To Maa…

For her advice, her patience, and her faith...

Without her nothing would have been possible….

DECLARATION

I, Koushik Barman, hereby state that the thesis entitled "Electrochemical Sensing of **Some Selected Bio-molecules Using Chemically Modified Gold Electrodes**" has not been submitted either in whole or in part earlier to any other institution for the award of any degree and does not contain any previously published material or written by other person, except where due reference is made in the text.

Kowshik Broman

Place: Silchar Koushik Barman

Date: 05.09.2017

Acknowledgements

First of all, I wish to express my sincere gratitude to my supervisor, Dr. Sk. Jasimuddin Sir, for his unwavering support, vital encouragement, immense care, and continuous valuable guidance throughout the duration of my post graduate study, project work and Ph.D. tenure. It has been his continuous inspiration and encouragement that has enabled me to complete my research work.

I also wish to express my gratitude to our Head of Department Dr. P. C. Paul for his support. Besides, my gratitude to all the teachers of Chemistry department from whom I have learned so many valuable lesions along with chemistry. I thank Prof. N.V.S. Rao, Prof. S. B. Paul, Prof. C. R. Bhattacharjee, Dr. P. Mandal, Dr. M. K. Paul, Dr. H. Acharya, Dr. S. Ghosh, Dr. D. Sengupta, Dr. S. Chowdhury, Dr. T. S. Singha, Dr. R. Panchadhyee and my supervisor for their inspiration, training and guidance during the entire period. Also, I am grateful to Dr. Mahuya Sengupta, Department of Biotechnology for her generous help.

Besides, I would like to express my thanks to the technical staff section Mr. P. Ramesh, Mr. S. Bhattacharjee, Mr. B. Nath, Mr. A. J. A. Barbhuya and Mr. Rajib Kurmi for their help and support during the course. I would also like to thank all of the official staffs of our Department of Chemistry Jamil da, Hmar da and Sanjiv for their kind help in every field that they possibly could to complete my Ph.D. research work.

I express my sincere thanks to my lab mates Abhinandan Mahanta, Bishwajit Changmai, Umme Solaem Akond and all other Research Scholars of the Department of Chemistry, for their active co-operation and friendship that made me pleased during this research work. Also, I am thankful to my friends Hirak Chatterjee, Rupam Chakrabarty, Hasimur Rahman, Samiran Garain, Sudip kumar Pal, Nayan Roy, Abhijit Dutta, Sandip kumar Saha, Nirmalendu Das and Dewan A. Islam for their help.

I acknowledge Department of Chemistry, Assam University, Silchar and UGC, New Delhi for providing infrastructures and financial support.

I wish to express my great appreciation and my heart-felt gratitude to my parents specially my mother for her support, advice, encouragement, understanding and the financial assistance, which have made my research study possible. Undoubtedly, I acknowledge and express my heartiest regards to my father, Late Mr. Hari Narayan Barman for his constant affection, motivation, inspiration and help. Without them, I would not been the person what I am today. I am very thankful and in the same time very much grateful to my all family members specially my aunty Mitali Bhattacherjee and uncle Sumanta Bhattacherjee, for their tremendous supports and valuable advices that has been shared to me during Ph.D. tenure.

Finally, I am thankful to God who has made all this possible to me.

Koushik Barman

TABLE OF CONTENTS

xiii

Annexure: List of publications and Conferences attended

Preface

The thesis entitled **"Electrochemical Sensing of Some Selected Bio-molecules Using Chemically Modified Gold Electrodes"** describes the results of a Ph.D. study initiated in September 2013. The study was on the modification of gold electrode surface with different aliphatic and aromatic thiol films having redox active species that include transition metal complexes and metal nanoparticles and the application of their electrochemical sensing of some selected biologically important molecules. The modified electrode surface was characterized by using microscopic (scanning electron microscopy), spectroscopic (energy dispersive X-ray analysis, Fourier transform infrared spectroscopy) and electrochemical (cyclic voltammetry, electrochemical impedance spectroscopy) techniques. The sensing property of the electrode material was investigated by two different electrochemical techniques, *viz*., differential pulse voltammetry and chronoamperommetry.

