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General Introduction

Nanotechnology is the precise reprogramming of matter at the atomic and molecular levels to nanoscale range i.e, 1–100 nm, and utilizing the well defined properties which are more tunable than that of bulk matter (Thanh et al., 2014). Restructuring the bulk phase metals to their nanorange analogues is a function of parameters like reduction potential, reactivity and stability of the metal. Noble-metal nanoparticle synthesis has attracted much attention during recent decades due to their interesting size dependent, optical, electronic, and catalytic properties (Haruta et al., 1989; Hutchings and Haruta, 2005; Tang and Cheng, 2015; Feng et al., 2018). Nanoparticles can further function as building blocks for the construction of highly-ordered superlattices that exhibit collective properties of individual nanoparticles (Zheng et al., 2006). The remarkable reactivity of nanoparticles, which makes them potential catalysts, is associated with the high fraction of surface area (Bonnet et al., 1999; Lee et al., 2009; Liu and Corma, 2018). The development of uniform nanometer sized particles has been intensively pursued

because of many technological and fundamental scientific interests associated with these nanoparticles (Kim et al., 2003). Synthetic strategies for the preparation of monodispersed, colloidal suspension of nanoparticles, mainly involve top-down or bottom-up approaches (Cheong et al., 2010; Lee et al., 2015). The method based on the solvated metal atom dispersion technique is suitable for preparation of metal nanoparticles on the large scale (Zheng et al., 2006; Ftouni et al., 2012). The noble metal nanoparticles are synthesized (Baber et al., 2017) through various physical (mechanical ball milling, physical vapour deposition), chemical (wet chemical reduction, inverse micelles,) and hybrid methods (electrochemical and chemical vapour deposition). During recent years the noble metal nanoparticles of palladium, platinum, gold and silver are synthesized (Maenosono et al., 2012) and exploited for excellent potential catalytic applications like electrochemical sensing (Yang et al., 2014; Tang et al., 2016), organic reactions, cell imaging (Chen et al., 2015), etc. Palladium nanoparticle synthesis and applications have been explored thoroughly due to their exhaustive properties and catalytic aptitude.

1.1. Synthesis of palladium nanoparticles and the role of stabilizers

Palladium nanoparticles are highly active catalytic materials, for practical applications like hydrogen evolution reaction, organometallic reactions (Astruc, 2007), electrochemical sensing, etc. Palladium nanoparticles have been widely studied for their synthesis using various chemical and electrochemical methods via electrostatic and steric stabilisation and for their immense catalytic potential (Qi et al., 2014). Particle diameter is of immense importance for catalytic processes, as homogeneous colloidal dispersion of precious noble metals are used as efficient nanocatalysts in various reactions (Quiros et al., 2002; Chen et al., 2011). During the recent years, methods like wet chemical synthesis has emerged as a highly versatile and powerful tool

for size and shape-controlled synthesis (Xiong et al., 2005; Niu et al., 2010; Ananikov et al., 2007). Nanoparticles are kinetically stabilized through various protective chemical stabilization techniques. The effective procedures for stabilization include, electrostatic or steric interactions or even both of them can be applied simultaneously (i.e, electrosteric forces) (Wu et al., 2006). Most common stabilizers used till now are organic ligands, surfactants, polymers and dendrimers (Corain et al., 2004; Tu and Liu, 2000). In a wet chemical reduction pathway, the stabilizers are mostly incorporated in the first step of synthesis i.e, along with the metal precursor. The type of interaction, between a metal ion, stabilizer and reducing agent is responsible for long-term stability of the colloidal dispersion.

1.1.1. Phosphine as stabilizing agent

The use of phosphorus-containing compounds as stabilising agents for the fabrication of nanoscaled materials commenced about a century ago. Several researchers have explored the role of phosphine derivatives as steric ligands to obtain the monodispersed colloidal sol of palladium nanoparticles (Kim et al., 2003; Wu et al., 2006; Chahdoura et al., 2013). Kim and coworkers reported the role of trioctlyphosphine (TOP) to yield highly dispersed nanoparticles. The average size obtained was approximately 3.5-7.5 nm as a function of reaction conditions applied (Kim et al., 2003). Son and coworkers demonstrated the effect of a range of multidentate phosphines as substitution to TOP (Son et al., 2004), such as optically active bidentate ligands like 2, 2′-bis(diphenylphosphino)- 1,1′-binaphthyl (BINAP). BINAP thioether-derivatives are utilized as single phase catalyst organic coupling reactions (Tamura and Fujihara, 2003). Other phosphine derivatives used are 1,2-Bis(diphenylphosphino)ethane (DPPE), 1,2-Bis(diphenylphosphino)

propane (DPPP), tris(2-cyanoethyl)phosphine (TCP), Tri(2-furyl)phosphine (TFP), triphenylphosphine disulphonate (TPPDS).

