

Contents

Title		Page No.
TITLE OF THESIS		i
CERTIFICATE		ii
DECLARATION BY THE CANDIDATE & CERTIFICATE BY THE SUPERVISOR		iii
COPYRIGHT TRANSFER CERTIFICATE		iv
Dedication		v
Acknowledgement		vi-viii
Contents		ix-xvi
List of Figures		xvii-xxii
List of Schemes		xxiii
List of Tables		xxiv
List of Symbols/Abbreviations		xxv-xxvi
Preface		xxvii-xxx
Chapter 1: General introduction		1-30
1.1	Noble metal nanoparticles: An introductory discussion	2
	1.1.1 Synthesis approach of noble metal nanoparticles	3
	1.1.1.1 Silver nanoparticles	3
	1.1.1.2 Palladium nanoparticles	4
	1.1.1.3 Gold nanoparticles	5
	1.1.2 Properties and applications of noble metal nanoparticles	7
	1.1.2.1 Properties of silver nanoparticles	7

		A.	Optical properties	7
		B.	Toxic properties	8
		C	Electrical properties	9
	1.1.2.2	Application of silver nanoparticles		10
		A.	Catalytic application	10
		B.	Sensing application	11
		C.	Photovoltaic applications	11
	1.1.2.3	Properties of palladium nanoparticles		12
		A	Electronic properties	12
		B	Catalytic properties	12
	1.1.2.4	Applications of palladium nanoparticles		13
		A.	Homogenous and heterogenous catalyst	13
		B.	Polymer membrane components	14
		C.	Sensors based on nanomaterials	14
		D.	SERS-active substrates	15
		E.	Nanosensitizers for fluorophore	15
	1.1.2.5	Properties of gold nanoparticles		16
		A.	Fluorescence quenching	16
		B.	Redox activity	16
		C.	Surface plasmon resonance (SPR)	17
	1.1.2.6	Applications of gold nanoparticles		17
		A.	Heavy metal ions detection	17
		B.	Colorimetric Sensing	18
		C.	Sensing based on fluorescence	18
		D.	Detection of small organic molecules	19

			E.	Hydrogenation reaction	19
			F.	Therapeutics	19
			G.	Detection of Anions	20
	1.2	Synthesis and application of multimetallic analogues of noble metal nanoparticles			20
		1.2.1	Bimetallic nanoparticles		21
		1.2.2	Trimetallic nanoparticles		22
	1.3	Challenges in the synthesis and application of noble metal nanoparticles and their multimetallic analogues			23
	1.4	Origin of the present research programme			24
	1.5	Objective of the present research investigation			25
	1.6	Work plan of the thesis			28
Chapter 2:					
Trialkoxysilane-functionalized synthesis of noble metal monometallic, bimetallic, and trimetallic nanoparticles mediated non-enzymatic sensing of glucose by resonance Rayleigh scattering					31-52
	2.1	Introduction			31
	2.2	Experimental section			33
		2.2.1	Materials and reagent		33
		2.2.2	Microwave-assisted synthesis of trialkoxysilane functionalized noble metal nanoparticles and their multimetallic analogues:		33
		2.2.2.1	Microwave-assisted 3-APTMS and 3-GPTMS mediated controlled synthesis of gold nanoparticles		33

		2.2.2.2	Microwave-assisted 3-APTMS and 3-GPTMS mediated synthesis of silver nanoparticles	34
		2.2.2.3	Microwave-assisted 3-APTMS and formaldehyde mediated controlled synthesis of palladium nanoparticles	34
		2.2.2.4	Microwave-assisted 3-APTMS and 3-GPTMS mediated controlled synthesis of Au-Ag bimetallic nanoparticles	34
		2.2.2.5	Microwave-assisted 3-APTMS, 3-GPTMS, and formaldehyde mediated controlled synthesis of Ag -Pd bimetallic nanoparticle	35
		2.2.2.6	Microwave-assisted 3-APTMS, 3-GPTMS, and formaldehyde mediated controlled synthesis of Au-Ag-Pd trimetallic nanoparticles	35
		2.2.2.7	Microwave-assisted 3-APTMS, 3-GPTMS, and formaldehyde mediated controlled synthesis of Au-Pd bimetallic nanoparticle	36
	2.2.3	Instrumentation		36
2.3	Results and discussion			36
	2.3.1	Functional trialkoxysilane mediated synthesis of AuNPs, AgNPs, and PdNPs and their multimetallic analogues		36
	2.3.2.	Synchronous fluorescence spectroscopy of functional trialkoxysilane -functionalized noble metal nanoparticles and multimetallic nanoparticles for non-enzymatic sensing of glucose		45
		2.3.2.1	Non-enzymatic sensing of glucose by AuNPs in the presence and absence of nafion	46

