Summary

The thesis entitled "Studies on 3-Aminopropyltrimethoxysilane mediated synthesis of Silver and Palladium nanoparticles and their application in chemical sensing" has been divided into following five chapters:

1. General Introduction
2. Synthesis and characterization of Silver nanoparticles.
3. Synthesis and characterization of Palladium nanoparticles.
4. Synthesis and characterization of Bimetallic nanoparticles and Nanocomposites.
5. Intrinsic peroxidase-like and Electrocatalytic activity of Nanomaterials.

Chapter 1 describes an overview of noble metal nanoparticles (NMNPs), bimetallic nanoparticles (BMNPs) and Nanocomposites. An extensive literature survey on synthesis of Silver nanoparticles (AgNPs), Palladium nanoparticles (PdNPs), BMNPs and Nanocomposites was reported. The use of these nanomaterials in electroanalytical applications as well as peroxidase-mimetic activity was critically reviewed followed by definition of the problem, objective of the present investigation together with the work plan.

Chapter 2 describes the synthesis and characterization of Silver Nanoparticles (AgNPs) mediated by involving the active participation of 3-APTMS and GPTMS. The mechanistic approach on the reduction of silver ions in the presence of these two alkoxysilanes is reported. The rate of AgNPs formation is faster on increasing GPTMS concentration whereas the similar increase in rate is observed on decreasing 3-APTMS concentrations. The size of AgNPs varies as a function of 3-APTMS and GPTMS concentration.The resulting AgNPs are dispersible in both aqueous and non-aqueous solvents based on the molar ratio of 3-APTMS and GPTMS. An increase in molar ratio of GPTMS to 3-APTMS results better dispersibility of AgNPs in water while decrease in molar ratio of GPTMS to 3-APTMS lead better dispersibility in toluene. The dispersion ability of AgNPs is attributed to the hydrophobic alkyl chain of the reaction product of GPTMS and 3-APTMS. The absorption maxima of the AgNPs are found as a function of refractive index of the various organic solvents.

The use of two alkoxysilanes during the synthesis of AgNPs may encounter problems during specific applications as such nanoparticles may be susceptible to autohydrolysis, condensation and polycondensation. Accordingly, efforts have been made to replace one of the alkoxysilane by suitable organic reducing agents that may overcome such limitations. The use of Cyclohexanone is therefore demonstrated that rapidly converts 3-APTMS capped silver ions in AgNPs. Since cyclohexanone relatively hydrophobic in nature and generate biphasic system beyond the micellar activity of 3-APTMS accordingly, another organic reagent namely Formaldehyde has been used during the synthesis of AgNPs from 3-APTMS capped silver ion. The hydrophilic nature of the reagent control the dispersibility of as made nanoparticles in specific applications. Such organic reducing agents also enables the formation of organic- inorganic hybrid that facilitated catalytic activity of the as made nanoparticles.

Chapter 3 describes the synthesis and characterization of Palladium Nanoparticles (PdNPs). The role of 3-APTMS during the synthesis of PdNPs has been evaluated from the use of cyclohexanone that allow the formation of PdNPs in presence or even in absence of 3-APTMS. In the absence of 3-APTMS, PdNPs having excellent polycrystallinity and hexagonal nanogeometry. While in the presence of 3-APTMS the polycrystallinity and nanogeometry of PdNPs is drastically changed. The polycrystallinity and nanogeometry of PdNPs are found as a function of 3-APTMS concentration. An increase in 3-APTMS concentration there is increase in nanogeometry and decrease in polycrystallinity while the shape of PdNPs becomes circular. Such variation in microstructure and polycrystallinity of PdNPs found mainly due to interaction of silanol residue with as generated PdNPs made in the presence of 3-APTMS. The as synthesized PdNPs dispersible in variety of solvents having different polarity index and shows excellent mimetic ability with Km value to the order of 3.6 mM indicating complete replacement of HRP. Simultaneously the synthesis of PdNPs in the presence of tetrahydrofuran hydroperoxide (THF-HPO) is reported that allow the conversion of Palladium ions into palladium nanoparticles only in the presence of suitable concentrations of 3-APTMS that allows the rapid synthesis of PdNPs under ambient conditions with variable nanogeometry. The nanogeometry of PdNPs is found as a function of 3-APTMS concentration. PdNPs dispersible in variety of solvents having different polarity index and applicable for heterogeneous catalysis.