1.1.2. Nitrogen as stabilizing agent

The unshared pair of electron present on nitrogen (such as bulky primary amines) undergo chemisorption on the surface of metal, and the bulky alkyl group prevents aggregation *via* steric stabilisation. Likewise, Palladium (II) cation was reduced in oleylamine in the presence of boron tributylamine (BTB) at 90ºC (Mazumdar and Sun, 2009), where double bond in oleylamine plays a major role in particle stabilisation. The role of primary amines in stabilization is dependent on initial Pd (II) to amine ratio (Li et al., 2009). Polymeric amino groups bind weakly with the surface groups which make them more convenient for catalysis purpose. Aromatic amines like porphyrins (Mayer-gall et al., 2008), pyridyl groups (Gittins and Caruso, 2001) and imidazole derivatives (Serpell et al., 2011), act as important ligands for the steric stabilisation of Palladium nanoparticles. Turkenburg and co-workers have explored the role of 4-dimethylaminopyridine (DMAP) ligand as stabilizer for metal nanoparticles (Turkenburg et al., 2005). Its efficiency has been documented in ligand exchange reactions. Serpell and coworkers have recently demonstrated the role of imidazole derivatives as effective stabilizers for palladium nanoparticles (Serpell et al., 2001).

1.1.3. Polymer as stabilizing agent

Polymers, such as poly (*N*-vinyl-2-pyrrolidone) (PVP) and poly (vinyl alcohol) (PVA), are broadly used as capping agents for the fabrication of colloids. Polymeric stabilizers support the dispersibility of nanoparticles in a variety of solvent systems including aqueous medium (Calo et

al., 2005). The use of polymers is often associated with the 'polyol method' (Maenosono et al., 2017), in which a metal precursor is dissolved and reduced at high temperatures by an alcohol (Stevens et al., 2005). The polymeric alcoholic derivatives effectively stabilize the nanoparticles and are considered most favorable because the by-products formed as their derivative do not hinder the structural as well as compositional features of the nanoparticles.

1.1.4. Dendrimer as stabilizing agent

Balogh et al and Zhao et al were the first to attempt the encapsulation of metal nanoparticles inside dendrimers of poly(amidoamine) (PAMAM) using template synthesis strategy (Balogh and Tomalia, 1998; Zhao et al., 1998). Dendrimers are efficiently used as stabilizers for the nanomaterial synthesis significant number of reports is available regarding this area of research (Crooks et al., 2001, Wu et al., 2006). In order to prepare palladium-encapsulated nanoparticles, metal ions are generally sorbed into the interior of the dendrimer. Badetti and coworkers used triolefinic 15-membered macrocycles which acted as coordinating agents for Palladium nanoparticles to form stable complexes (Badetti et al., 2008). Consequent nanoparticles remain surrounded by dendrite like structures in all the directions which prevent the particles from aggregation (Gomez et al., 2008). Typically, homogeneous colloidal solution of metal nanoparticles with average particle diameter of 2-4 nm, having a large fraction of easily available, and highly exposed metal sites are obtained by using this synthetic pathway (Andreas et al., 2007). The interior and periphery of the dendrimers are tuned by Chechik and coworkers are modifed to allow dispersibility of nanoparticles in organic (Chechik et al., 1999), aqueous (Niu et al., 2001), supercritical carbon dioxide (Yueng et al., 2001), or fluorous media (Balogh and Tomalia, 1998).

