

CONTENTS

	Page No.
List of Figures	xv
List of Tables	xxvi
List of Abbreviations	xxvii
Preface	xxix
CHAPTER I General Introduction	1-18
1.1. Synthesis of Palladium nanoparticle and the role of stabilizers	2
1.1.1. Phosphine as stabilizing agent	3
1.1.2. Nitrogen as stabilizing agent	4
1.1.3. Polymer as stabilizing agent	4
1.1.4. Dendrimer as stabilizing agent	5
1.2. Properties of Palladium Nanoparticles	6
1.2.1. Electronic properties	6
1.2.2. Catalytic properties	6
1.3. Applications of palladium nanoparticles	7
1.3.1. Homogenous and Heterogenous catalyst	7
1.3.2. Constituent of Polymer memberanes	8
1.3.3. Nanomaterial for sensor designs	8
1.3.4. Nanosensitizer for fluorophores	9
1.3.5. Active substrates for SERS	9
1.3.6. Fuel cell applications	10

1.4. Synthesis and applications of multimetallic analogues of palladium nanoparticles	11
1.4.1. Bimetallic nanoparticles	11
1.4.2. Trimetallic nanoparticles	12
1.5. Challenges in the synthesis of palladium nanoparticles and its multimetallic analogues	13
1.6. Origin of the research programme	14
1.7. Objective of the present research programme	15
1.8. Work plan of the thesis	17
CHAPTER II Functional alkoxy silane mediated synthesis of Palladium nanoparticles and their role as Metal Enhanced Fluorescence Resonance or Fluorescent Energy Transfer	19-51
2.1. Introduction	19
2.2. Experimental	22
2.2.1. Materials	22
2.2.2. EETMS /GPTMS mediated synthesis of palladium nanoparticles	23
2.2.3. Interaction of fluorophores with nanoarrays	24
2.2.4. Instrumentation	25
2.3. Results	26
2.3.1. Synthesis and characterization of nanoparticles	26
2.3.2. Metal–Fluorophore Interactions	30
2.3.2.1. Effect of Pd/EETMS and Pd/GPTMS systems on Fluorescence intensity variations	31
2.3.2.2. Effect of APTMS and APTMS-GPTMS-AuNPs systems	34

on Fluorescence intensity variations	
2.3.2.3. Effect of APTMS and APTMS-GPTMS AgNPs systems	40
on Fluorescence intensity variations	
2.4. Discussion	
2.4.1. Role of EETMS in fabrication of palladium nanoparticles	46
2.4.2. Effect of alkoxysilanes on metal nanoparticle fluorphore	48
interaction	
2.5. Conclusion	50
CHAPTER III Studies on graphene oxide and alkoxysilane functionalized PdNPs	52-70
for the fabrication of silica-alginate beads: Catalyst for selective	
decomposition of hydrazine into hydrogen	
3.1. Introduction	52
3.2. Experimental	56
3.2.1. Materials	56
3.2.2. Synthesis of graphene oxide (GO)	57
3.2.3. Graphene oxide mediated synthesis of palladium nanoparticles	58
3.2.4. Fabrication of silica alginate beads and doping of nanocrystals	58
3.2.5. Synthesis of Au/GO nanohybrids	60
3.2.6. Instrumentation	60
3.3. Results	61
3.3.1. Synthesis of palladium-GO nanocomposites	61
3.3.2. Characterisation of Pd/GO nanocomposites	62
3.3.3. Fabrication and characterization of mesoporous silica	65
alginate beads doped with palladium nanocomposites	
3.3.4. Decomposition of hydrazine	68

and Ag@PdNPs

5.2.3. Thin film deposition and electrochemical measurements

5.2.4. Characterization of bifunctional nanomaterials

5.3. Results

5.3.1. Binary nanoparticle synthesis and characterisation

5.3.2. Fabrication of solvent dependent thin films

5.3.3. Electrochemical catalysis using thin film modified electrodes

5.3.4. Differential pulse voltammetric measurements

5.4. Discussion

5.4.1. Functional alkoxy silane mediated synthesis of
bifunctional nanoclusters

5.4.2. Synergistic action of solvents and alkoxy silanes in
thin film formation

5.4.3. Electrochemical oxidation of L-Tryptophan

5.4.4. DPV analysis

5.5. Conclusion

CHAPTER VI Functional alkoxy silane mediated synthesis of multimetallic analogues of PdNPs