Chapter 4 describes the synthesis and characterization of Bimetallic Nanoparticles (BMNPs) and Nanocomposites. The synthesis of BMNPs of Pd-Au/Au-Pd involves the active role of hydrophilic organic reagent THF-HPO and 3-APTMS capped metal ions at desired ratio via two processes Simultaneous and Sequential under ambient conditions. During the synthesis of BMNPs of Pd-Au and Au-Pd justifies potential affinity of PdNPs with silanol group whereas AuNPs do not show such affinity. In Sequential synthesis, initial reduction of palladium ions followed by reduction of gold ions during the synthesis of bimetallic nanoparticles results in negligible interaction of the silanol residue and PdNPs justifying an increase in polycrystallinity whereas simultaneous reduction of the same enable a decrease in polycrystallinity. Subsequently, initial reduction of gold ions causes aggregation of the same forming larger nanoparticles and reveals negligible interaction with silanol content under similar conditions. The BMNPs of Ag-Au or Au-Ag using cyclohexanone and 3-APTMS exhibit improved catalytic performance because of both synergistic and electronic effects. The use of the use of common reducing agent like 3-APTMS and cyclohexanone also enables the synthesis of polycrystalline PBNPs that allows the formation of nanostructured composites with a crystallized framework having excellent tuning with Au-Ag nanoparticles for colorimetric and electrocatalytic applications.

Chapter 5 divided into two sections, first section deals with the Intrinsic-peroxidase like activity of nanomaterials and the second section describes the electrocatalytic activity of nanomaterials. In first section the intrinsic peroxidase like activity of Nanocomposites of PBNP-AgNPs/Au-Ag and PdNPs, capable of catalyzing the oxidation of o-dianisidine by H_2O_2 to give the same colour change as natural peroxidase. Major findings of this section concluded as follows: (i) the PBNP-Au-AgNP nanocomposite show an enhanced catalytic efficiency as compared to that of PBNPs and PBNP-AgNP made under similar conditions; (ii) The relative variation in the kinetic catalytic activity of PBNP-AgNP and PBNP-Au-AgNP was examined for H_2O_2 detection and found in the order of: PBNP-Au-AgNP > PBNP-$AgNP_2$ > PBNP-$AgNP_1$ > PBNP-AgNP (I) > PBNPs; (iii) The results justified the better kinetic catalytic behavior of PBNP-Au-AgNP as compared to that of PBNPs and PBNP-AgNP revealed the bimetallic nanocomposite is more catalytic than monometallic nanocomposite as well as PBNPs; (iv) the catalytic property of PdNPs made with increasing concentrations of 3-APTMS and cyclohexanone on the oxidation of *o*-dianisidine-H_2O_2 system; (v) the K_m value of PdNPs increases with increase in 3-APTMSconcentrations; and (vi) the relative variation in the kinetic catalytic activity of PdNPs was examined for H_2O_2 detection and found in the order of: $PdNP_1$>$PdNP_2$>$PdNP_3$> $PdNP_4$.

In second section the applicability of above synthesized nanometerials in electrocatalytic sensing of two biologically important analytes viz., H_2O_2 and Ascorbic Acid (AA). The electro-analytic findings reported in this chapter provided deeper insight on electrochemical sensing specifically: (i) an efficient H_2O_2 sensor has been fabricated based on application of PBNPs and its nanocomposite with AgNP (I); (ii) the PBNP-AgNP (I) nanocomposite significantly increased the sensitivity of H_2O_2 analysis as compared to that of PBNPs, reflecting the contribution of AgNP (I) in electrocatalysis; (iii) 3-APTMS is found to influence the redox electrochemical behavior of Fc-COOH in polar medium; (iv) PdNPs synthesized through 3-APTMS and THF-HPO gradually improves the electrochemistry of Fc-COOH as a function of nanogeometry and usability in synthesizing the electrochemical sensor design; (v) These findings indicate admirable reproducible and stable electrochemical behavior of the Fc-COOH-PdNPs during AA detection.