		2. 3.2.2	Non-enzymatic sensing of glucose by using Au-Pd bimetallic nanoparticles with different metal ratio in the presence of nafion	47
		2.3.2.3	Non-enzymatic sensing of glucose by using Ag and Pd monometallic nanoparticles	49
		2. 3.2.4	Non-enzymatic sensing of glucose by using Ag-Pd, Au-Ag bimetallic and Au-Ag-Pd trimetallic nanoparticles	51
2. 4	Conclusions			52
Chapter 3: Functional trialkoxysilane mediated controlled synthesis of fluorescent gold nanoparticles and fluoremetric sensing of dopamine				53-73
3.1	Introduction			53
3.2	Experimental section			55
	2.2.1	Materials and reagent		55
	3.2.2	3-APTMS and 3-GPTMS-mediated synthesis of Au-NPs		56
	3. 2.3	Quantum yield determination		56
	3. 2. 4	Sensing of DA using AuNPs		57
	3.2.5	Detection of DA in biological fluid		58
	3.2. 6.	Instrumentation		58
3. 3	Results and discussion			58
	3.3.1	Microwave assisted 3-APTMS and 3-GPTMS mediated controlled synthesis of fluorescent gold nanoparticle		58
	3.3.2	Characterization of synthesized fluorescent AuNPs		60

	3.3.3	Optical characteristics of the fluorescent AuNPs	63
	3.3.4	DA sensing	66
	3.3.5.	Real sample analysis	68
	3.3.6	Selectivity and interference studies	68
	3.3.7	Fluorescence Quenching mechanism	69
	3.3.8	Fluorescence Life time decay analysis	71
3.4	Conclusions		72
Chapter 4: Trialkoxysilane-functionalized synthesis of mesoporous supported palladium-nickel nanocatalyst for selective hydrazine decomposition and sensing			74-90
4.1.	Introduction		74
4.2	Experimental section		76
	4.2.1	Materials and reagents	76
	4.2.2	Instrumentation	77
	4.2.3	Synthesis of AuNPs-1	77
	4.2.4	Synthesis of AuNPs-2	78
	4.2.5	Functional trialkoxysilane mediated synthetic incorporation of palladium nanoparticles within mesoporous silica and mesoporous silica nanoparticles	78
	4.2.6	Synthesis of Pd-Ni NPs-1 and Pd-Ni NPs-2 bimetallic nanoparticle inserted MSNPs	79

	4.2.7.	Hydrous hydrazine decomposition	79
4.3.	Results and discussion		79
	4.3.1	Microwave-assisted 3-APTMS and 3-GPTMS mediated controlled synthesis of gold nanoparticles	79
	4.3.2	Synchronous fluorescence spectroscopy of Functional trialkoxysilane-functionalized gold nanoparticles in hydrous hydrazine sensing	82
	4.3.3	Synthesis and characterization of Pd-Ni bimetallic nanocrystallite inserted mesoporous silica nanoparticles	84
	4.3.4	Decomposition of hydrous hydrazine	88
4.4.	Conclusions		90
Chapter 5:			91-118
Synthetic incorporation of palladium-nickel bimetallic nanoparticles within mesoporous silica/silica nanoparticles as efficient and cheaper catalyst for both cationic and anionic dyes degradation			
5.1	Introduction		91
5.2	Experimental Section		96
	5.2.1	Materials and reagent	96
	5.2.2	Synthetic incorporation of palladium nanoparticles within mesoporous silica (MSPs) and mesoporous silica nanoparticles (MSNPs)	96
	5.2.3	Synthesis of Pd-Ni bimetallic nanoparticles inserted MSNPS/MSPs	96
	5.2.4	Instrumentation	96

