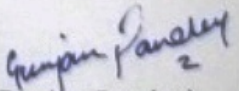


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(Gunjan Pandey)

## PREFACE

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Extensive use of colloidal gold in the field of sensing, therapeutics and catalysis is due to the unique physical and chemical properties they possess, that has led to a surge in its synthesis protocols. There are several techniques available for the synthesis of AuNPs, like Turkevich, Brust-schiffrin and Martin methods. However, such conventional methods have few limitations; (i) generally the AuNPs are produced as aqueous suspension (Turkevich method) and the use of such NPs in organic solvent causes agglomeration. Similarly, the AuNPs having compatibility with organic solvent (Brust- Schiffrin method) are not compatible in aqueous system; (ii) The AuNPs fabricated through conventional routes are generally produced as dilute solution i.e. the initial concentration of AuNPs precursor ( $\text{Au}^{3+}$ ) is very low; (iii) Attempt to convert the homogenous suspension of AuNPs to heterogeneous matrix by adsorbing over some solid support ( $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  etc.) causes an increase in size of the AuNPs or undergo agglomeration. Thus, there is a need to devise a method that can produce stable, concentrated colloidal suspension of AuNPs with the ability to convert from homogeneous suspension to heterogeneous catalyst (in powder form or as thin film) without compromising the catalytic behavior. This constitutes the theme of the present thesis work involving the active participation of functional alkoxy silanes which has shown its potentiality in yielding novel nanostructured material.

Functional Alkoxy silanes like 3-Glycidoxypropyltrimethoxysilane (3-GPTMS), 3-Aminopropyltrimethoxysilane (3-APTMS), epoxy cyclohexyltrimethoxysilane, trimethoxysilane etc. have been used for the synthesis of nanomaterials through sol-gel

process. Some of these alkoxysilanes have behaved as a potential reducing agent for  $\text{PdCl}_2$  allowing the introduction of Pd within nanostructured network of organically modified silicates. Such findings established the role of functional alkoxysilanes (3-APTMS and 3-GPTMS) as reducing agent of noble metal ions and led the way for the use of such functionality during the synthesis of AuNPs and its multimetallic analogue. 3-APTMS capped noble gold ion can be precisely converted to AuNPs in the presence of another alkoxysilane 3-GPTMS or variety of organic reducing agents (THF-HPO, cyclohexanone, formaldehyde, acetaldehyde, acetone, t-butylmethylketone), thus controlling the dispersibility of as made NPs in variety of solvents covering wide range of polarity index. The study has been further extended to the 3-APTMS mediated synthesis of bimetallic (AuPd) and trimetallic (AgAuPd) NPs. 3-APTMS used for the synthesis of AuNPs have following properties: (i) 3-APTMS is **amphiphilic** in nature. Thus, the NPs made using 3-APTMS can be dispersed or fabricated in organic as well as aqueous solvents (ii) The reversible **imine** (-C=N-) linkage formed between amine group of 3-APTMS and organic reducing agent like formaldehyde (-C=O) during AuNPs synthesis has a great propensity to play attractive role in the synthesis of AuNPs. (iii) The 'trimethoxysilyl' group [-Si(OMe)<sub>3</sub>] of 3-APTMS can be utilized for the conversion of homogenous nanoparticle suspension to **heterogeneous** solid matrix without addition of any external support like  $\text{TiO}_2$ . The trimethoxysilyl group can also be utilized for casting film of the nanomaterial through sol-gel processing.

These considerations, inter alia, prompted me to take up the present work. The thesis is organized into seven chapters with 'Summary and Future Projection' at the end. Chapter (I) 'General Introduction' reviews the current status of the subject and gives the reasons for

embarking upon the present study. Chapter (II) deals with the synthesis and dispersibility of the AuNPs synthesized using 3-APTMS and 3-GPTMS where the synthesized AuNPs were dispersible in organic solvents at all concentration of 3-APTMS and 3-GPTMS while dispersibility in water required low concentration of either 3-APTMS or 3-GPTMS. Chapter (III) explores the suitability of THF-HPO as reducing agent with 3-APTMS to form the AuNPs in aqueous medium. Imine linkage (Organic-inorganic hybrid) formed between 3-APTMS and GBL assists AuNPs in displaying peroxidase mimetic ability as the linkage is catalytic in nature. The improved dispersibility (both in water and organic solvents) and stability of AuNPs in the presence of 3-APTMS and cyclohexanone is described in Chapter (IV). Further, the AuNPs suspension is converted to homogenous nanocomposite suspension with PBNPs and ruthenium bipyridyl solution [AuNPs-PBNPs-Ru(bpy)] justifying even better catalytic ability than that of HRP. The next chapter (Chapter V) deals with the use of homologous series of carbonyl group (“-C=O”) containing organic reducing agents i.e. formaldehyde (HCHO), acetaldehyde (CH<sub>3</sub>CHO) and acetone (CH<sub>3</sub>COCH<sub>3</sub>) for the fabrication of 3-APTMS mediated AuNPs. The pH- and Salt- sensitivity of AuNPs has been monitored as a function of reducing agent and 3-APTMS concentration. A typical example on the role of AuNPs in homogenous catalysis during potassium ferricyanide mediated oxidation of ascorbic acid is also reported. Chapter (VI) describes the “one pot two step” rapid synthesis of trimetallic (Ag/Au/Pd) NPs utilizing 3-APTMS and formaldehyde. The synthesized trimetallic NPs behave as excellent catalyst for the reduction of PNP to PAP both in homogenous suspension and as heterogenous solid matrix. Bifunctionality of 3-APTMS has been utilized in the last chapter (VII) for the fabrication of hybrid between AuNPs and porous siloxane matrix. Solvent induces the formation of the hybrid which is mainly obtained in the case of organic

solvents. Use of water as synthesis media yields spherical AuNPs without the formation of siloxane polymer. The reversible imine linkage between 3-APTMS [ $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OMe})_3$ ] and acetone [ $\text{CH}_3(\text{CO})\text{CH}_3$ ] is exploited for AuNPs synthesis both in suspension and over a solid support. AuNPs layer made over solid support is used repeatedly for the reduction of PNP in the presence of excess  $\text{NaBH}_4$ .

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