1.2. Properties of Palladium Nanoparticles

Nanodimensional Palladium is well known for its unique properties in different scientific areas. The investigations regarding the versatile properties of palladium nanoparticles have been taken up widely in different interdisciplinary areas of research. The considerable efforts have been put to understand the effect of different reaction conditions, morphological features of the nanoparticles on their behavior in variety of important areas. Though the properties of palladium nanoparticles are highly explored, but still it remains much active area of research.

1.2.1. Electronic properties

Unsupported palladium nanoparticle catalysts are conveniently used as anode for direct formic acid fuel cell for preparing micropower energy devices such as cell phones, laptopts, etc (Zhou et al., 2006). Palladium nanoparticles with specific crystallographic orientations, 100 and 110 are effectively used as working electrode on gas permeable membrane, for oxygen reduction reaction in an ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Tang et al., 2016). Similarly, anisotropic nanostructured palladium dendrites are used as electrocatalyst for the oxidation of formic acid (Kannan et al., 2014).

1.2.2. Catalytic properties

Consequently, the properties of palladium nanoparticles have been thoroughly studied in a wide range of catalytic applications including hydrogenations (Semagina et al., 2007, Wilson et al., 2006), oxidations (Hou et al., 2005), carbon–carbon bond formation (Narayan and El-Sayed, 2005), and electrochemical reactions in fuel cells (Cheon and Suh, 2009; Yang et al, 2014) and various other reactions (Zhang et al., 2015; Huang et al., 2014). Palladium attached to the

vacancy defective sites of graphene act as efficient recyclable catalyst for the production of complex organic molecules (Yang et al., 2016). Thin film stabilized single atom palladium, fabricated by atomic layer deposition act as catalyst for methanol decomposition (Piernavieja-Hermida et al., 2016). In-situ placed palladium nanoparticles in magnetic carbon nanocages show superior catalytic activity towards cleavage reaction of *N*-butyl-4-NHAlloc-1,8-naphthalimide (Chen et al., 2015).

1.3. Applications of palladium nanoparticles

1.3.1. Homogenous and Heterogenous catalyst

Palladium can be used both as homo and heterogeneous catalyst in various chemical and electrochemical reactions. Palladium nanoparticles being very small in size can usually be dissolved in reaction media, which exposes the reactant molecules to catalytic sites, thus they can be used as excellent homogeneous catalyst. In addition, the stereochemistry and regiochemistry of the reaction products is controlled in one phase reactions. Stevens and coworkers used homogenous palladium catalyst for Suzuki, Heck, and Sonogashira cross-coupling reactions. (Stevens et al., 2005; Li and El-Sayed, 2001). Rahim and coworkers used PAMAM-dendrimer encapsulated palladium nanoparticles as homogeneous catalysts for the Heck reaction (Rahim et al., 2001). The reactions such as hydrogenation of ethyl pyruvate, hydrogenation of arenes, carbonylation of methanol, the intra- and intermolecular reactions, and hydrogenation of alkenes are catalysed using palladium nanoparticles supported on solid matrix. Bruening et al demonstrated the remarkable intramolecular selectivity in the hydrogenation of alkenes by incorporating palladium nanocatalyst in multilayer polyelecrolyte films (Bhattacharjee and Bruening, 2008). In addition to new types of catalysts or precatalysts such as Pd - carbene

complexes (Liu et al., 2008; Meyer et al., 2009) or phospha-palladacycles (Alonso et al., 2000; Frey et al., 2005), increasingly being used in carbon coupling reactions.

1.3.2. Constituent of Polymer memberanes

The encapsulation of monometallic palladium nanoparticles (PdNPs) in polymeric matrix, grants stability and protecting effects towards PdNPs, polymers enhance the availability of substrate molecules to the active sites of metal nanoparticles (Kidambi et al., 2004). The reduction of Pd^{2+} ions to PdNPs within the polymeric memberane network allows the fabrication as well as catalysis process to undergo simultaneously, which further accelerates the rate of respective reaction (Dotzauer et al., 2006; Macanas et al., 2010). Some common polymers such as cellulose acetate, hydrophilized polysulfone, polyacrylic acid-modified polyethersulfone, polyvinylidene fluoride, have been successfully employed for the synthesis of PSMNPs (Smuleac et al., 2010) and materials including polyelectrolyte brushes (Mei et al., 2005; Bergbreiter and Li, 2003) polystyrene microspheres (Dokoutchaev et al., 1999) and polyelectrolyte multilayers (Dai and Bruening, 2002; Kidambi and Bruening; 2005), which are widely used as membrane materials. Porous membranes provide an alternative support for nanoparticle immobilization and are very attractive for catalysis using layer by layer adsorption technique (Dotzauer et al., 2006).