	5.2.5	Measurement of cationic and anionic dyes Degradation	97
		5.2.5.1 Pd-Ni inserted MSNPs mediated degradation of Congo red	97
		5.2.5.2. Pd-Ni inserted MSNPs mediated degradation of Rhodamine (Rh B)	97
5.3	Results and discussion		98
	5.3.1	Synthesis and characterization of Pd-Ni bimetallic nanocrystallite inserted MSNPs/MSPs	98
	5.3.2	Catalytic degradation of both cationic and anionic dyes	103
	5.3.3	Mechanism of nanocatalyst supported mesoporous silica mediated dye degradation	109
	5.3.4	Degraded end product analyzed by high resolution mass spectroscopy of both cationic and anionic dyes	111
	5.3.5	Catalyst recyclability	115
	5.3.6	Catalytic degradation of a real sample collected from the textile industry	115
	5.3.7	Degradation Congo red based effluent	116
	5.3.8	Degradation Rh B based effluent	117
6.4	Conclusion		117
Summary			119-122
Future Recommendations			123-124
References			125-174
List of Publications			175-176

List of Figures

Figure No.	Title	Page No.
Figure 2.1.	UV-Vis spectra of the nanoparticles (a)gold nanoparticles (b) silver nanoparticles (c) palladium nanoparticles (d) bimetallic (Au-Ag) nanoparticles (e) trimetallic (Au-Ag-Pd) nanoparticles.	37
Figure 2.2	(a) & (b) TEM images (c) SAED pattern and (d) particle size distribution graph of gold nanoparticles.	38
Figure 2.3	(a) & (b) TEM images (c) SAED pattern and (d) particle size distribution graph of silver nanoparticles.	38
Figure 2.4	(a) & (b) TEM images (c) SAED pattern of palladium nanoparticles.	39
Figure 2.5	(a) & (b) TEM images (c) SAED pattern and (d) particle size distribution graph of Au-Ag bimetallic nanoparticles.	41
Figure 2.6	(a) & (b) TEM images (c) SAED pattern and (d) particle size distribution graph of Ag-Pd bimetallic nanoparticles.	42
Figure 2.7	(a) & (b) TEM images (c) SAED pattern and (d) particle size distribution graph of Au-Pd bimetallic nanoparticles	42
Figure 2.8	(a) & (b) TEM images (c) SAED pattern and (d) particle size distribution graph of Au-Ag-Pd trimetallic nanoparticles.	43
Figure 2.9	XRD profile of XRD profile of (a) PdNPs, (b) AgNPs, (c) AuNPs	44
Figure 2.10	XRD profile of (a) trimetallic (Au-Ag-Pd) NPs, (b) bimetallic (Au-Ag) NPs, (c) bimetallic (Au-Pd) NPs, and (d) bimetallic (Ag-Pd) NPs.	45

Figure 2.11	(a) Synchronous fluorescence spectra at $\Delta\lambda=0$ nm, the spectra were recorded at various concentrations of glucose. (b) Synchronous fluorescence intensity of AuNPs in the presence of glucose and ascorbic acid. (c) Synchronous fluorescence spectra at $\Delta\lambda=0$ nm, the spectra were recorded at different concentrations of glucose with nafion. (d) Synchronous fluorescence intensity of AuNPs with nafion in the presence of glucose and ascorbic acid.	47
Figure 2.12	Synchronous fluorescence spectra at $\Delta\lambda=0$ nm; the spectra were recorded at various concentrations of glucose. (a) Synchronous fluorescence intensity of bimetallic (AuPd) NPs with an Au:Pd ratio of 20:80. (b) Synchronous fluorescence intensity of bimetallic (Au-Pd) NPs with an Au:Pd ratio of 80:20. (c) Synchronous fluorescence intensity of bimetallic (Au-Pd) NPs with an of ratio Au:Pd 80:20 with nafion. (d) Synchronous fluorescence intensity of bimetallic (Au-Pd) NPs with an Au:Pd ratio of 80:20 with nafion in the presence of glucose and ascorbic acid.	48
Figure 2.13	Linear plot (a) Concentration of glucose versus synchronous fluorescence spectroscopy (SFS) intensity in the presence of AuNPs with nafion. (b) The concentration of glucose versus SFS intensity in the presence of bimetallic Au-Pd nanoparticles with an Au:Pd ratio of 80:20 with Nafion.	49
Figure 2.14	Synchronous fluorescence spectra at $\Delta\lambda = 0$ nm, recorded at various concentrations of glucose. (a) AgNPs (b) Synchronous fluorescence intensity of AgNPs in the presence of glucose and	50