14

6.1. Introduction

6.2. Experimental

6.2.1. Materials

6.2.2. Synthesis of Ag@Ru@PdNPs

6.2.3. Characterization of trimetallic nanoparticles

6.2.4. Electrochemical investigations

6.3. Results	150
6.3.1. Synthesis of multilayered nanoparticles	150
6.3.2. Characterisation of triple-layered nanoparticles	151
6.3.3. Fabrication of nanoparticle linked organically modified silicates	156
6.3.4. AFM analysis of nanoparticle linked ormosil films	157
6.3.5. Redox electrochemistry of nanoparticle modified electrodes	158
6.3.6. Electrooxidation of Ascorbic acid	161
6.4. Discussion	162
6.4.1. Role of alkoxysilanes in synthesis of multimetallic nanoparticles	162
6.4.2. Characterisation of nanomaterials	163
6.4.3. Electrochemical analysis	164
6.4.4. Electrocatalytic behavior of modified electrodes	165
6.5. Conclusion	168
CHAPTER VII Alkoxysilane functionalized hybrid Ni-Pd nanocatalysts as efficient electrolyser for hydrogen evolution reaction	170-192
7.1. Introduction	170
7.2. Experimental	173
7.2.1. Materials	173
7.2.3. Synthesis of Nickel-Palladium binary nanoparticles	173
7.2.4. Electrochemical measurements	174
7.2.5. Instrumentation	175
7.3. Results	175
7.3.1. Synthesis of Ni _x Pd _y NPs	175
7.3.2. Characterisation of Ni _x Pd _y NPs	177
7.3.3. Electrochemical investigations on hydrogen evolution	182

7.4. Discussion	183
7.4.1. Synthesis of bifunctional nanoparticles $\text{Ni}_x\text{Pd}_y\text{NPs}$	183
7.4.2. Structural analysis	184
7.4.3. Evaluation of HER	184
7.5. Conclusion	191
Summary and Future Outlook	193
References	200

LIST OF FIGURES

Figure No.	Figure caption	Page No.
Figure 2.1.	TEM images, SAED pattern and particle size distribution, of PdNPs arranged in increasing order of the concentration of EETMS, (a-e) 0.1 M, (f-j) 0.5 M, (k-o) 1.5 M, (p-t) 2.5 M.	29
Figure 2.2.	TEM image (a), SAED pattern (b) of PdNPs synthesized using GPTMS.	29
Figure 2.3.	TEM images, SAED pattern and particle size distribution, of gold (a-e) and silver nanoparticles (f-j).	30
Figure 2.4.	XPS profiles of monometallic (a) PdNPs, (b) AuNPs and (c) AgNPs.	30
Figure 2.5.	Fluorescence emission spectra of fluorescein in the presence of PdNPs. The variations in the emission intensity when (i) the concentration of K_2PdCl_4 is varied from 2 – 10 mM at constant EETMS, (ii) the EETMS is varied over the range 0.1 – 4.32 M and (iii) GPTMS is varied from 1 – 6 M, at constant K_2PdCl_4 (10 mM) for both (ii) and (iii).	32
Figure 2.6.	Plots of enhancement factor (EF) or fluorescence intensity change (I/I_0) with respect to the concentrations of EETMS, for the fluorophores (a) Rhodamine B and (b) Fluorescein.	33
Figure 2.7.	Fluorescence emission spectra of Rhodamine B in the presence of PdNPs. The variations in the emission intensity when (i) the concentration of K_2PdCl_4 is varied from 0.5 – 10 mM at constant EETMS, (ii) the EETMS is varied over the range 0.1 – 4.32 M and (iii) GPTMS is varied from 1 – 6 M, at constant K_2PdCl_4 (10 mM) for both (ii) and (iii).	34
Figure 2.8.	Fluorescence emission spectra of L-Tryptophan in the presence of PdNPs. The variations in the emission intensity when (i) the concentration of K_2PdCl_4 is varied from 0.5 – 10	35

mM at constant EETMS, (ii) the EETMS is varied over the range 0.1 – 4.32 M and (iii) GPTMS is varied from 1 – 6 M, at constant K_2PdCl_4 (10 mM) for both (ii) and (iii).

