PREFACE

Nanoscaled metal colloids have attracted much attention over recent decades for their potential applications in science and technology. Nanorange particles particularly palladium nanoparticles (PdNPs) possess size and shape dependent unique properties, in contrast to those of bulk materials and direct for thorough search on the synthesis and applications of the same on these lines. Designing the palladium nanocrystals with homogeneous nucleation and well controlled morphological characteristics has been a challenging task. Ongoing progress in synthetic techniques has led to the derivation of various encouraging methods to prepare the PdNPs with various geometrical shapes and sizes. PdNPs have been obtained using various strategies like top-down approach, which includes mechanical scrapping of metals and stabilization by surfactants, bottom-up approach which involve wet chemical synthesis by following methods like chemical vapour infiltration, arc discharge, polyol reduction, thermal decomposition of organometallic complexes, intermatrix synthesis (IMS), electrochemical deposition, digestive ripening, and chemical reduction using $NaBH_4$. Most of the above cited procedures, observe certain obvious limitations like they do not confirm the dispersibility of resulting nanoparticles in wide range of solvents, which is of absolute importance in deciding their utility for the practical purposes. Additionally, these involve the complex synthetic multistep pathway which last for hours and lead to broad particle size distributions. Thus the current research program is integrated to develop an effective mechanism for preparing the PdNPs in order to deal with the stringent issues.

The present study describes the synthesis of PdNPs, derived using the functionalized alkoxysilanes like 3-glycidoxytrimethoxysilane (GPTMS) and 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane (EETMS), in the presence of polymeric stabilizer (PVP). EETMS mediated preparation results in well dispersed, stabilized and monodispersed nanoparticles with higher palladium content. Alkoxysilanes (APTMS, GPTMS, EETMS and TMS) have gained considerable attention over recent past, for their potentiality in nanostructured thin film formation and synthetic utility. APTMS in combination with various organic reducing agents like aldehydes, ketones, tetrahydrofuran-hydroperoxide (THF-HPO) and also other alkoxysilanes (GPTMS) for fabricating an array of mono as well as multimetallic noble metal (Ag, Au and Pd) nanoparticles. Further, the alkoxysilanes like APTMS, EETMS and TMS along with HCl lead to the formation of organically modified silicates (ORMOSIL), keeping up the balance over hydrophilic and hydrophobic components. Therefore an attempt has been made to recognize the role of alkoxysilanes (EETMS, GPTMS) in generating PdNPs with exceptional characteristics. The constructed nanoparticles have been exploited in a versatile manner for some relevant applications that are deliberately discussed in the withstanding thesis.

The thesis has been divided into seven odd chapters, where the role of EETMS has been explored from different viewpoints in an elementary manner. Chapter I subsume the critical overview of the research area focusing on the synthesis mechanisms, catalytic properties and potential applications, along with a precise account of the origin, objectives and work plan of the respective research program. A detailed discussion on the synthesis of PdNPs using EETMS as the reducing agent, including the concentration (EETMS) dependent changes in the structural features has been incorporated in Chapter II. Also the systematic investigations on morphology dependent enhancement in Raman cross sections, using PdNPs as SERS substrates have been reported here.

Chapter III describes the effect of graphene oxide (GO) on the synthesis of PdNPs using EETMS and GPTMS as reducing agents. The role of organic functionalities of graphene sheets on the dispersibility and the stability of the nanocomposites (Pd/GO/EETMS and Pd/GO/GPTMS), which enables their encapsulation in microgel beads also been undertaken. Developed material has been used as an efficient catalyst for the decomposition of hydrazine hydrate.

Chapter IV involves the discussion on assembling the artificial enzyme carrier system by incorporating the EETMS stabilized PdNPs into the polysaccharide network of sodium alginate. Alkoxysilane (EETMS) adds rigidity by contributing hydrophobic nature to the system, which prevents the leaching of enzyme.

Chapter V elucidates the synthesis of multimetallic analogues of PdNPs (Ag@PdNPs, Au@PdNPs) in aqueous and non aqueous media, by adopting the template approach. Colloidal particles are assembled over electrodes in ordered fashion to generate uniform thin film by the bifold action of APTMS and EETMS. Modified electrodes are used as electrocatalyst for the pH dependent oxidation of an important bioanalyte, L-Tryptophan.

Chapter VI describes the strategic synthesis of triple layered metal colloids (Ag@Ru@PdNPs) using two step template approach, through sequential pathway. The as-designed nanoparticles are employed as model catalyst for studying the electrochemical oxidation of Ascorbic acid.

Chapter VII deals with the development of an efficient route to obtain bimetallic Ni-Pd catalyst in order to stabilize the nickel nanoparticles under the concerted action of EETMs and PVP. As-synthesized material is used as versatile and efficient electrolyser for the water splitting reaction in basic medium. The activity of the catalyst is also investigated after several calcination events by converting it to solid pellets.

Chapter VIII describes the epitaxial growth of gold nanoparticles (AuNPs) over the exfoliated sheets of graphene and reduced graphene oxide. The synthesized AuNPs are used for both hetero and homogeneous catalytic reactions. Their nanocomposites with PdNPs are observed to effectively catalyse the electrochemical reduction of H_2O_2.

The contents of the thesis have been published in *Advanced Science, Engineering and Medicine*, 2016, *8*, 271-283, *RSc Adv*, 2016, 6, 80549-80556, *Journal of Materials Research*, 2017, *32*, 3574-3584, *Journal of Sol-Gel Science and Technology*, 2018, 86, 650–663.

designed nanoparticles are employed as model catalyst for studying the electrochemical oxidation of Ascorbic acid.

Chapter VII deals with the development of an efficient route to obtain bimetallic Ni-Pd catalyst in order to stabilize the nickel nanoparticles under the concerted action of EETMs and PVP. As-synthesized material is used as versatile and efficient electrolyser for the water splitting reaction in basic medium. The activity of the catalyst is also investigated after several calcination events by converting it to solid pellets.

Chapter VIII describes the epitaxial growth of gold nanoparticles (AuNPs) over the exfoliated sheets of graphene and reduced graphene oxide. The synthesized AuNPs are used for both hetero and homogeneous catalytic reactions. Their nanocomposites with PdNPs are observed to effectively catalyse the electrochemical reduction of H_2O_2.

The contents of the thesis have been published in *Advanced Science, Engineering and Medicine*, 2016, *8*, 271-283, *RSc Adv*, 2016, 6, 80549-80556, *Journal of Materials Research*, 2017, *32*, 3574-3584, *Journal of Sol-Gel Science and Technology*, 2018, 86, 650–663.