueous media.

2.3.4. Peroxidase Mimetic behavior of AuNPs

NPs that mimic enzymes have become popular as they have potentiality for bio-signal amplification, mainly because of their large surface area, high catalytic activity, and low cost (Zhang et al., 2012; Zeng et al., 2012; Pandey and Pandey, 2013). In a typical o-dianisidine oxidation process, the color of the transparent substrate (o-dianisidine and buffer solution) turns brown after the addition of catalysts (AuNPs) and H_2O_2 as shown in Fig. 2.11A, and the maximum absorbance at 430 nm increases during this reaction (Fig. 2.11 B).

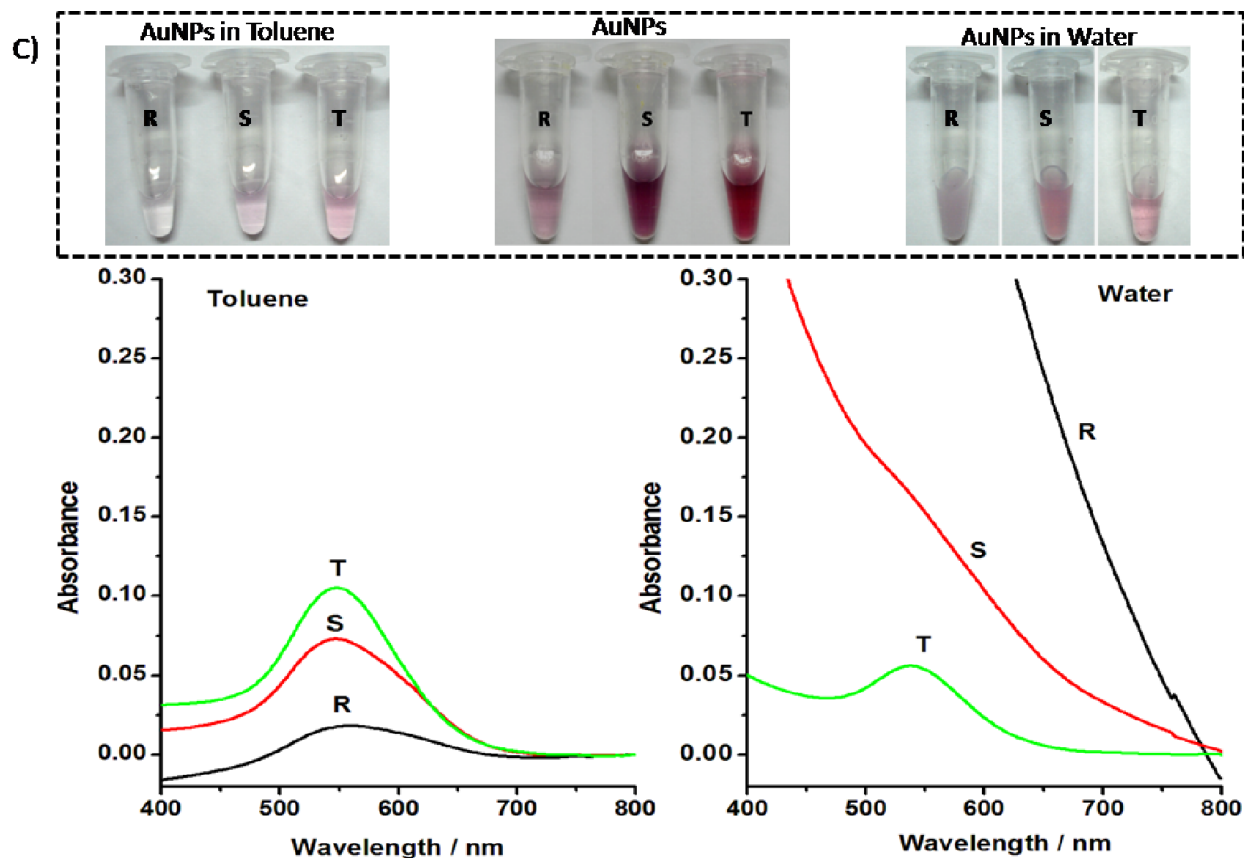


Figure 2.6. The visual photographs of AuNPs made by using constant concentration of 3-GPTMS (1.0 M) and varying concentrations of 3-APTMS (R) 0.6 M, (S) 0.4 M, and (T) 0.2 M and their dispersibility in toluene and water. The lower portion shows the UV-Vis spectra of the corresponding sols in toluene and water.