- Figure 2.9.** Fluorescence emission spectra of Fluorescein in the presence of AuNPs. The variations in the emission intensity when (i) the concentration of $HAuCl_4$ is varied from 2 – 25 mM at constant APTMS, (ii) the APTMS is varied over the range 0.5 – 5.41 M at constant $HAuCl_4$ (10 mM) (iii) the APTMS is varied over the range 0.5 – 5.41 M at constant $HAuCl_4$ (10 mM) (iv) the concentration of $HAuCl_4$ is varied from 10 – 50 mM at constant GPTMS
- Figure 2.10.** Plots of enhancement factor (EF) or fluorescence intensity change (I/I_0) with respect to the concentrations of EETMS, for the Fluorescein at (a) 10 mM and (b) 20 mM $HAuCl_4$.
- Figure 2.11.** Fluorescence emission spectra of L-Tryptophan in the presence of AuNPs. The variations in the emission intensity when (i) the concentration of $HAuCl_4$ is varied from 2 – 25 mM at constant APTMS, (ii) the APTMS is varied over the range 0.5 – 5.41 M at constant $HAuCl_4$ (10 mM) (iii) the APTMS is varied over the range 0.5 – 5.41 M at constant $HAuCl_4$ (10 mM) (iv) the concentration of $HAuCl_4$ is varied from 10 – 50 mM at constant GPTMS.
- Figure 2.12.** Fluorescence emission spectra of Rhodamine B in the presence of AuNPs. The variations in the emission intensity when (i) the concentration of $HAuCl_4$ is varied from 2 – 25 mM at constant APTMS, (ii) the APTMS is varied over the range 0.5 – 5.41 M at constant $HAuCl_4$ (10 mM) (iii) the APTMS is varied over the range 0.5 – 5.41 M at constant $HAuCl_4$ (10 mM) (iv) the concentration of $HAuCl_4$ is varied from 10 – 50 mM at constant GPTMS.
- Figure 2.13.** Plots of enhancement factor (EF) or fluorescence intensity change (I/I_0) with respect to the concentrations of APTMS, for the Rhodamine B at (a) 10 mM and (b) 20 mM $HAuCl_4$.
- Figure 2.14.** Fluorescence emission spectra of Fluorescein in the presence of AgNPs. The variations in the emission intensity when (i) the concentration of $AgNO_3$ is varied from 5 – 20 mM at constant APTMS, (ii) the APTMS is varied over the range 0.5 – 5.41 M at constant $AgNO_3$ (5 mM) (iii) the APTMS is varied over the range 0.5 – 5.41 M at constant $AgNO_3$ (10 mM) (iv) at

constant 4 M GPTMS.

- Figure 2.15.** Plots of enhancement factor (EF) or fluorescence intensity change (I/I_0) with respect to the concentrations of APTMS, for the Fluorescein at (a) 5 mM and (b) 10 mM AgNO_3 . 43
- Figure 2.16.** Fluorescence emission spectra of L-Tryptophan in the presence of AgNPs. The variations in the emission intensity when (i) the concentration of AgNO_3 is varied from 5 – 20 mM at constant APTMS, (ii) the APTMS is varied over the range 0.5 – 5.41 M at constant AgNO_3 (5 mM) (iii) the APTMS is varied over the range 0.5 – 5.41 M at constant AgNO_3 (10 mM) (iv) at constant 4 M GPTMS. 44
- Figure 2.17.** Fluorescence emission spectra of Rhodamine B in the presence of AgNPs. The variations in the emission intensity when (i) the concentration of AgNO_3 is varied from 5 – 20 mM at constant APTMS, (ii) the APTMS is varied over the range 0.5 – 5.41 M at constant AgNO_3 (5 mM) (iii) the APTMS is varied over the range 0.5 – 5.41 M at constant AgNO_3 (10 mM) (iv) at constant 4 M GPTMS. 45
- Figure 2.18.** Plots of enhancement factor (EF) or fluorescence intensity change (I/I_0) with respect to the concentrations of APTMS, for the L-Tryptophan at (a) 5 mM and (b) 10 mM AgNO_3 . 46
- Figure 2.19.** Plots of enhancement factor (EF) or fluorescence intensity change (I/I_0) with respect to the concentrations of APTMS, for the Rhodamine B at (a) 5 mM and (b) 10 mM HAuCl_4 . 46
- Figure 2.20.** Infrared spectra of 2-(3,4-Epoxy cyclohexyl) ethyltrimethoxysilane (1) and Palladium nanoparticle dispersion (2) with major peaks at (a) 1642 cm^{-1} (s; C – C), (b) 2920 cm^{-1} (C–H), (c) 1087 cm^{-1} (s; Si–O), (d) 3400 cm^{-1} (O – H) (e) 1190 cm^{-1} (epoxy ring), (f) 891 cm^{-1} (s (epoxy ring)), respectively. 48
- Figure 2.21.** DLS profiles of the variations in hydrodynamic radii (R_H) on the interaction between the alkoxy silane functionalized nanoparticles and the corresponding flourophores (a) Fluorescein, (b) Rhodamine and (c) L-Tryptophan. 49
- Figure 3.1.** Absorbance spectra of conversion of Pd^{2+} to Pd^0 under different conditions. 61