This thesis consists of seven chapters. In the introductory chapter (**Chapter 1)**, a brief description of bio-molecules, their sensing techniques, chemically modified electrodes, different electrode modifications and characterization techniques and a short review on the electrochemical sensing of some selected bio-molecules using self-assembled thiol monolayer modified gold electrodes along with the present investigation proposal. In **Chapter 2,** a brief account of the chemicals and reagents used for the synthesis purpose and a brief description of various techniques used for the characterization or electrochemical sensing application of the chemically modified gold electrode has been included. **Chapter 3** and **Chapter 4** contains the preparation and characterization of selfassembled aromatic thiols $(4-(2^2\text{-midazolylazo})$ thiophenol and 4 -(pyridine-4 $\frac{1}{2}$ amido)thiophenol) layer modified gold electrode containing transition metal (copper and vanadium) complexes, respectively. The copper(II) complex modified gold electrode was utilized for the sensing of purine bases - adenine and guanine, whereas, the vanadium(IV) complex modified electrode was applied for the detection of glucose and hydrogen peroxide. In **Chapter 5** and **Chapter 6**, we describe the synthesis of CTAB and PVP capped silver nanoparticles and their immobilization on self-assembled aliphatic thiols, L-cysteine, and penicillamine monolayer modified gold electrode, respectively. The electrodes modified with nanoparticles were used for the electrochemical sensing of vitamin, ascorbic acid and catecholamine neurotransmitters, dopamine and epinephrine. In **Chapter 7**, the significant results of the research work have been summarized and the future scopes of the work stated.

I am happy to state that the work has been published in national and international journals (List of Publications).

As usual practice, findings of other investigators have been duly acknowledged throughout the thesis. Finally, I take the responsibility of any unintentional errors which might have escaped notice despite due precautions.

Abbreviations

List of Figures

- Fig. 3.1. Schematic representation for the fabrication of gold electrode and the electrochemical oxidation mechanism of adenine and guanine 34
- Fig. 3.2. SEM images of bare (A), 4-ATP modified (B), IATP modified (C) , Cu^{2+} -IATP modified gold electrode 36
- Fig. 3.3. EDAX spectrum of bare (A), 4-ATP modified (B), IATP modified (C) , Cu^{2+} -IATP modified gold electrode 36
- Fig. 3.4. FTIR spectra of (a) 4-ATP modified (b) IATP modified (b) and (c) Cu^{2+} -IATP modified gold electrode 37
- Fig. 3.5. Cyclic voltammograms (A) and Nyquist plot $(-Z¹$ versus Z' (B) of 0.5 mM K₄[Fe(CN)₆] in 0.1M PBS at pH 7 using different working electrode [bare Au (red), ATP - Au (light blue), $ATP-N^{+2}$ - Au(dark blue) and IATP - Au (black)]. [Inset: enlarge figure of two overlapping curve for ATP $-N^{+2}$ - Au (dark blue) and IATP - Au (black)] 38
- Fig. 3.6. (A) Overlaid cyclic voltammograms of bare Au (red line), ATP-Au (blue line), Cu^{2+} -IATP-Au (violet line) modified electrode and (B) cyclic voltammogram of IATP-Au electrode in varying concentration of CuSO⁴ [0.1 mM -0.7 mM] in 0.1 M PBS at pH 7.0 39
- Fig. 3.7. Plot of pH versus cathodic peak current (I_{pc}) for copper complexation with IATP-Au electrode in 0.1 M PBS solution 40
- Fig. 3.8. Overlaid cyclic voltammogram and Nyquist plot (inset) of 1 mM Guanine (A) and 1 mM adenine (B) in 0.1 M PBS solution at pH 7 using different working electrodes. [Bare Au (red), IATP - Au (blue) and Cu^{2+} - IATP - Au (green)] 41
- Fig. 3.9. Overlaid DPV with increasing guanine concentration (150 - 600 μ M) in 0.1 M PBS (pH 7). [Inset: Plot of current as a function of concentration of guanine with 42

linear trend line $(R^2 > 0.99)$]

- Fig. 3.10. Overlaid DPV with increasing Adenine concentration (150 - 600 μ M) in 0.1 M PBS (pH 7). [Inset: Plot of current as a function of concentration of adenine with linear trend line $(R^2 = 0.985)$] 42
- Fig. 3.11. Overlaid DPV for each increment of 10 μ M G to 100 μ M A at Cu^{2+} - IATP SAM modified gold electrode in 0.1 M PBS buffer solution at pH 7.0 43
- Fig. 3.12. DPVs obtained for each 10 μ M A to 100 μ M G at Cu²⁺ -IATP SAM modified gold electrode in 0.1 M PBS buffer solution at pH 7.0 44
- Fig. 3.13. (A) DPV obtained for A and G with each increment of 50 μ M each A and G at Cu²⁺-IATP-Au SAM electrode in 0.1 M PBS ($pH = 7$). [(B) Plot of current as a function of concentration of adenine with linear trend line $(R^2 =$ 0.992), (C) Plot of current as a function of concentration of guanine with linear trend line $(R^2 = 0.99)$] 44
- Fig. 3.14. Plot of accumulation time *versus* oxidation peak current for adenine (blue line) and guanine (red line) 46
- Fig. 3.15. Plot of accumulation potential *versus* oxidation peak current for adenine (blue line) and guanine (red line) 46
- Fig. 3.16. Overlaid Cyclic voltammogram of adenine (A) and guanine (B) with different scan rate (10-90 mV/s) at Cu^{2+} -IATP-Au electrode [Inset (A) Plot of current as a function of scan rate of adenine with linear trend line (R^2) $= 0.9939$) and (B) Plot of current as a function of scan rate of guanine with linear trend line ($R^2 = 0.9925$) 47
- Fig. 3.17. DPV obtained for 1.0 mM adenine (A) and 1.0 mM guanine (B) at Cu^{2+} -IATP-Au electrode in different pH $(3.0 - 9.0)$. (C) The Plot of the oxidation peak potential 48