Table 2.4. Dispersibility of nanoparticles having varying concentrations of 3-APTMS and constant concentrations of 3-GPTMS (4 M).

Sample Name	3-APTMS Conc. (M)	3-GPTMS Conc. (M)	Dispersibility	
			Toluene	Water
R	0.6	1	++++	---
S	0.4	1	+++	--
T	0.2	1	++	+
U	0.1	1	+	++

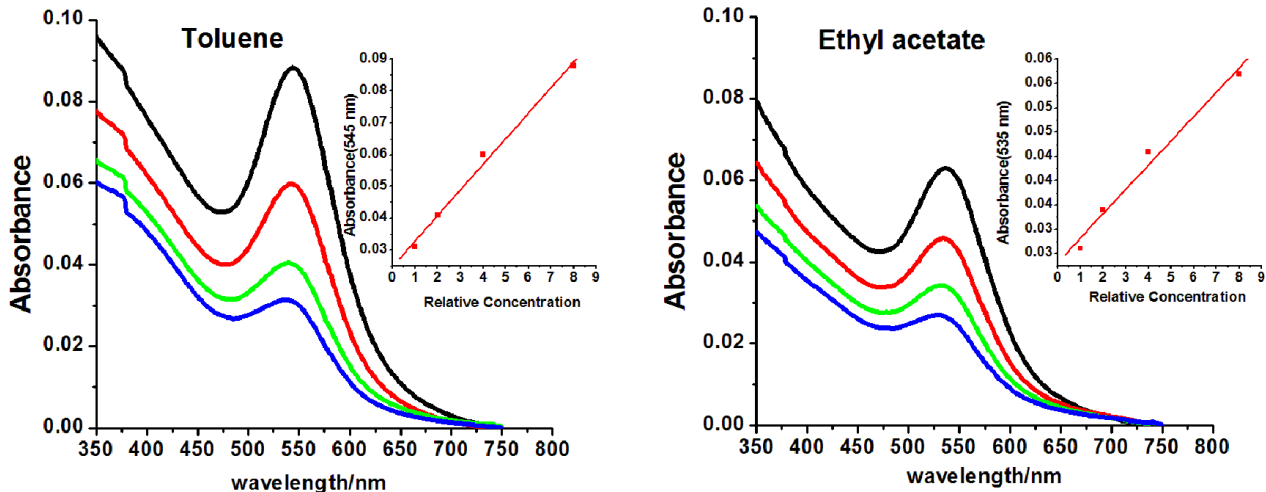


Figure 2.7. UV-Vis spectra of AuNPs in (i) toluene, (ii) ethyl-acetate, inset shows the dependence of absorption maxima (λ_{max}) on relative concentration.

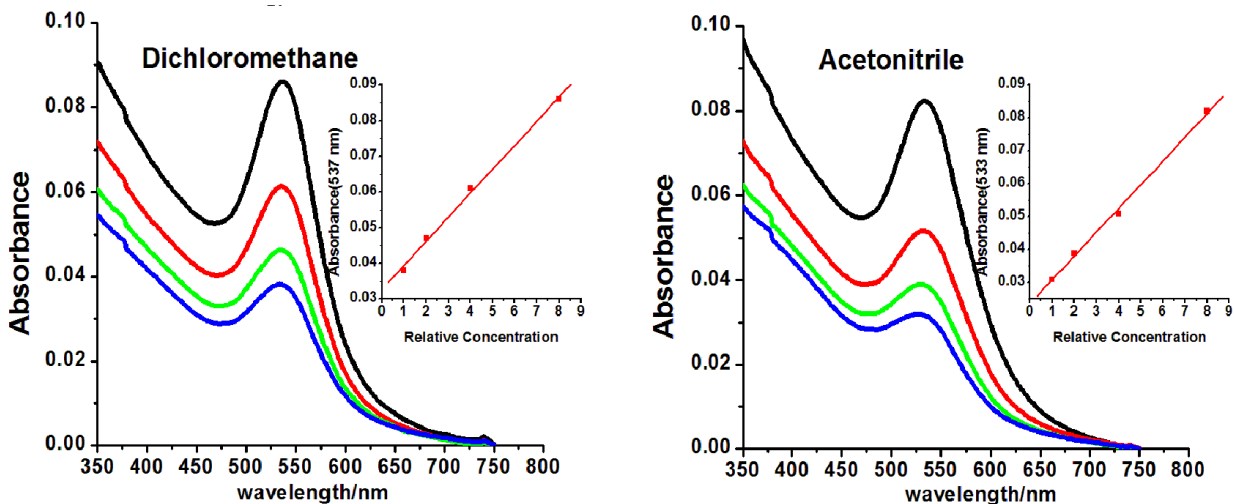


Figure 2.8. UV-Vis spectra of AuNPs in (i) dichloromethane, (ii) acetonitrile, inset shows the dependence of absorption maxima (λ_{max}) on relative concentration.

