3-Aminopropyltrimethoxysilane mediated synthesis of Gold Nanoparticles and its Multimetallic analogue

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By

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SUMMARY AND FUTURE PROJECTION

The thesis entitled “3-Aminopropyltrimethoxysilane mediated synthesis of Gold Nanoparticles and its Multimetallic analogue” has been devided into seven chapters.

(i) General Introduction

(ii) Functionalized alkoxysilane mediated synthesis of Gold Nanoparticles dispersible in aqueous and non-aqueous medium.

(iii) 3-Aminopropyltrimethoxysilane and Tetrahydrofuranhydroperoxide mediated synthesis of Gold Nanoparticles : Application in glutathione sensing

(iv) Cyclohexanone role during the synthesis of 3-Aminopropyltrimethoxysilane mediated Gold Nanoparticles and its comparison with other mild reducing agents.

(v) 3-Aminopropyltrimethoxysilane and organic carbonyl moiety role during the synthesis of Gold Nanoparticles specific to pH- and salt- Tolerance.

(vi) 3-Aminopropyltrimethoxysilane Mediated rapid synthesis of Ag@AuPdTrimetallic Nanoparticles.

(vii) 3-Aminopropyltrimethoxysilane mediated solvent induced synthesis of Gold Nanoparticles.

Chapter I

Chapter 1 “General introduction” opens up with the brief introduction about nanoparticles (NPs) and gold nanoparticles (AuNPs). The famous methods available for the synthesis of

AuNPs like turkevisch method, brust-schiffrin method, martin method have also been discussed in detail. Various shapes of AuNPs (nanocages, nanospheres, nanoshells, nanorods etc.) that can be obtained following different synthesis protocols have also found mention in the introductory chapter. The unique physical and chemical properties (redox activity, surface plasmon resonance and fluorescence quenching etc.) of AuNPs that have led to the exploitation of these NPs in the field of sensing (colorimetric sensing, fluorescence-based sensing, electrical sensing, electrochemical sensing), therapeutics and catalysis is discussed in detail. Finally, the origin, motivation and work plan for the present thesis work is also discussed.

Chapter II

Functional alkoxysilanes, specifically 3-Aminopropyltrimethoxysilane (3-APTMS) and 3-Glycidoxypropyltrimethoxysilane (3-GPTMS), mediated synthesis of AuNPs in methanolic medium has been dealt with in detail in chapter II. It has been found that the interaction between 3-APTMS and 3-GPTMS is important for the synthesis of AuNPs as neither of them resulted in AuNPs when used alone with methanolic solution of gold ion (Au^{3+}). Also, experimental findings have revealed that the interaction between 3-APTMS and 3-GPTMS is enhanced in the presence of Au^{3+}compared to the interaction of same without Au^{3+}. Such reaction results into a hydrophobic reaction product, that control the dispersibility of resulting AuNPs in both aqueous and various organic solvents. Dispersibility of the AuNPs, in aqueous and various organic solvents, made using 3-APTMS and 3-GPTMS was monitored under different conditions. The results demonstrate that AuNPs having lower value for molar ratio of 3-APTMS to 3-GPTMS have a much better dispersibility in aqueous medium whereas the higher molar ratio favored the dispersibility of the same in organic solvents. The absorption maxima of the NPs are found to vary 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.

Chapter III

In chapter (III) 3-APTMS and Tetrahydrofuranhydroperoxide (THF-HPO) have been used for the synthesis of AuNPs in aqueous medium. The effect of reactant concentrations i.e. 3-APTMS and THF-HPO, on the size of AuNPs is monitored and an increase in the size of the AuNPs with increasing 3-APTMS concentration whereas decrease in size with increasing THF-HPO concentration is observed. Nanogeometry of as synthesized AuNPs can further be manipulated by addition of 3-APTMS even after the synthesis of AuNPs. The flexibility in the synthesis technique allows formation of AuNPs of desired size at desired 3-APTMS and THF-HPO concentrations. It has been observed that during the synthesis of AuNPs, THF-HPO is converted to γ-butyrolactone (GBL) which itself participates in nanoparticle formation under optimum concentration and forms imine derivative of GBL with 3-APTMS. The as synthesized amine functionalized AuNPs also display peroxidase mimetic behaviour and has an additional advantage as amine functionality assists the AuNPs in its catalyzing/sensing ability. The nanoparticles synthesized differ from other conventional nanoparticles in its catalyzing ability that increases with increasing size which is attributed to the combined effect of nanogeometry and functionality (catalytic imine linkage). When the effect of size was studied alone by keeping amine functionality constant it showed the conventional (smaller size higher catalysis) behavior towards catalysis. The as synthesized AuNPs with tunable functionality and nanogeometry has been used further for glutathione sensing in the present chapter and may be used for various applications in the future.

Chapter IV

Cyclohexanone is used with 3-APTMS for the synthesis of AuNPs and a comparative study on the role of organic reducing agents (3-GPTMS, THF–HPO and cyclohexanone) during 3-APTMS mediated controlled synthesis of AuNPs is presented in Chapter IV. The AuNPs differ from each other in properties such as dispersibility, catalysis, stability etc. thus making them available for use in various applications. In a bid to get 3-APTMS mediated AuNPs having better stability and dispersibility than with THF–HPO and 3-GPTMS, cyclohexanone was used. AuNPs can be dispersed in different solvents (organic or aqueous) by adjusting the constituents (3-APTMS/cyclohexanone) ratio. Thus, the use of different reducing agents having compatibility with different solvents results in AuNPs with significant variation in properties from each other, presenting the option to select AuNPs for specific applications either in aqueous or organic media. These nanoparticles display functional ability to form monophasic nanocomposites for homogenous catalysis with Prussian blue nanoparticles and ruthenium bipyridyl for specific application as peroxidase mimetic. In addition to that, the nanoparticles also enable the formation of nanocomposites with Prussian blue useful as heterogeneous redox catalysts displaying excellent electrochemical properties as a function of nanogeometry. Both mimetic and electrocatalytic ability could be explored for probing glucose oxidase catalyzed reactions, justifying the potential viability in biomedical applications.