1.3.3. Nanomaterials for sensor designs

Palladium-doped SnO_2 hollow nanofibers were prepared by single capillary electrospinning and were investigated for their gas sensing characteristics for 100 ppm H_2, 100 ppm CO, 500 ppm CH_4, and 100 ppm C_2H_5OH (Choi et al., 2010). In hydrogen gas (H_2) sensors, nanoscale gaps in palladium nanowires have been widely used to study sensor mechanisms (Favier et al., 2001) and

to develop reversible gas sensing capabilities, which is an important step forward in rational sensor design (Dasari and Zamborini, 2008; Yang et al., 2010). In another approach, a nanogap based sensing method, where nanogaps in palladium are used to effectively detect the hydrogen gas. Palladium nanoparticles supported on carbon aerogel significantly act as electrochemical sensors for biologically important molecules (Rajkumar et al., 2017). In another approach, palladium nanoparticle-graphene nanohybrids are also used for non-enzymatic glucose sensing reaction (Lu-min et al., 2011).

1.3.4. Nanosensitizers for fluorophores

The nanoscaled metal surfaces have been proved to influence the visual properties of the chromophore (Vukovic et al., 2008; Wang et al., 2013). It has been found that rugged metal surfaces and nanoclusters can magnify the molecular optical properties, markedly fluorescence emission intensity. Fluorescence with metal interactions has been widely investigated as an interspace phenomenon (Zhang et al., 2017), as the amplitude of oscillations and flouroscence lifetime vary according to the distance of flourophore from the metal nanoclusters. The metal enhanced fluorescence is considered as the function of plasmonic activity and the local field generated due to the collective oscillations of electrons of the metal nanoparticles (Lakowicz et al., 2008). Metals with weaker Surface Plasmon Resonance like palladium (Li et al., 2017), platinum, also play a crucial role in fluorescence enhancement.

1.3.5. Active substrates for SERS

The Raman signal is enhanced when the vibrating molecule interacts with metal surface and generates oscillating electromagnetic field. (Wang et al., 2013, Wang et al., 2018) Recently,

transition metal nanostructured substrates have been designed to maximize the electromagnetic field near the analytes and bolster their polarizability. SERS involves higher effective Raman cross sections in the presence of nanoparticle surfaces; this additional response is due to the existence of hot spots and Raman resonating effect (Kneipp et al., 2006; Indrasekara et al., 2014). Recent advancements in synthetic strategies have put forward a range of possibilities to precisely tune the nanoarchitechtures to obtain the material with desired functionality (Huang et al., 2018) and structural orientations which could serve for selective enhancement (Zhang et al., 2006; Wang et al., 2008). Further studies have been done to fabricate SERS nanosensors, integrating the anisotropy in morphology of particles with improved surface properties for selective detection (Sau and Murphy, 2004; Wang et al., 2014).

1.3.6. Fuel cell applications

Fuel cells may help to reduce our dependence on fossil fuels and diminish poisonous emissions into the atmosphere, since fuel cells have higher electrical efficiencies compared to heat engines. Recently, PdNPs based catalysts were found to possess superior performances in formic acid oxidation, as the anode of polymer electrolyte membrane fuel cells (PEMFCs) with greater resistance to CO than Pt catalysts (Larsen et al., 2006). Vulcan supported palladium (Pd/C) and carbon nanotube modified (CNT-PdNPs) catalysts has been often used as electrocatalysts for various kinds of fuel cells due to their high surface area, good electrical and thermal conductivity, suitable porosity to allow for a good reactant flow, and high stability in the acidic conditions (Bianchini and Shen, 2009; Sun et al., 2008).

1.4. Synthesis and applications of multimetallic analogues of Palladium nanoparticles

Nanoparticles with multiple compositions (bimetallic, trimetallic) have grabbed much attention due to the exceptional catalytic properties in contrast to their monometallic counterparts (Wang and Yamauchi, 2010; Maenosono et al., 2014) as discussed vide infra.