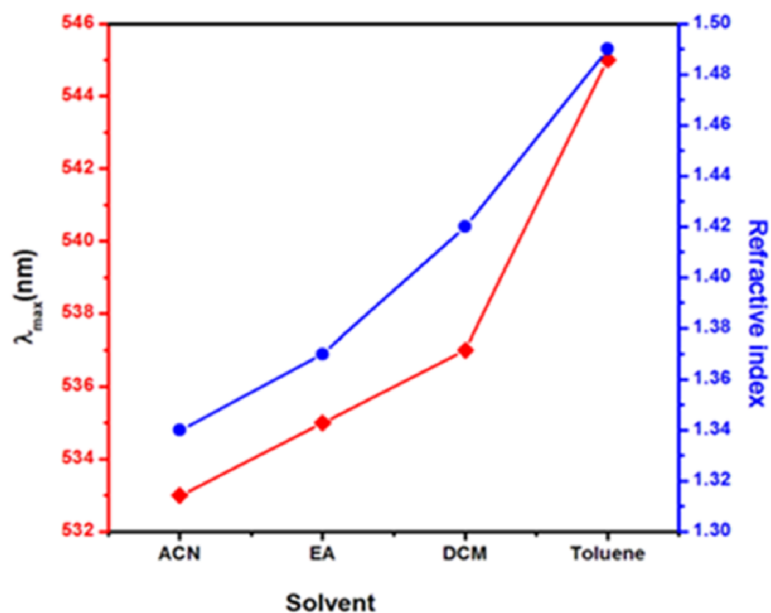


Figure 2.9. Shows the dependence of absorption maxima (λ_{\max}) on refractive index of solvents (acetonitrile, ethylacetate, dichloromethane and toluene).

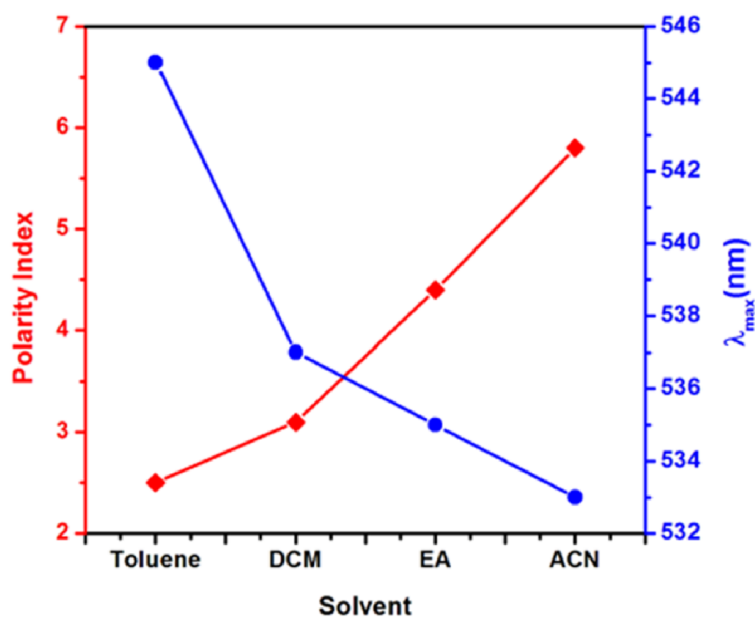


Figure 2.10. Shows the dependence of absorption maxima (λ_{\max}) on polarity index of solvents (toluene, dichloromethane, ethylacetate and acetonitrile).