Chapter V

Aldehydes (formaldehyde, acetaldehyde) and Ketones (acetone, t-butylmethylketone) have been used as mild reducing agent with 3-APTMS for the synthesis of AuNPs. Chapter describes that the 3-APTMS capped Au^{3+} can be precisely converted into respective nanoparticle in the presence of formaldehyde, acetaldehyde, acetone and t-butylmethylketone having pH- and salt- tolerance ability. An increase in alkyl content significantly influence the dispersibility in various working medium. A decrease in hydrocarbon content of the organic reducing agent nanoparticles causes increased compatibility with water. Besides imparting desired compatibility to the AuNPs, the organic reducing agents also affect the pH sensitivity of the AuNPs with aldehydic AuNPs (made using 3-APTMS and formaldehyde/acetaldehyde) being more pH-tolerant compared to ketonic AuNPs (made using 3-APTMS and acetone/t-butylmethylketone). Also, an increase in 3-APTMS concentration increases the salt- and pH-tolerance of the AuNPs. These findings have been exploited in justifying charge tranport dynamics at electrochemical interface resulting from the electrochemical behavior of $Fe(CN)_6^{3-}/Fe(CN)_6^{2-}$redox system. The presence of AuNPs facilitates the charge transport process and introduces electrocatalysis in reacting system.

Chapter VI

A simple and rapid method has been described for the synthesis of PdNPs under ambient conditions, from 3-APTMS and formaldehyde which is further extended to Ag@(PdAu) trimetallic nanoparticles via (AuPd) bimetallic nanoparticles. The as-synthesized monometallic, bimetallic and trimetallic nanoparticles are characterized by UV-Vis spectroscopy, TEM and XPS. The trimetallic nanoparticle suspension is found to be highly catalytic for PNP reduction to PAP with a rate constant value of 0.14 ± 0.0025 s^{-1}. 3-APTMS used serves dual purpose: (1) as a stabilizer and (2) as a precursor to the solid matrix. The point that further favors the conversion of the homogenous suspension to the solid matrix is that the nanoparticles do not get affected by HCl addition. Upon addition of a small amount of acid, Si–O–Si linkages are formed leading to the solid matrix being embedded with nanoparticles. This is used as a heterogeneous catalyst which can be recycled easily and can be used as a catalyst again.

Chapter VII

Amphiphilic and bifunctional nature of 3-APTMS has been utilized in this chapter for the fabrication of AuNPs in different solvents and for the formation of hybrid between AuNPs and siloxane matrix respectively. 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. The characterization data reveal the formation of "siloxane-gold" NPs in case of organic solvents while discrete AuNPs were seen in case of water as a solvent. The siloxane polymer formed from 3-APTMS and acetone has been used for the synthesis of AuNPs over siloxane polymer both in suspension and solid state utilizing the reversible imine linkage formed between the amine group of 3-APTMS and carbonyl group of acetone. The AuNPs made in solid state is used as catalyst for the reduction of PNP to PAP in the presence of excess $NaBH_4$ whereas the AuNPs produced as suspension can be made into excellent thin films.

FUTURE PROJECTION

The present study deals with the synthesis of functionalized monometallic AuNPs, bimetallic (AuPd)NPs and trimetallic Ag/(AuPd)NPs involving the functional activity of 3-APTMS and a variety of other organic reducing agents including 3-GPTMS. Depending on the reducing agents used these NPs differ in the solvent being used for synthesis and solvents for dispersing the NPs.

The concentration of the precursor ion and hence of AuNPs can be varied from as low as 0.25mM to as high as 25mM. The AuNPs can be used in suspension form, as thin film or in powder form as reusable catalyst. Thus, we see that the AuNPs made this way evades many unnecessary steps that have to be overcome to make the AuNPs (conventional) suitable for particular application for use in aqueous and non aqueous system. Accordingly, the NPs derived through such processes can be used as a catalyst in many synthetic reactions that needs to be explored in due course.

Functional alkoxysilanes have been exploited for the formation of nanostructured materials/thin film for use in various chemical sensor and biosensor fabrication. Accordingly, the NPs derived through current process can be further explored for in-situ encapsulation within nanostructured matrix having potential application in electrocatalysis/biocatalysis.

Alkoxysilane have been used in making mesoporous silica nanoparticles having potentiality for in-vivo biomedical application since such materials are not cytotoxic. The present process can aid the incorporation of AuNPs and other biocompatible metal nanoparticles within mesoporous silica nanoparticles. Due to the unique merits of as derived materials, the number of studies can be conducted for *in-vivo* biomedical applications specifically in drug delivery, bioimaging etc.

Silica part of 3-APTMS is used for the formation of mesoporous silica while the amino group can be used to form important biological linkage via imine linkage. AuNPs have also proved their worth in many diseases more importantly cancer. Thus a combination of two can have far better results in curing the disease.

Thus the present thesis largely deals with the synthesis routes and properties of 3-APTMS mediated nanoparticles and application of such nanomaterials in various important fields remain unexplored and needs to be addressed in future.