1.4.1. Bimetallic nanoparticles

Bimetallic nanoparticles containing two metals are of great interest since they exhibit distinct catalytic, electronic, and optical properties in contrast to the corresponding monometallic equivalents (Ferrer, 2007; Xu et al., 2015; Zhang et al., 2016). Pd-Au bimetallic nanoparticle catalysts attracted great attention, due to their similar lattice parameters they are easily fixed in any ratio (Crooks et al., 2001; Lu et al., 2015). Au-Pd bimetallic nanoclusters act as catalysts for a variety of reactions like, direct synthesis of hydrogen peroxide from H_2 and O_2, for hydrodesulfurization of thiophene, the oxidation of alcohols to aldehydes (Mejia-Rosales et al., 2006), effective agents for the remediation of various inorganic and organic groundwater contaminants (Nutt et al., 2005). Bimetallic nanoparticles are mostly synthesized via wet chemical reduction method using two different approaches: sequential and simultaneous pathways (Pei et al., 2015). The precursor metal ions are reduced according to their reduction potentials and there is a possibility of the formation of variety of structures via simultaneous route. However, sequential reduction is usually carried out to prepare core shell structured bimetallic nanoparticles (An et al., 2017). This involves the deposition of one metal element on pre-formed monometallic nanoparticles of another metal seems to be very effective. Harada and coworkers attempted to prepare the PVP-stabilized Au-Pd bimetallic nanoparticles was made by

the successive reduction procedure. Synthesis of Au nanoparticles proceeded with the reduction of Pd ion, results into the mixtures of Pd and Au monometallic nanoparticles (Kareem et al., 2018). While, when the reduction of palladium ions is preceded by gold ions, bimetallic nanoparticles were obtained (Harada et al., 1993; Darabdhara et al., 2016). Heterogeneous seeded growth represents an effective means of coupling the optical or catalytic properties of one metal with those of another metal, thereby forming multifunctional nanocrystals (Lim et al., 2010). Habas and coworkers demonstrated the shaping of a variety of binary nanoparticles to form polyhedral nanocrystals (Habas et al., 2007; Lee et al., 2009). Similarly, the nanodendrites consisting of branched arms made of one metal supported on a core of another metal (Lim et al., 2009; Peng andYang, 2009).

1.4.2. Trimetallic nanoparticles

Multicomposition core shell-structured trimetallic nanocatalyst systems are usually prepared by a multistep seed-mediated growth method in which the particle size and shape are uncontrollable without the use of a preformed uniform seed (Mazumder, 2010; Xu et al., 2018). Wang and coworkers synthesized the Au@Pd@Pt triple-layered coreshell structured nanoparticles, consisting of a Au core, a Pd inner layer, and a nanoporous Pt outer shell, in a poly(vinylpyrrolidone) (PVP)-based aqueous solution (Wang and Yamauchi, 2011; Khanal et al., 2013; Zhang et al., 2018). Ternary catalysts are highly active towards various catalytic applications like methanol oxidation, formic acid oxidation. Ge and coworkers designed the sandwiched sensor based on folic acid by integrating the fabricated dendritic Au@PtPd trimetallic nanoprobe, for the recognition of cell surface folate receptor expression (Ge et al., 2015). Another report by Kondrat and research group attempted the base-free selective oxidation

of glycerol using trimetallic (Au–Pd–Pt) nanoparticles. Similarly, Abazari and coworkers demonstrated the preparation of Pt/Pd/Fe trimetallic nanoparticle using a water-in-oil microemulsion system and utilized it for the hydrodehalogenation (HDH) of halogenated organic compounds (HOCs) (Abazari et al., 2012).

