

**Study of 2-(3, 4-epoxycyclohexyl)ethyltrimethoxysilane mediated synthesis and Catalytic applications of Palladium nanoparticles and its multimetallic analogues**



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**By**

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# SUMMARY

The thesis entitled "Study of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane mediated synthesis and catalytic applications of Palladium nanoparticles and its multimetallic analogues" has been divided into seven chapters.

- General Introduction
- Fabrication of monometallic palladium nanoparticles and investigations on the effect of alkoxysilanes on the Fluorescence emission intensity
- Mesoporous silica beads encapsulated with graphene oxide and alkoxysilane functionalized palladium nanoparticles: Novel catalyst for selective hydrogen evolution
- Flexible approach to design Organosilane Modified Microscaled Carrier to Facilitate Homogeneous Enzyme Loading for Glucose Detection
- Solvent Dependent Fabrication of Bifunctional Nanoparticles and Nanostructured Thin Films by Self Assembly of Organosilanes
- 2-(3,4-Epoxycyclohexyl)Ethyltrimethoxysilane Intervened Synthesis of Functional PdNPs and Heterometallic Nanocrystallites; Deployed Into Catalysis
- Alkoxysilane Functionalized Hybrid Ni-Pd Nanocatalysts as Efficient Electrolyser for Hydrogen Evolution Reaction

## Chapter I

Chapter one gives a brief overview of the synthesis, properties and catalytic applications of Palladium nanoparticles (PdNPs). Various known methods of synthesis have been comprehensively discussed in the chapter. The effect of steric and electrostatic stabilisation on the particle size and heterogeneity of the colloidal dispersion has been thoroughly reviewed. The remarkable properties (electronic, catalytic, etc) and viable applications of PdNPs (like, electrochemical catalysis, sensor designing, homogenous and heterogenous catalysis of organic reactions, etc) have been taken up briefly. The synthesis and the importance of multimetallic analogues over the monometallic ones have been equally focused. Conclusively, the objective, origin and the work plan of the study have been stated precisely.

## Chapter II

A facile one step route to solution phase synthesis of anisotropic palladium nanoparticles using EETMS as reducing agent has been described in this chapter. EETMS acts as reducing, stabilizing as well as structure directing agents, which controls the morphology and crystallinity of PdNPs. Particle size is the exact function of the molar concentration of EETMS, large polyhedron nanostructures are transformed to tiny spherical particles depending on the amount of EETMS supplied. The model anisotropic nanoparticles are utilized as effective MEF substrates, to study the precise variations in the fluorescence emission intensity, due to alkoxy silanes which are responsible for regulating the distance related effects and coupling with different fluorophores. They can be utilized as potential probes for several fluorescence based applications in future.

## Chapter III

A novel and highly effective methodology to fabricate the mesoporous silica alginate beads with precisely controlled pore sizes (2–10 nm) has been demonstrated in this chapter. Graphene oxide (GO) and EETMS functionalized palladium nanoparticles are introduced into the polysaccharide matrix of alginate hydrogel to form silica modified microspheres, with controlled hydrophilicity and improved rigidity. The fabricated composites have exceptionally tunable catalytic properties and were utilized as heterogeneous catalysts, specifically for hydrogen evolution from the decomposition of hydrazine. Out of different systems (silica beads encapsulated with Pd/GPTMS, Pd/EETMS, Pd/GO/GPTMS, and Pd/GO/EETMS), one with Pd/GO/EETMS nanoparticles, is found to be highly active material, justifying the role of alkoxy silane in improving the properties of the materials. When treated at elevated temperatures, silica beads

with Pd/GO/EETMS nanoparticles attained mesoporous framework with enhanced rigidity and are found to exhibit the highest level of catalytic activity. This miniaturized machinery can be reliably adopted for various other applications. Also, an investigation on the fabrication of graphene oxide (GO) mediated gold nanohybrids, has been discussed in this chapter. The synthetic procedure involved active participation of GO, 3-aminopropyltrimethoxysilane and formaldehyde. APTMS acts as a surface modification and capping agent while GO sheets provide nucleation sites for epitaxial growth of gold nanoparticles. Graphene oxide and APTMS have a mutual control over the particle size and do not permit the agglomeration.

#### **Chapter IV**

The designing of mesoporous framework of silica-alginate beads as a suitable support material for enzyme encapsulation has been illustrated in this chapter. The fabrication of such biohybrid assembly involves a simple two-step straight forward process, which ultimately results in ordered pore structure with outstanding chemical stability. Introduction of alkoxy silane functionalized nanoparticles induces direct chemical cross-linking between residual functional moieties of alkoxy silane, alginate hydrogel, and the protein molecules (glucose oxidase). The hydrophilic alginate hydrogel is transfigured to relatively hydrophobic material on interaction with lipophilic domains of organosilane, in order to reinforce the enzyme carrying properties of polysaccharide matrix. Enzyme encapsulated beads are used as biohybrid catalyst for the conversion of glucose to hydrogen peroxide, which is further decomposed by a well known peroxidase mimetic, Prussian blue nanoparticles. These findings emphasize on the generation of materials with flexible properties of different aspects.