versus the solution pH for A and G. (D) The Plot of the oxidation peak current *versus* the solution pH for A and G

- Fig. 3.18. DPV of A and G in presence of 1000 fold excess of Ascorbic acid 49
- Fig. 3.19. Overlaid DPVs of 0.1 M PBS solution (red), herring sperm DNA solution (blue) and after addition of standard A, G solution in herring sperm DNA solution (green) 50
- Fig. 4.1. FE-SEM images (top) of different electrode systems bare Au (A), ATP -Au (B), PATP- Au (C), $[VO(acac)_2]$ -4-PATP modified gold electrode (D) (10 μ m scale bar) and elemental mapping images (bottom) of $[VO(acac)₂]$ -4-PATP modified gold electrode(1µm scale bar) 60
- Fig. 4.2. (A) Cyclic voltammograms and Nyquist plot $(-Z¹$ versus Z') (inset) of 0.5 mM K₄[Fe(CN)₆] in 0.1M PBS at pH 7 using different working electrode [bare Au (black), ATP -Au (red), PATP- Au (green)]. (B) Cyclic voltammograms in 0.1M PBS at pH 7 before (red) and after (green) immobilization of $[VO(acac)_2]$ 61
- Fig. 4.3. Cyclic voltammograms obtained with bare, PATP and $[VO(acac)_2]$ -4-PATP modified gold electrode in 0.1 mM glucose (A) and 0.5 mM hydrogen peroxide (B) in 0.1 M PBS solution (pH 7.0) 62
- Fig. 4.4. (A) Overlaid CV obtained with (red curve) and without (blue curve) 0.1 mM glucose at the $[VO(acac)₂]$ -4-PATP-Au electrode in 0.1 M PBS solution ($pH = 7.0$). (B) Overlaid DPV obtained with bare (brown curve), PATP (green curve) and $[VO(acac)_2]$ -4-PATP (black curve) modified gold electrode in 0.1 mM glucose in 0.1 M PBS solution ($pH = 7.0$) 62

Fig. 4.5. Overlaid cyclic voltammogram obtained with (red curve) 63

and without (blue curve) 0.5 mM H_2O_2 at the $[VO(acac)_2]$ -4-PATP-Au electrode in 0.1 M PBS solution $(pH = 7.0)$

64

- Fig. 4.6. Overlaid Nyquist plot of 0.1 mM glucose (A) and 0.5 mM H_2O_2 (B) in 0.1 M phosphate buffer solution (pH = 7.0) using bare and modified gold electrodes. $E_{ac} = 10$ mV, frequency range: 0.01-100000 Hz. For glucose, bare Au (blue curve), $R_{ct} = 4.0 \times 10^4 \Omega$; PATP - Au (red curve), $R_{ct} = 4.8 \times 10^4 \Omega$; [VO(acac)₂]-4-PATP-Au (green curve, $R_{ct} = 1.3 \times 10^4 \Omega$ and for H₂O₂, bare Au (blue curve), $R_{ct} = 2.6 \times 10^5 \Omega$; PATP-Au (red curve), R_{ct} $= 6.4 \times 10^5 \Omega$; [VO(acac)₂]-4-PATP-Au (green curve), $R_{\rm ct}$ = 1.2 \times 10⁵ Ω
- Fig. 4.7. (A) Chronoamperograms with increasing concentration of glucose $(0.1 \text{ to } 0.5 \text{ mM})$ in 0.1 M PBS (pH 7.0) at $[VO(acac)_2]$ -4-PATP-Au electrode at $+$ 0.65 V *vs* Ag/AgCl. LOD= $0.1 \mu M$. (B) Plot of resulting current in chronoamperometry at 30 seconds *versus* concentration of glucose $(0.1 - 0.5$ mM) 65
- Fig. 4.8. (A) Chronoamperograms with increasing concentration of glucose (1.0 μ M to 5.0 μ M) in 0.1 M PBS (pH 7.0) at $[VO(acac)_2]$ -4-PATP-Au electrode at $+$ 0.65 V *versus* Ag/AgCl. (B) Plot of concentration of glucose *versus* oxidation peak current. Detection limit 0.1 μ M (S/N = 3) 66
- Fig. 4.9. (A) Overlaid Differential pulse voltammogram with increasing glucose concentration (1-14 mM) in 0.1 M PBS ($pH = 7.0$) at $[VO(acac)₂]$ -4-PATP-Au electrode (B) Plot of current as a function of concentration of glucose with linear trend line ($R^2 > 0.99$) 66
- Fig. 4.10. (A) Chronoamperograms with increasing concentration 67