- Figure 3.2.** FTIR spectra of Pd/GO nanocomposite. 62
- Figure 3.3.** (a) TEM image, (b) descriptive SAED pattern of Pd/EETMS nanocomposites. Inset to picture (a) shows the corresponding size distribution. 63
- Figure 3.4.** (a) TEM image, (b) descriptive SAED pattern of Pd/GO/EETMS nanocomposites. Inset to picture (a) shows the corresponding size distribution. 63
- Figure 3.5.** (a) TEM image, (b) descriptive SAED pattern of Pd/GPTMS nanocomposites. Inset to picture (a) shows the corresponding size distribution. 64
- Figure 3.6.** (a) TEM image, (b) descriptive SAED pattern of Pd/GO/GPTMS nanocomposites. Inset to picture (a) shows the corresponding size distribution. 64
- Figure 3.7.** (a) SEM image of dried silica alginate beads entrapped with nanocomposites and (b) corresponding EDX map showing the distribution of the palladium in the beads along with Si and C. 66
- Figure 3.8.** FTIR spectra of hydrazine solution before (a) and after the decomposition (b), (c) with time degradation of N–N bond stretching, (d) magnified view of the dissipation of the band at 1069 cm^{-1} . 67
- Figure 3.9.** N_2H_4 conversion as a function of time using Pd/GO/EETMS (623 K), Pd/GO/EETMS (423 K), Pd/GO/EETMS, Pd/GO/GPTMS, Pd/EETMS, Pd/GPTMS catalysts at initial hydrazine concentration of 1.19 M. 68
- Figure 3.10.** Comparative hydrogen selectivity of the prepared catalysts, TOF on decomposition of hydrazine by different catalysts. 68
- Figure 3.11.** Absorbance spectra of the reduction of methylene blue (MB) to leucomethylene blue (leucoMB), (b) kinetic analysis of the process without (1) and with (2) temperature treatment of catalyst. 70
- Figure 3.12.** FTIR (1) and UV-Vis (3) spectra of Au/GO nanocomposite. 71

Figure 3.13.	TEM images of graphene sheet (a), Au/GO nanohybrids (b) and (d), AuNPs (c) Inset shows the magnified image of a nanoparticle with visible fringes.	72
Figure 3.14.	Plots showing the lattice spacings of Au/GO (A) and AuNPs (B).	72
Figure 3.15.	Optical micrographs showing the enlarged view of the silica beads, showing the variation in pore sizes with the concentration of silica, 1) 0.5 M and 2) 2.5 M.	76
Figure 3.16.	Variation in absorbance spectra of synthesis of a). AuNPs and c). GO-AuNPs. Bar daigrams c) and d) representing the increase in absorbances recorded in relation to time.	78
Figure 3.17.	EDS spectrum of Au/GO nanocomposite. Inset figure gives the zeta potential of the Au/GO nanocomposites.	79
Figure 3.18.	Absorbance spectra of p-nitroaniline reduction using (a) Pd/GPTMS, (b) Pd/EETMS, (c) Pd/GO/GPTMS, and (d) Pd/GO/EETMS. Solid line represents the p-nitroaniline.	82
Figure 3.19.	Bar diagrams representing the variation in absorbance and completion of reaction, in relation to time for (a) Pd/GPTMS, (b) Pd/EETMS, (c) Pd/GO/GPTMS, and (d) Pd/GO/EETMS.	84
Figure 3.20.	Absorption spectra of reduction of p-nitrophenol using heat treated catalyst (a) at 423 K and (b) 623 K and corresponding bar diagrams (c) and (d).	85
Figure 3.21	Stability test before (a) and after 5–6 days (b), (i) and (ii) represent the variation in absorbance relative to time (c) recyclability assessment over 5 experimental cycles for the silica alginate beads entrapped with nanocomposites. Stability and recyclability was examined through p-nitroaniline reduction with 1.19 M hydrazine	86
Figure 4.1.	Variation in zeta potential with pH for pure alginate polymer solution (AA), organosilane (PdNPs) modified alginate polymer solution with (AA + GOx) and without (AA + Pd) glucose oxidase GOx in 0.1 M phosphate buffer.	94

