PREFACE

Nanomaterials derived through sol-gel processing of alkoxysilanes have received great attention bridging chemistry, physics, biology, medical and engineering disciplines. Such nanomaterials not only provide suitable matrix for encapsulating sensing element but also introduce catalysis in sensing events when used in chemical sensor design. The presence of suitable organic functionality in alkoxysilanes introduce extra event in controlling the wettability of nanomaterial alongwith options for anchoring the targeted sites within organically modified silicates (ORMOSIL) network. In addition to that specific interaction between palladium chloride and 3-glycidoxypropyltrimethoxysilane (GPTMS) and Trimethoxysilane allow introducing palladium within nanostructured network together the existence of palladium-silicon linkage that facilitate in displaying excellent redox electrochemistry of ormosil-encapsulated electron transfer mediator even better than that recorded in homogeneous solution. Similarly the role of amino-functionality linked to alkoxysilanes (3-APTMS) has been demonstrated to enhance the stability of metal nanoparticles for practical applications. These finding demonstrated the reducing ability of functional alkoxysilanes and directed us to understand whether such functional activity could be exploited in controlled synthesis of noble metal nanoparticles specifically silver (AgNPs) and palladium (PdNPs) nanoparticles which has been undertaken in the current research program.

Indeed interesting finding on the controlled conversion of 3-APTMS capped silver ions into AgNPs in the presence of GPTMS is recorded yielding a novel route of functional noble metal nanoparticles synthesis (NMNPs) that can be converted into nanostructured thin film or may be used as homogeneous suspension with tunable functionality and nanogeometry due to micellar behavior of 3-APTMS. The choice of small organic reducing agent in place of GPTMS during such process of NMNPs synthesis may also introduce extra event through the formation of organic-inorganic hybrid that may further enhance the catalytic activity of as synthesized NMNPs. The findings on the conversion of 3-APTMS capped silver and palladium ions into AgNPS and PdNPs in the presence GPTMS/tetrahydrofuran hydroperoxide/cyclohexanone/formaldehyde are studied in details having better potentiality for practical applications. The new process not only allows the formation of monometallic nanoparticles but also enabled rapid synthesis of bimetallic nanoparticles synthesis (BMNPs). The synthesis of bimetallic nanoparticles of Ag-Au and Pd-Au are studied in details herein. The use of common reducing agents and the micellar activity of 3-APTMS also allow in the formation of nanocomposite with other functional material tuning the catalytic activity of parent components. The nanocomposite of AgNPs, Ag-Au and Prussian blue (PBNPs) nanoparticles are reported in the present thesis.

Accordingly, the present thesis describes a new route for the synthesis of Metal nanoparticles (AgNPs/PdNPs/Pd-Au/Au-Pd/Au-Ag/Ag-Au) and Nanocomposites (PBNP-AgNP/PBNP-Au-Ag) involving the active participation of 3-APTMS and GPTMS/formaldehyde/cyclohexanone/ tetrahydrofuran hydroperoxide from their corresponding salts. The various parameters like nanogeometry, polycrystallinity, functional ability, dispersibilty in various polar and non-polar solvents and processability for nanocomposite formation are precisely controlled during synthesis through the suitable choice of reacting components and reported in the thesis. The catalytic activity as peroxidase mimetics of as synthesized Nanocomposites and PdNPs have been examined for justifying the functional ability and tuning of parent components during nanocomposite formation. In addition to that the ability of as made nanomaterials has also been examined as electrocatalyst for use in chemical sensor design. The thesis has been divided into five chapter's namely; (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 deals with the general introduction including the results of earlier studies done on synthesis and applications of Noble metal nanoparticles (silver, palladium, gold and their bimetallic) in chemical sensing.

Chapter 2 describes the synthesis of AgNPs from 3-APTMS capped silver ions. The role of 3-APTMS compatible reducing agents like GPTMS, tetrahydrofuran hydroperoxide, formaldehyde and cyclohexanone has been studied to control the AgNPs synthesis displaying specific properties as a function of organic reducing agents. The as synthesized AgNPs has been characterized by UV-Vis and transmission electron microscopy.

Chapter 3 describes the synthesis of 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 even in absence of 3-APTMS. 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. The characterization of as made PdNPs are precisely evaluated from UV-Vis spectroscopy and electron transmission microscopy.

Chapter 4 describes the synthesis of BMNPs (Pd-Au/Au-Pd/Au-Ag/Ag-Au) and Nanocomposites (PBNP-AgNP/PBNP-Au-Ag). Simultaneous and sequential mode of Pd-Au/Au-Pd synthesis is investigated from the use of 3-APTMS and THF-HPO. In addition to that the use of common reducing agent like 3-APTMS and cyclohexanone has been studied for the synthesis of PBNPs and Ag-Au that enable the formation of nanocomposite having potentiality for both homogeneous and heterogeneous catalysis.

Chapter 5 describes the typical applications of as made AgNPs/PdNPs/ BMNPs/nanocomposite. Two specific applications namely as peroxidase mimetics and electrocatalysis of hydrogen peroxide and ascorbic acid are studied. The findings revealed excellent catalytic activity even better than that of Horseradish peroxidase for practical applications. In addition to that the redox electrochemistry of ferrocene monocarboxylic acid has been also evaluated as a function of palladium nanogeometry for electrocatalytic applications.

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