## Chapter V

A flexible approach to synthesize binary nanoscaled materials and self-assemble the bifunctional materials on solid substrates by means of well-defined orientation of organofunctionalised alkoxysilanes into nanostructured thin films, via a multistep guided process has been elucidated in this chapter. Initially, EETMS stabilized Palladium nanoparticles (PdNPs) are synthesized in water, methanol, and 2-propanol, further hybrid bifunctional nanomaterials (Au@PdNPs, Ag@PdNPs) are prepared through sequential synthesis using PdNPs as the template, and are stabilized by the micellar behavior of APTMS. The hydrodynamic radius of the objects formed; vary according to the interactions between alkoxysilanes and solvents. EETMS/APTMS based Au@PdNPs in propanol has the lowest hydrodynamic radii and polydispersity index. Bulk micellar solutions generated the ordered pattern of nanoporous thin films with solvent dependent morphologies. Hence, we manifest a route to manipulate the surface topography of the film, thereby controlling the composition of precursors and solvent selection. The self-configured assembly of the bifunctional materials into a patterned array, with precisely controlled nanogeometry of the constituent particles is considered the possible arrangement for potential catalytic applications.

## Chapter VI

A well programmed template synthesis of multimetallic nanocrystals Ru@Pd(BNPs) and Ag@Ru@Pd(TNPs) respectively, over presynthesized EETMS functionalized Palladium nanoparticles (PdNPs) has been comprehensively discussed in this chapter. The functional ability of as made nanomaterials enable their use in heterogeneous catalysis. They can be easily assembled as thin film of organically modified silicates (ormosil), having potential for

encapsulating the small molecules like potassium ferricyanide. The ormosil-encapsulated potassium ferricyanide display gradual improvement in redox electrochemistry as a function of monometallic, bimetallic and trimetallic nanoparticles. Catalytic activity of active electrode systems has been studied via electrochemical sensing of ascorbic acid, the significant improvement in anodic peak current density is observed in the presence of trimetallic nanoparticles (Ag@Ru@PdNPs). Thus it is worth suggesting that the fabricated nanoparticles have enormous potential, to discover their utility in future applications.

## Chapter VII

A facile chemical reduction pathway to synthesise Ni doped BNPs of palladium, Ni<sub>3</sub>PdNPs and NiPdNPs following the seed mediated growth phenomenon has been discussed in this chapter. These nanoscaled BNPs are highly stabilised due to the intervention of functional alkoxysilane (EETMS), in lieu of NiNPs which are susceptible to aggregation. Bifold action of EETMS, (a) Sol-gel processing and (b) steric stabilisation along with PVP, controls the nucleation of Nickel nanoparticles over the surfaces of PdNPs. These nanocatalysts serve as powerful bimetallic electrolysers for HER reaction in alkaline media, at an optimum loading of 0.1 mg/cm<sup>2</sup>, produced 10 mAcm<sup>-2</sup> current density at an overpotential of -90 mV. Further, the calcinated hybrid catalyst have shown remarkable improvement in results, with drastic amplification in current density (20 mAcm<sup>-2</sup>) at an overpotential of -56 mV. Trivial potential losses were observed in the stability analysis. The characteristic features like remarkable catalytic potential, stability and smooth fabrication techniques promotes their versatile applications in catalysis, in addition to electrochemical water splitting.

## FUTURE OUTLOOK

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In this Ph.D. thesis, potential role of alkoxysilane based palladium nanoparticles has been studied. The flexibility of the system directed us to carry out in-depth investigations involving different aspects and draw conclusions regarding the capabilities of the fabricated materials. The solution phase synthesis of palladium nanoparticles (PdNPs) involved organically functionalized alkoxysilanes (EETMS, GPTMS) as stabiliser, efficient reducing agent and polymeric chain stabiliser (PVP) as secondary capping agent along with variable concentration of metal precursor. EETMS along with PVP effectively controlled the morphological properties, promoted the directional growth of nanoparticles. PdNPs were significantly used as ready-seeds for producing multifunctional nanoparticles by template approach. Further, the epoxy moiety of functionalized PdNPs actively interacted with foreign molecules like graphene oxide and polysaccharide matrices and generated a new class of nanohybrids and microscaled composites. All the as-synthesised nanoparticle model systems had shown promising catalytic performances for a range of reactions, with enhanced selectivity and efficiency.

However, there are considerable challenges in adopting these techniques as reliable tools to guarantee the real time requirements of the catalyst. Although EETMS functionalised PdNPs are quite stable, and have turned up as adequate substitute over those resulting from conventional routes, for the applications discussed *vide infra*, a more technical approach is required to frame even better system for significant practical purposes. Future efforts will be more focussed on developing a more catalytically efficient model of nanoparticles to achieve high sensitivity. Furthermore, the studies on zeolites (aluminosilicates) based stabilisation and enhancement in

catalytic performance of nanoparticles are lined up and will be concluded possibly in future. Zeolites are highly crystalline and porous in nature, with well oriented metal ions, which support the alignment of nanoscaled particles about specific crystallographic axes. The confinement of EETMS functionalized nanoparticles in zeolite help to accommodate more nanodimensional metal particles and further controls the aggregation possibilities. The arrangement of cavities on the zeolite matrix assist the exposure of monometallic as well as multimetallic nanoparticles on the surface as well as those settled in the bulk, for catalysis. Considering the significant interaction of nanoparticles with the solid matrix of zeolite, we anticipate that the newly constructed material, nanoparticles confined into microporous framework of zeolite, might be more application oriented and also commercially viable.

Taking into account the advantages of immobilising the metal nanoparticles into the aluminosilicate network for potential uses, it is considered as the future extension of the present thesis work.