- Figure 4.2.** (a) TEM image, (b) SAED pattern of Palladium nanoparticles. 96
- Figure 4.3.** Hydrodynamic radii of alginate polymer solutions at different stages of modification using different concentrations of organosilane [2-(3,4-(epoxycyclohexyl)ethyltrimethoxysilane (EETMS)]. 96
- Figure 4.4.** FTIR spectra of (a) alginate hydrogel, (b) alginate hydrogel with alkoxysilane functionalized palladium nanoparticles, (c) spectra of silica modified alginate hydrogel encapsulated with glucose oxidase enzyme, with peaks at 1653 and 1541 cm^{-1} , referring to the IR stretching bands of amide I (C=O) and amide II (N-H and C-H). 97
- Figure 4.5.** HR-SEM images of alginate hydrogel beads (a). Beads with (b) and (c) 0.01M EETMS, while (d) and (e) 2.5 M EETMS. 99
- Figure 4.6.** TGA (a) and DTA (b), curves for modified and unmodified alginate polymeric beads. 100
- Figure 4.7.** (a) Schematic illustration of catalytic activity of enzyme immobilised beads, (b) Luminescence spectra showing the variation in absorbance, as a function of concentrations of enzyme (1) 6 mg, (2) 4 mg (3) 2 mg in 0.2 mL phosphate buffer. 100
- Figure 4.8.** Colorimetric detection of oxidation of TMB in the presence of Prussian blue (PBNPs) nanoparticles. (a) Concentration dependent absorbance of TMB at 650 nm in different reaction systems. (b) Characteristic peak at 370 nm at pH = 1 of the reaction medium. Inset pictures (i) variation in color of reaction medium, (ii) appearance of yellow color upon addition of acid. 100
- Figure 4.9.** Colorimetric detection of formation of quinoneamine in the presence of Prussian blue (PBNPs) nanoparticles. (a) Concentration dependent absorbance 527 nm in different reaction systems. (b) Corresponding calibration plot of absorbance Vs concentration of glucose, (c) picture shows the 100

variation in color as a function of concentration of glucose.

Figure 4.10.	Evaluation of storage modulus at different concentrations of EETMS from (1-4).	111
Figure 4.11.	Kinetic analysis of PBNPs activity with in situ generated H_2O_2 as substrate.	112
Figure 5.1.	UV-Vis absorption spectra of bimetallic Au@PdNPs at different concentrations of precursors ($H AuCl_4/APTMS$), in (a) propanol, (b) methanol and (c) water.	121
Figure 5.2.	UV-Vis absorption spectra of bimetallic Pd-AgNPs at different concentrations of precursor (APTMS), in (d) propanol, (e) methanol and (f) water.	122
Figure 5.3.	TEM images (a)-(b), and corresponding SAED pattern of PdNPs (c). Inset to picture (a) shows the particle size distribution analysis.	123
Figure 5.4.	TEM images (a)-(b), and corresponding SAED pattern of Au@PdNPs (c). Inset to picture (a) shows the particle size distribution analysis. Inset to images (b) displays the lattice fringes.	123
Figure 5.5.	TEM images (a)-(b), and corresponding SAED pattern of Ag@PdNPs (c). Inset to picture (a) shows the particle size distribution analysis. Inset to images (b) displays the lattice fringes.	124
Figure 5.6.	EDS profile of Au@PdNPs. Inset shows the TEM image (i) elemental maps of Au and (ii) Pd in Au@PdNPs.	125
Figure 5.7.	EDS profile of Ag@PdNPs. Inset shows the TEM image (i) elemental maps of Ag and (ii) Pd in Ag@PdNPs.	125
Figure 5.8.	X-ray diffraction patterns of (a) PdNPs, (b) Au@PdNPs and (c) Ag@PdNPs.	126
Figure 5.9.	XPS spectra of Pd 3d in (a) PdNPs, (b) Au@PdNPs and (c) Ag@PdNPs; (d) Au 4f in Au@PdNPs and (e) Ag 3d in Ag@PdNPs respectively.	128