of H_2O_2 (0.5 to 0.9 mM) in 0.1 M PBS (pH 7.0) at [VO(acac)2]-4-PATP-Au electrode at - 0.11 V *versus* Ag/AgCl. LOD = $0.03 \mu M$. (B) Plot of resulting current in chronoamperometry at 30 seconds *versus* concentration of H_2O_2 (0.5 – 0.9 mM)

- Fig. 4.11. (A) Chronoamperograms with increasing concentration of H_2O_2 (20 to 40 μ M) in 0.1 M PBS (pH 7.0) at [VO(acac)2]-4-PATP-Au electrode at - 0.11 V *versus* Ag/AgCl. (B) Plot of concentration of H₂O₂ versus reduction peak current. Detection limit 0.03 μ M (S/N = 3) 67
- Fig. 4.12. (A) Overlaid cyclic voltammograms with increasing hydrogen peroxide concentration in 0.1 M PBS ($pH =$ 7.0) at $[VO(acac)₂]$ -4-PATP-Au electrode (B) Plot of current as a function of concentration of hydrogen peroxide with linear trend line $(R^2 > 0.99)$ 69
- Fig. 4.13. (A) Cyclic voltammograms of 0.1 mM glucose in 0.1 M PBS (pH 7.0) at different scan rate using $[VO(acac)₂]$ -4-PATP-Au electrode (B) Plot of oxidation peak current *versus* square root of scan rate 69
- Fig. 4.14. (A) Cyclic voltammograms of 0.5 mM H_2O_2 in 0.1 M PBS (pH 7.0) at different scan rate using $[VO(acac)₂]$ -4-PATP-Au electrode (B) Plot of oxidation peak current of 0.5 mM H2O2 *versus* square root of scan rate 70
- Fig. 4.15. Plot of scan rate-normalized current $(I_p/v^{1/2})$ with scan rate (v) 70
- Fig. 4.16. Plot of accumulation time *versus* oxidation peak current of glucose and reduction peak current of H_2O_2 in 0.1 M PBS at pH 7 at $[VO(acac)_2]$ -4-PATP-Au electrode 71
- Fig. 4.17. (A) Plot of applied potential *versus* oxidation peak current of 0.1 mM glucose in 0.1 M PBS (pH 7) at 72

 $VO(acac)₂-4-PATP-Au$ electrode. (B) Plot of applied potential *versus* reduction peak current of 0.5 mM H_2O_2 in 0.1 M PBS (pH 7) at $VO (acac)₂-4-PATP-Au$ electrode

- Fig. 4.18. (A) Overlaid DPV of 0.1 mM glucose at different pH using $[VO(acac)_2]$ -4-PATP-Au electrode (B) Plot of oxidation peak potential of 0.1 mM glucose *versus* pH 73
- Fig. 4.19. (A) Overlaid CV of 0.5 mM H_2O_2 at different pH obtained with $[VO(acac)_2]$ -4-PATP-Au electrode in 0.1 M PBS. (B) Plot of reduction peak current of 0.5 mM H2O2 *versus* pH 73
- Fig. 4.20. (A) Plot of oxidation peak current of 0.1 mM glucose *versus* pH at [VO(acac)₂]-4-PATP-Au electrode in 0.1 M PBS. (B) Plot of reduction peak potential of 0.5 mM H₂O₂ *versus* pH at [VO(acac)₂]-4-PATP-Au electrode in 0.1 M PBS 74
- Fig. 4.21. Plot of electrocatalytic current obtained for glucose and hydrogen peroxide with time using $[VO(acac)₂]$ -4-PATP-Au electrode 75
- Fig. 4.22. Amperometric response of 0.1 mM glucose at an applied potential of $+ 0.65$ V (A) and 0.1 mM $H₂O₂$ at an applied potential of - 0.11 V (B) at $[VO(acac)_2]$ -4-PATP-Au electrode on subsequent addition, 1.0 mM AA, 1.0 mM UA, 1.0 mM Cys, 1.0 mM l-Dopa, 1.0 mM CA, 1.0 mM NaCl, 1.0 mM KCl, 0.1 mM glucose under stirring condition 76
- Fig. 4.23. Overlaid DPVs of human blood sample solution and after addition of standard glucose solution in blood sample solution 76
- Fig. 5.1. Schematic representation of the electrode modification process 84
- Fig. 5.2. (A) UV-VIS spectra and (B) TEM [HRTEM (inset)] 85