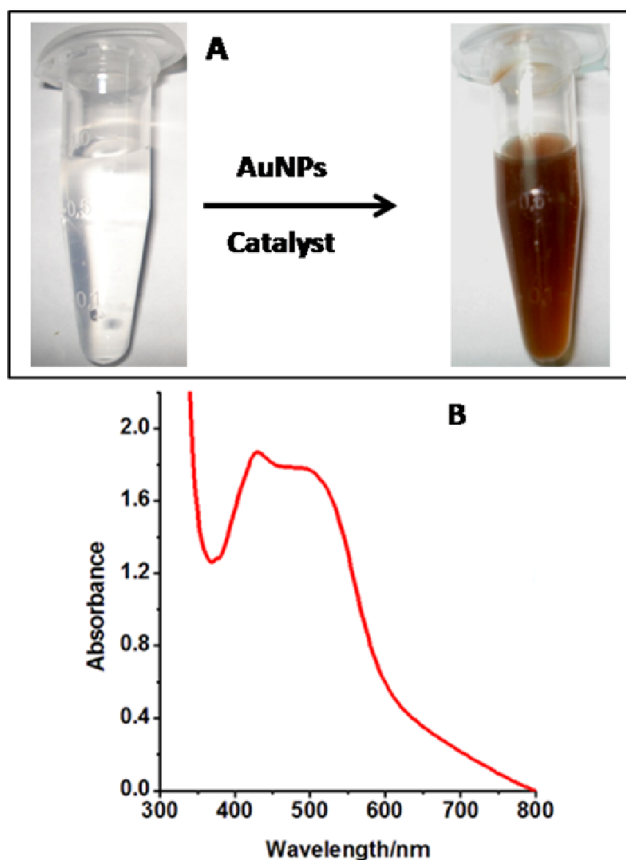


Figure 2.11. Color evolutions upon addition of AuNPs to o-dianisidine- H_2O_2 system (A); Typical UV-Vis spectra of o-dianisidine H_2O_2 -AuNPs reaction system (B).

2.4. DISCUSSION

2.4.1. Chemistry of 3-APTMS and 3-GPTMS interaction

In order to realize the chemistry of 3-APTMS and 3-GPTMS interaction, the hydrophobic and hydrophilic contribution of the reaction system need to be precisely understood. 3-APTMS and 3-GPTMS are hydrophilic and hydrophobic in nature respectively. It is found that 3-GPTMS on mixing with water generate two separate layers whereas a homogenous single layer is observed when methanolic solution of 3-GPTMS is put in water. In this process methanol is acting as a reactant converting hydrophobic 3-GPTMS to hydrophilic

methanolic solution. The results based on Fig. 2.1(A&B) and Fig. 2.2(A&B) reveal significant role of gold ions and clearly demonstrate the followings;

(1) the addition of 3-APTMS to 3-GPTMS present in reaction system enable faster interaction between glymo- and amino-residue as compared to that of 3-GPTMS to 3-APTMS, justifying the requirement of more 3-GPTMS molecules per 3-APTMS molecule,

(2) When 3-GPTMS is added to 3-APTMS in presence of HAuCl_4 the new absorbance peak at 280 nm is more facilitated than that of the same without HAuCl_4 , validating that gold ion is catalyzing the reaction between glymo and amino-residues.

(3) Addition of 3-APTMS to HAuCl_4 treated 3-GPTMS doesn't result a new absorbance peak recorded at 280 nm again justifying the role of available number of 3-GPTMS molecules per 3-APTMS at the site of glymo- and amino residue interaction.

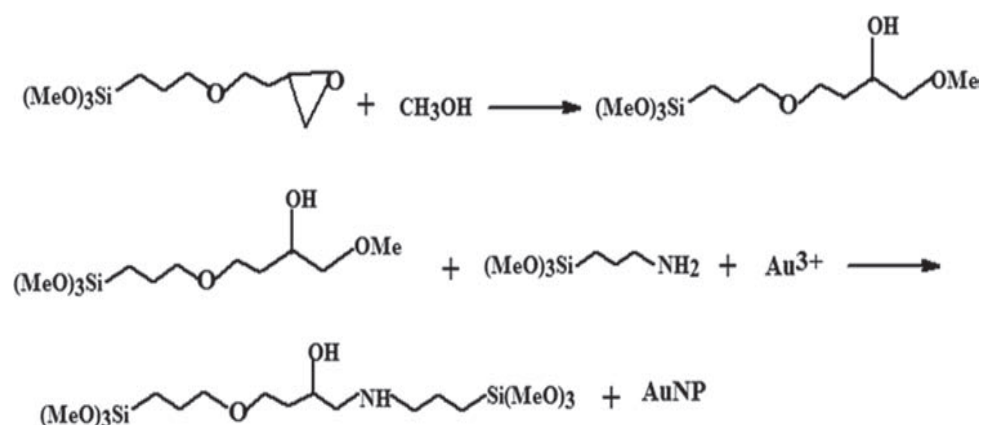
2.4.2. Proposed mechanism for interaction between 3-APTMS and 3-GPTMS during AuNPs synthesis