- Figure 5.10.** AFM topographies of (a) Au@PdNPs, (b) Ag@PdNPs and (c) PdNPs, in water. (d)-(f) The grain size distribution analysis of Au@PdNPs, Ag@PdNPs and PdNPs. Inset to the figures (a)-(c) shows the pore size distribution. 130
- Figure 5.11.** AFM topographies of (a) Au@PdNPs, (b) Ag@PdNPs and (c) PdNPs, in methanol. (d)-(f) The grain size distribution analysis of Au@PdNPs, Ag@PdNPs and PdNPs. Inset to the figures (a)-(c) shows the pore size distribution. 130
- Figure 5.12.** AFM topographies of (a) Au@PdNPs, (b) Ag@PdNPs and (c) PdNPs, in 2-propanol (d)-(f) The grain size distribution analysis of Au@PdNPs, Ag@PdNPs and PdNPs. Inset to the figures (a)-(c) shows the pore size distribution. 131
- Figure 5.13.** DLS profiles of Pd/EETMS and Pd/APTMS. (a) Average hydrodynamic radius of objects in water, methanol and 2-propanol. DLS profiles of Au@PdNPs and Ag@PdNPs. (a) Average hydrodynamic radius of objects in water, methanol and 2-propanol. 132
- Figure 5.14.** Cyclic voltammograms of 10 mM L-Trp in 0.1 M (a) phthalate buffer (pH-4.0), (b) phosphate buffer (pH-7.0), (c) borate buffer, (pH-9.0) on (1) and (2) bare GPE with and without analyte, (3) Pd/GPE, (4) Au@Pd/GPE and (5) Ag@Pd/GPE, at a scan rate of 2 mVs⁻¹. 133
- Figure 5.15.** FTIR spectra of (a) bimetallic colloidal solutions in different solvents, (b) magnified view of figure (a), and (c) comparison of the interactions between EETMS and APTMS, in the presence and absence metallic species. 134
- Figure 5.16.** DPV curves of L-Trp on Pd/GPE at (a) pH 4, (b) pH 7 and (c) pH 9, with concentrations ranging from 0.1 μM to 1000 μM. (d)-(f) Corresponding calibration curves of L-Trp. 140
- Figure 5.17.** DPV curves of L-Trp on Au@PdNPs/GPE at (a) pH 4, (b) pH 7 and (c) pH 9, with concentrations ranging from 0.1 μM to 1000 μM. (d)-(f) Corresponding calibration curves of L-Trp. 141
- Figure 5.18.** DPV curves of L-Trp on Ag@PdNPs/GPE at (a) pH 4, (b) pH 7 and (c) pH 9, with concentrations ranging from 0.1 μM to 142

1000 μ M. (d)-(f) Corresponding calibration curves of L-Trp.