	ascorbic acid. (c) PdNPs, (d) Synchronous fluorescence intensity of PdNPs in the presence of glucose and ascorbic acid.	
Figure 2.15	Synchronous fluorescence spectra at $\Delta\lambda = 0$ nm recorded at various concentration of glucose: (a) bimetallic (Ag-Pd) NPs, (b) bimetallic (Ag-Au) NPs, and (c) trimetallic (Au-AgPd) NPs.	51
Figure 3.1	(a) TEM image with the inset showing the fringes of the fluorescent AuNPs (b) particle size distribution histograms were obtained from the TEM image. (c) SAED pattern and (d) EDAX analysis of the fluorescent AuNPs.	60
Figure 3.2	(a) Full scan XPS spectrum (b) Au 4f spectra (c) C1s spectra (d) N1s spectra (e) O1s spectra (f) Si2p spectra of the fluorescent AuNPs.	61
Figure 3.3	(a) XRD pattern (b) zeta potential of the fluorescent AuNPs.	63
Figure 3.4	(a) UV-visible absorption spectrum (black line) and fluorescence emission spectrum (blue line). (b) Fluorescence emission spectra showing the different excitation wavelength (290-420nm). (c) Image of CIE coordinates showing the blue color of fluorescent AuNPs. (d) Fluorescence emission intensity at various pH ranging from 1 to 11.	64
Figure 3.6	(a) Fluorescence emission intensity decreases with increasing DA concentration from 0 to 96 μ M. (b) The linear calibration graph for the concentration ranges from 0 to 96 μ M with inset showing the concentration range from 0 to 0.6 μ M.	67

Figure 3.7	(a) Shows the selectivity of various metal ions and other compounds. (b) interference study of various metal ions and biomolecules in the presence and presence of DA.	69
Figure 3.8	Time resolved fluorescence decay of fluorescent AuNPs in the absence and presence of DA.	71
Figure 4.1	TEM images and SAED patterns of AuNPs-1(a, b) and AuNPs-2 (d, e), respectively. The particle size distribution for AuNPs-1 and AuNPs-2 are shown in Figure 4.1c and Figure 4.1f, respectively.	81
Figure 4.2	(a) and (b) show the UV-VIS spectra of AuNPs-1 and AuNPs-2, respectively.	81
Figure 4.3	Synchronous fluorescence spectra at $\delta\lambda=0$ recorded in the absence and the presence of different concentrations of hydrous hydrazine with AuNPs-1 (a) and AuNPs-2(c). Synchronous fluorescence spectrum intensity versus hydrous hydrazine concentration for AuNPs-1 (b) and AuNPs-2 (d) respectively.	83
Figure 4.4	TEM images and SAED pattern of Pd-Ni inserted mesoporous silica nanoparticles made at Pd:Ni ratios of 1:1 (a, b and c), for Pd-Ni metal ratio of 1:5 (d, e and f) respectively.	86
Figure 4.5	(a) and (e) show the EDX results of bimetallic Pd-Ni inserted MSNPs at a 1:1 and a 1:5 Pd-Ni metal ratio. (b-d) and (f-h) show the elemental mapping of Pd-Ni at a 1:1 and 1:5 metal ratio, respectively.	87
Figure 4.6	(a) Synchronous fluorescence spectra at $\Delta\lambda=0$ nm recorded before (ii) and after (iii) hydrous hydrazine decomposition; (i)	88