1.5. Challenges in the synthesis and applications of PdNPs and its multimetallic equivalents

The fabrication of palladium nanoparticles (PdNPs) has been thoroughly pursued for its exclusive properties and applications, by the researchers on global scenario, using different traditional methods available in literature. There are large fractions of reports dedicated to the preparation of nanoscaled palladium alone, where the different aspects on controlling the size and shape of the particles have been put forth. The general methods for PdNPs synthesis like, chemical reduction using $NaBH_4$, although leads to rapid synthesis of PdNPs at lower atomic wt % of Pd, but it is often associated with issues like quick agglomeration, remote dispersibility and several more that restrict the use of nanoparticles in relevant applications. Similarly, diverse solution-phase syntheses of monodisperse PdNPs, using ligand or steric stabilizers like trialkyl-phosphines, 1-alkanethiols, BINAP, imidazole-based ionic liquids, cyclodextrins, polynucleotides (RNA, DNA), dendrimers [poly(amidoamine), poly(propyleneimine)] invole bulky reagents to induce the interatomic repulsions, which possibly end up with large average particle diameter and also compromise with the catalytic performance of the prepared colloids, since the palladium nanoparticles are specifically known for their immense catalytic potential. In addition the practical formulation of PdNPs normally require diverse phase boundary conditions specifically in heterogeneous catalysis, like the conversion of colloidal solutions to catalytically active solid thin films, multidimensional nanocomposites, where the stabilization of

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nanogeometry play a central role and most of the conventional protocols for PdNP synthesis fail to comply such requirement. Therefore, efforts in the area to discover feasible methods for the preparation of palladium nanoparticles is desirable, in order to likely curtail the limitations introducing the role of functional materials and this constitutes the origin of current program as discussed vide infra.

1.6. Origin of the research programme

Fabrication of sol-gel glass has been explored thoroughly over the decades mainly in electrocatalysis (Kimura et al., 1997; Lev et al., 1997; Pandey et al., 1999). The sol−gel derived thin films are fabricated to design electrochemical biosensors and also ion sensor (Pandey et al., 2001a). Organofunctionalised silanes like trimethoxysilane (TMS), glycidoxypropyltrimethoxy silane (GPTMS), 2-(3,4-(epoxycyclohexyl) ethyltrimethoxysilane (EETMS), 3-aminopropyltrimethoxysilane (APTMS) were utilized to form nanostructured matrix in a favorable ratio as a function of their hydrophilicity and hydrophobicity (Pandey et al., 2003a; Pandey et al., 2003b; Pandey et al., 2001a; Pandey et al., 2001b). A series of work has been done applying this concept in our laboratory [Ph.D. thesis: Vijay Shyam Tripathi (2002); Bhupendra Singh (2007); Arvind Prakash (2014); Richa Singh (2015); and Gunjan Pandey (2016)]. The matrix being nanoporous allows the maximum exposure to the analytes, together with limited mass transfer kinetics. Therefore attempts have been made to facilitate the mass transfer and electron transfer dynamics, across the ormosil film, through incorporation of water leachable materials within nanostructured domains along with incorporation of electron transfer relays like ferrocene monocaboxylic acid and potassium ferricyanide. Subsequent efforts were made to integrate nanoelectrocatalyst like palladium in organically modified silicate network to

manipulate the electrochemical sensing process for real applications. Nevertheless novel findings on the specific interaction of palladium chloride with glycidoxy-residue of functional alkoxysilane have been investigated that allowed the formation of (-Pd-C-) palladium linked organically modified silicate. In addition the specific interaction of trimethoxysilane and palladium chloride further added the formation of -Pd-Si- linkage which together with -Pd-C-linked ormosil's precursors enabled the formation of novel nanostructured matrix behaving as solid-solution for commercial electrochemical biosensor design (Tripathi et al., 2006; Pandey et al., 2001a; Pandey et al., 2001b). Apart from being a vital constituent of ormosil, GPTMS along with APTMS is found to behave as reducing agent for rapid conversion of Au^{3+} to Au^0 (Pandey and Chauhan, 2012). Similarly, the role of APTMS was explored in the preparation of gold, silver and palladium nanoparticles (Pandey and Pandey, 2014; Pandey and Singh, 2015; Pandey et al., 2015), owing to its micellar behavior it works as a capping agent to stabilize and control the size and morphology of the nanoparticles. Undertaking the well established and promising role of different organofunctionalised alkoxysilane moieties in various fields, it was intended to thoroughly explore the utility of 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane (EETMS) in the controlled synthesis of PdNPs and its multimetallic analogues which has not been paid much attention so far and constitute the origin of present research program.