The findings discussed above provide valuable information related to the synthesis of nanoparticles. It is again necessary here to understand the reactivity of functional constituents to study the mechanism of such process. The specific interaction between 3-APTMS and [2-(3,4-Epoxy cyclohexyl)ethyl] trimethoxysilane results into the formation of solid-state network of organically modified thin film allowing the precise control of hydrophobic and hydrophilic components (Pandey et al., 2003a; Pandey et al., 2001a,2001b). These observations also predict that 3-APTMS may facilitate the reducing ability of 3-APTMS-compatible reducing agent which is a key point during 3-GPTMS mediated synthesis of metal nanoparticles. The epoxide linkage of 3-GPTMS may open in

the presence of methanol as evidenced from the homogenous layer in water after the addition of methanol and such epoxide ring opening leads to hydroxyl and methoxy group functional 3-GPTMS. The interaction of 3-APTMS with metal ions also justify reducing ability of 3-APTMS to metal ions under appropriate reaction conditions. A mechanism of 3-GPTMS mediated synthesis of gold nanoparticles in the presence of 3-APTMS is hypothesized. The proposed mechanism for 3-APTMS and 3-GPTMS mediated synthesis of nanoparticle based on the above observations is shown in Scheme 2.1.

2.4.3. Dispersibility of AuNPs as a function of alkoxy silanes molar ratio

From the results based on the dispersibility of AuNPs, made using varying concentration of 3-APTMS and 3-GPTMS, in solvents of different polarity index as shown in Fig.2.4, Fig.2.5 and Fig.2.6 it can be concluded that the molar ratio of 3-APTMS to 3-GPTMS is a critical factor affecting the dispersible efficiency in organic and aqueous phase. The product formed from the interaction between 3-APTMS and 3-GPTMS is highly hydrophobic due to increased hydrocarbon content as shown in Scheme-2.1.



Scheme 2.1. Mechanism of 3-GPTMS and 3-APTMS assisted formation of AuNPs

Thus, the lower molar ratio is found to be better for the water dispersibility of AuNPs due to relatively less amount of hydrophobic alkyl chain residue. Similarly, the higher molar ratio is found to impart better dispersion efficiency, to the AuNPs, in organic solvent due to increase in the hydrophobic alkyl chain (reaction product of 3-GPTMS and 3-APTMS). To further assess the AuNPs compatibility in different solvents increasing concentration of AuNPs were added to the solvent and UV-Vis spectra were recorded as shown in Fig. 2.7 and Fig. 2.8. The results show linear relation as a function of AuNPs concentrations in toluene and ethyl acetate. The results obtained in Fig. 2.9 and Fig. 2.10 on the variation in λ_{\max} as a function of refractive index and polarity index of different solvents further strengthens the claim for the use of AuNPs made using 3-APTMS and 3-GPTMS indifferent solvents without compromising the stability.

2.5 CONCLUSION

The experimental findings show that HAuCl_4 treated 3-APTMS catalyzes the interaction of 3-APTMS and 3-GPTMS more efficiently as compared to that of the same without HAuCl_4 which is a key point of AuNPs synthesis through proposed reaction scheme. Such reaction results into a hydrophobic reaction product, that control the dispersibility of resulting AuNPs in both aqueous and various organic solvents. Different ratio of alkoxy silane enabling AuNPs to disperse in both aqueous and non-aqueous solvents is discussed. The results demonstrate that AuNPs having higher molar ratio of 3-APTMS to 3-GPTMS have a much better dispersibility in organic solvents whereas the same having lower molar ratio enable the dispersibility in aqueous medium. The observed result justify that the dispersion ability of AuNPs depends on the composition of

reacting functional alkoxy silanes. The absorption maxima of the AuNPs are found as a function of refractive index of the various organic solvents. An application of these nanomaterials is discussed as intrinsic peroxidase-like activity representing the usability towards HRP or HRP-AuNPs coupled catalyzed reaction.