	shows the control. (b) N ₂ adsorption-desorption isotherms of Pd-Ni metal ratio 1:1 inserted mesoporous silica nanoparticles.	
Figure 5.1.	TEM images of synthetically inserted noble metal nanoparticles within mesoporous silica nanoparticles: (a) Gold nanoparticles, (b) Au-Ag bimetallic nanoparticles, and (c) (Au-Ag-Pd) trimetallic nanoparticles.	100
Figure 5.2	The plot of absorbance versus wavelength for the reduction of methylene blue in the presence of NaBH ₄ and gold inserted MSNPs.	101
Figure 5.3	The plot of absorbance versus wavelength for the reduction of methylene blue in the presence of NaBH ₄ and Au-Ag bimetallic inserted MSNPs.	102
Figure 5.4	The plot of absorbance versus wavelength for the reduction of methylene blue in the presence of NaBH ₄ and (Au-Ag-Pd) trimetallic inserted MSNPs.	103
Figure 5.5	Fig. 5.5. UV-vis absorption spectra of (a) PdNPs (b) Pd-Ni NPs-1 (c) Pd-Ni NPs-2 inserted mesoporous silica particle (MSPs) of diameter 50 μm mediated degradation of 15 ppm Rh B.	104
Figure 5.6	Fig. 5.6. UV-vis absorption spectra of (a), PdNPs (b), Pd-Ni NPs-1 (c) Pd-Ni NPs-2 inserted mesoporous silica particle (MSPs) of diameter 50 μm mediated degradation of 55 ppm Congo red.	105
Figure 5.7	Fig. 5.7. Plot between the ln(C ₀ /C _t) Vs time curve and linear fitting for (a) Rh B and (b) Congo red show for PdNPs, Pd-Ni NPs-1, and Pd-Ni NPs-2 inserted mesoporous particles supported nanocatalysts.	105

Figure 5.8	Fig. 5.8. UV-vis absorption spectra of Pd-Ni NPs-1 inserted mesoporous silica nanoparticles (MSNPs) diameter 200 nm mediated degradation of (a) Rh B and (b) Congo red. Plot between the $\ln(C_0/C_t)$ Vs time curve and linear fitting for (c) Rh-B and (d) Congo red, show for Pd-Ni NPs-1, inserted mesoporous silica nanoparticles (MSNPs) diameter 200 nm supported nanocatalysts.	106
Figure 5.9	Fig. 5.9. (a) N ₂ adsorption-desorption isotherms of PdNPs (i) and Pd-Ni NPs-1 (ii) inserted mesoporous silica particle; (b) Pore volume distribution curve of PdNPs and Pd-Ni NPs-1 inserted mesoporous silica particle.	109
Figure 5.11	HR-MS spectrum of Congo red(a) before and (b) after degradation.	112
Figure 5.12	Fig. 5.12. HR-MS spectrum of Rh B (a) before and (b) after degradation.	113
Figure 5.13	Fig. 5.13. (a), (b) shows the UV-Vis absorption spectra of the real textile sample in the absence and the presence of Pd-Ni NPs-1 inserted MSPs, for Congo red and for Rh B. The samples were collected from the washout of stencil used in fabric printing using dye embedded with binder and thinner.	116

List of Schemes

Scheme No.	Title	Page No.
Scheme 3.1	The schematic illustration of fluorescence emission intensity quenching of fluorescent AuNPs with DA and as well as the diagram depicts the reaction mechanism of DA to DQ via electron transfer from DA to fluorescent AuNPs and the donation of those electrons to DQ, which results in fluorescence quenching.	70
Scheme 5.1	Mechanism of Rh B degradation	114
Scheme 5.2	Mechanism of CR degradation	114

List of Table

Table No.	Title	Page No.
Table 3.1	Fluorescence quantum yield determination of functional trialkoxysilane mediated synthesized fluorescent AuNPs with reference to quinine Sulphate at excitation wavelength 360 nm from the equation (1).	57
Table 3.2	Comparison performance of various reported methods for DA detection.	67
Table 3.3	Detection of DA in spiked CSF.	68
Table 4.1	Show the data on specific surface area, pore volume and average pore diameter of Pd-Ni inserted mesoporous support.	88
Table 5.1	Summary of the apparent rate constants for the reduction of CR and Rh B in the presence of nanocatalyst inserted mesoporous silica and mesoporous silica nanoparticles.	107
Table 5.2	Pore parameter of nanocatalyst inserted mesoporous silica of size 50 μ m.	109