- Figure 6.1.** UV spectrum of (1) Pd nanoparticles (2) bimetallic and trimetallic nanocomposites. 151
- Figure 6.2.** TEM image (a), SAED pattern (b) of PdNPs. 152
- Figure 6.3.** TEM image (a), electron diffraction pattern of (b) Ru@PdNPs. 152
- Figure 6.4.** TEM image (a), electron diffraction pattern of (b) Ag@Ru@PdNPs. 153
- Figure 6.5.** EDS spectra of PdNPs (a), Ru@PdNPs (b) and Ag@Ru@Pd (c) respectively at corresponding binding energies. 154
- Figure 6.6.** Elemental maps of (a) Pd, (b) Ru in bimetallic Ru@Pd nanoparticles. 154
- Figure 6.7.** Elemental maps of (a) Pd, (b) Ru and (c) Ag in trimetallic Ag@Ru@Pd nanoparticles. 155
- Figure 6.8.** XPS spectra of Palladium in monometallic (PdNPs) (a) corresponding bimetallic nanoparticles (Ru@Pd) and in (c) trimetallic nanoparticles (Ag@Ru@Pd). 156
- Figure 6.9.** XPS spectra of Ruthenium in Ru@PdNPs (a) and Ag@Ru@PdNPs (b). Spectrum of Silver in Ag@Ru@PdNPs (c). 156
- Figure 6.10.** AFM images of potassium ferricyanide encapsulated Ormosil (a), Ormosil-PdNPs (b), Ormosil-Ru@PdNPs (c) and Ormosil-Ag@Ru@PdNPs. 158
- Figure 6.10.** AFM images of potassium ferricyanide encapsulated Ormosil (a), Ormosil-PdNPs (b), Ormosil-Ru@PdNPs (c) and Ormosil-Ag@Ru@PdNPs. 158
- Figure 6.11.** Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ encapsulated within ormosil (a), ormosil-PdNPs (b), ormosil-Ru@PdNPs (c) and ormosil-Ag@Ru@PdNPs modified electrodes in 0.1 M 160

phosphate buffer pH 7 containing 0.5 M KCl at the scan rates between 1-600 mVs⁻¹

- Figure 6.12.** Cyclic voltammogram of Fe(CN)₆^{3-/4-} encapsulated (a) Ormosil, (b) Ormosil-PdNPs, (c) Ormosil-Pd-RuNPs and (d) Ormosil-Pd-Ru-AgNPs in absence (1), and presence (2) of Ascorbic acid (1 mM, 30 L) in phosphate buffer (.1 M, pH 7.0) at a scan rate of 10 mV/s. 161
- Figure 6.13.** Comparison of conventional and present synthetic routes in terms of stability and templating properties. 163
- Figure 6.14.** Plots of anodic and cathodic peak current densities against the scan rates for (a) Ormosil, (b) Ormosil-PdNPs, (c) Ormosil-Ru@PdNPs and (d) Ormosil-Ag@Ru@PdNPs. Inset pictures show the plots of anodic and cathodic peak current densities vs the square root of scan rates for (a) Ormosil, (b) Ormosil-PdNPs, (c) Ormosil-Ru@PdNPs and (d) Ormosil-Ag@Ru@PdNPs. 167
- Figure 6.15.** Chronoamperograms of Fe(CN)₆^{3-/4-} encapsulated (a) Ormosil, (b) Ormosil-PdNPs, (c) Ormosil-Ru@PdNPs and (d) Ormosil-Ag@Ru@PdNPs in absence (1), and presence (2) of AA (1 mM, 30 L) in phosphate buffer (0.1 M, pH 7.0) at a scan rate of 10 mV/s. Inset: I_{Ana}/I versus $t_{1/2}$ plots. 168
- Figure 7.1.** Stability analysis of mono and bimetallic nanoparticles by zeta potential measurements (a), EDS map of bimetallic nanoparticle (Ni₃PdNPs) suspension (b). 176
- Figure 7.2.** TEM image (a) and SAED pattern of PdNPs (b) corresponding particle size distribution (c). 178
- Figure 7.3.** TEM image (a), SAED pattern of NiNPs (b), and corresponding particle size distribution of NiNPs (c). 178
- Figure 7.4.** TEM images (a) & (e), SAED pattern (d) of Ni₃PdNPs and corresponding particle size distribution of Ni₃PdNPs (h). Magnified view of different shapes of Ni₃PdNPs particles (b, c, f, g). 179
- Figure 7.5.** XRD profile of (a) PdNPs, (b) NiNPs, (c) Ni₃PdNPs and (d) calcinated Ni₃PdNPs. 180