1.7. Objective of the present research programme

Taking into account the effective role of glycidoxy moiety in directing the conversion of bulk palladium to zero valent form, it was intended to investigate the reactivity of epoxy functional group from different angles, which is the ultimate objective of the projected thesis. The rational objectives are as follows:

- To examine the reducing and stabilizing ability of epoxy moiety linked to alkoxysilane typically 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (EETMS), for the facile conversion of Pd^{2+} to Pd^0.

- Fabricating the palladium nanoparticles using EETMS in the absence and presence of a known stabilizer (PVP), in order to figure out the specific role of EETMS in stabilization.

- To understand the effect of EETMS on the topographical features and catalytic behavior of nanocrystals, at different concentrations.

- Investigate the possibility of encapsulating the nanoparticles into nanostructured framework of organically modified silicates (Ormosil).

- Developing insight on the effective role of EETMS as spacer for regulating the distance between fluorophore and metal nanoparticle surface, for the metal enhanced fluorescence (MEF) or fluorescence resonance energy transfer (FRET) studies.

- To describe the role of bound and free EETMS, along with the by-products of transformation (Pd^{2+} to Pd^0) in facilitating the epitaxial growth of subsequent layers of metal (Au, Ag, Ni, Ru) to produce multimetallic analogues.

- Investigate the possibility of arranging the multimetallic nanoparticles on conducting substrates by self assembly of organofunctionalised silanes (EETMS, APTMS).

- Studying the specific interactions between epoxycyclohexyl and glycidoxy moiety of alkoxysilanes (EETMS, GPTMS) and molecules like isolated sheets of graphene oxide in order to develop two dimensional nanocomposites of palladium,

- Investigating the compatibility of epoxy and glycidoxy functionalized palladium nanoparticles with the polysaccharide matrix, to fabricate the three dimensional systems

like silica modified microspheres, and further examine the ease of enzyme immobilization in chemically tuned hydrogel based microspheres,

- Investigate the catalytic potential of alkoxysilane functionalized nanohybrids, nanocomposites, nanoarchitectured thin films in relevant applications.

1.8. Work plan of the thesis

The role of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (EETMS) has been explored thoroughly in the synthesis of palladium nanoparticles. The effect of EETMS has been demonstrated in the fabrication process as well as the catalytic potential of various nanohybrids of PdNPs. The research programme covers the following aspects:

[1] The epoxy functional moiety present in the EETMS molecule is responsible for its reducing ability and stabilisation of nanoparticle dispersion.

[2] To synthesize PdNPs using PVP, EETMS and the potassium tetrachloropalladate under ambient conditions.

[3] To understand the effect of different solvents on the size and morphology of the nanoparticles.

[4] To study the fluorescence intensity variations as a function of the concentration of organofunctionalised alkoxysilanes (EETMS, GPTMS) responsible for the stabilisation and fabrication of palladium nanoparticles.

[5] To synthesize the bimetallic counterparts of palladium nanoparticles such as, Au@PdNPs, Ag@PdNPs using APTMS, formaldehyde and the presynthesised PdNPs as seed for further synthesis.

[6] To synthesise bimetallic nanoparticles of Ru@PdNPs and Ni@PdNPs using PVP, NaBH$_4$ and presynthesized PdNPs as seed.

[7] To synthesize triple layered colloids with metal constituents in the sequence, Ag@Ru@Pd.

[8] To further investigate the effect of graphene oxide in the preparation of gold nanoparticles.

[9] To investigate the role of PdNPs in facilitating the successful immobilization of enzyme in the polysaccharide matrix.

[10] To investigate the catalytic potential of palladium nanoparticles, its corresponding multimetallic analogues and various nanocomposites in following applications:

i. On board hydrogen evolution from the decomposition of hydrazine hydrate at room temperature

ii. Hydrogen evolution from electrochemical water splitting reaction.

iii. Glucose oxidation using glucose oxidase (GOx) immobilized silica-alginate beads.

iv. Reduction of p-nitroaniline to p-diaminobenzene

v. Electrochemical behavior of modified electrodes in the presence of redox mediator like potassium ferricyanide

vi. Electroanalysis of bio-analytes like ascorbic acid, L-Tryptophan, hydrazine.

vii. Casting solvent assisted sol-gel thin film by self assembly of organosilanes

viii. Variations in fluorescence emission intensity of probe molecules in proximity to the metal nanoparticle surfaces.