- Figure 7.6.** XPS spectrum of Pd in: (a) PdNPs, (b) NiPdNPs. Spectra of Ni in (c) NiNPs, (d) Ni₃PdNPs.
- Figure 7.7.** AFM images showing the grain size distribution in thin films of (A) PdNPs (B) NiNPs and (C) Ni₃PdNPs. Corresponding aspect ratio plots (A') PdNPs, (B') NiNPs and (C') Ni₃PdNPs.
- Figure 7.8.** Polarisation curves (a) and corresponding Tafel plots (i) of NiNPs, PdNPs, NiPdNP and Ni₃PdNP in 0.1 M KOH.
- Figure 7.9.** Polarisation curves (b) and corresponding Tafel plots (ii) of NiNPs, PdNPs, NiPdNP and Ni₃PdNP in 0.5 M KOH.
- Figure 7.10.** Polarisation curves of NiNPs, PdNPs, NiPdNP and Ni₃PdNP (a) in 1 M KOH and corresponding tafel plots (b).
- Figure 7.11.** Polarisation curves of calcinated NiNPs, PdNPs, and Ni₃PdNP (a) in 1 M KOH, tafel plots (b).
- Figure 7.12.** Nyquist plots of Ni₃PdNPs, NiNPs and PdNPs modified electrodes in 1 M KOH, (a) before and (b - d) after calcination at 473 K, (b) Ni₃PdNPs, (c) PdNPs and (d) NiNPs.
- Figure 7.13.** Stability evaluation of Ni₃PdNP electrode, by recording LSV polarisation curves over 1000 experimental cycles (a).

LIST OF TABLES

Table No.	Table caption	Page No.
Table 3.1.	Summary of values of d-spacing corresponding to the lattice planes obtained in synthesized Palladium nanocomposites.	72
Table 3.2.	Content of Au and other constituents in Au/GO nanohybrids.	80
Table 5.1.	Solvent dependent DLS profile of different nanoparticle systems.	136
Table 5.2.	Comparision of solvent dependent properties of thin films.	138
Table 6.1.	Compositions of four different types of electrode systems.	157
Table 6.2.	Summarized topographical features of different ormosil films obtained through AFM scans.	159
Table 6.3.	Chronoamperometric characteristics of different chemically modified electrodes.	166
Table 7.1.	Summarises the value of d-spacing, corresponding to the lattice planes present in the nanoparticles.	180
Table 7.2.	Summary of elemental composition of the Ni _x Pd _y NPs at different ratios.	181

LIST OF ABBREVIATIONS

BNPs	: Bimetallic Nanoparticles
N_2H_4	: Hydrous Hydrazine
GO	: Graphene Oxide
MWCNTs	: Multiwalled Carbon Nanotube
EETMS	: 2-(3, 4-epoxycyclohexyl)ethyltrimethoxysilane
3-APTMS	: 3-aminopropyltrimethoxysilane
GPTMS	: 3-glycidoxypropyltrimethoxysilane
TMS	: Trimethoxysilane
MB	: Methylene Blue
LeucoMB	: Leuco Methylene Blue
PNA	: para – Nitroaniline
THF-HPO	: Tetrahydrofuranhydroperoxide
PdNPs	: Palladium nanoparticles
SAED	: Selected Area Electron Diffraction
TEM	: Transmission Electron Microscopy
EDX	: Energy Dispersive X-Ray Analysis
FTIR	: Fourier Transform Infrared Spectroscopy
PEI	: Polyethyleneimine
TMB	: 3,3,5,5-tetramethyl benzidine
K_2PdCl_4	: Potassium tetrachloropalladate
PVP	: Polyvinylpyrrolidone
PBNPs	: Prussian blue Nanoparticles

DTA	: Differential Thermal Analysis
TGA	: Thermogravimetric analysis
AFM	: Atomic Force Spectroscopy
ITO	: Indium Titanium Oxide
AgNO ₃	: Silver nitrate
GCE	: Glassy Carbon Electrode
DPV	: Differential Pulse Voltammetry
L-Trp	: L-Tryptophan
XPS	: X-ray Photoelectron Spectroscopy
DLS	: Dynamic Light Scattering
CMC	: Critical Micelle Concentration
EDL	: Electrical Double Layer
R _H	: Hydrodynamic radius
TNPs	: Trimetallic Nanoparticles
NaBH ₄	: Sodium Borohydride
HER	: Hydrogen Evolution Reaction
RHE	: Reverse Hydrogen electrode
PVA	: Polyvinylalcohol
XRD	: X-ray Diffraction
TOF	: Turn Over Frequency
R _{ct}	: Charge Transfer Resistance
EIS	: Electrochemical Impedance spectroscopy
RhB	: Rhodamine B
L-Trp	: L-Tryptophan