images of CTAB stabilized silver nanoparticles

- Fig. 5.3. Cyclic voltammograms of 0.5 mM $K_4[Fe(CN)_6]$ at pH 7 using different working electrodes. [(Blue) bare Au electrode, (brown) modified Au/L-cysteine electrode, (red) modified Au/L-cysteine/AgNPs electrode] 85
- Fig. 5.4. Cyclic voltammogram of AgNPs, immobilized on Ag/Lcysteine electrode,in 0.1 M PBS solution [(1) pH 2.0, (2) pH 4.0, (3) pH 6.0, (4) pH 7.0] 87
- Fig. 5.5. Cyclic voltammogram of 0.5 mM ascorbic acid in 0.1 M PBS solution at *pH* 7 using different working electrodes. [(Brown) bare Au electrode, (blue) modified Au/Lcysteine electrode, (red) modified Au/L-cysteine/AgNPs electrode] 87
- Fig. 5.6. Nyquist plot $(-Z^{\prime\prime})$ versus Z^{\prime} of 0.5 mM ascorbic acid in 0.1 M PBS solution at pH 7 using various working electrodes obtained from impedance measurements. [(Brown) bare Au electrode, (red) modified Au/Lcysteine electrode, (blue) modified Au/L-cysteine/AgNPs electrode] 88
- Fig. 5.7. (A) Overlaid DPV and (B) CA (at the potential level, $+$ 0.34 V *vs* Ag/AgCl, corresponding to AA anodic oxidation) with increasing ascorbic acid concentration $(0.05 - 0.35 \mu M)$ in 0.1 M PBS (pH 7) at Au/Lcysteine/AgNPs modified electrode. [Inset: Plot of current as a function of concentration of ascorbic acid with linear trend line $(R^2 > 0.99)$] 89
- Fig. 5.8. Bar diagram of oxidation current for 0.5µM ascorbic acid and 0.5 mM cysteine, citric acid, tartaric acid and glucose 90
- Fig. 5.9. Overlaid DPV of orange juice before (blue) and after addition of ascorbic acid (red) in 0.1 M PBS 91
- Fig. 6.1. TEM images of AgNPs (scale bar 20 nm) (a), Particle 99

size distribution histogram of AgNPS (b), HRTEM image showing lattice fringes (c), and a typical SAED of AgNPs (d)

- Fig. 6.2. UV-Vis spectra of PVP stabilized AgNPs. [Blue line: $AgNO₃ + PVP + Ascorbic acid + EtOH; Red line:$ $AgNO₃ + PVP + EtOH$] 100
- Fig. 6.3. FE-SEM images of bare (a), PCA modified (b) AgNPs-PCA modified gold electrode (c) and elemental mapping of AgNPs-PCA modified gold electrode (d)
- Fig. 6.4. Cyclic voltammograms obtained at bare and AgNPs-PCA modified gold electrode in 0.1 M PBS (pH 7.0) 101
- Fig. 6.5. Overlaid cyclic voltammograms obtained with increasing scan rate at AgNPs-PCA-Au electrode in 0.1 M PBS (pH 7.0) (a). Plot of current as a function of scan rate with a linear trend line $(R^2 > 0.99)$ (b), Bar diagram of current *versus* scan rate (c) 102
- Fig. 6.6. Cyclic voltammograms of 0.5 mM $K_4[Fe(CN)_6]$ in 0.1 M PBS at pH 7.0 using different working electrode (bare Au, PCA-Au and AgNPs-PCA-Au electrode) (a). Bar diagram of cathodic peak current at different electrode system, (b) Five times measurement $(n = 5)$ were taken 103
- Fig. 6.7. Nyquist plot $(-Z^{\prime\prime}$ *versus* Z[']) of 0.5 mM K₄[Fe(CN)₆] in 0.1 M PBS at pH 7.0 using different working electrode (bare Au, PCA-Au and AgNPs-PCA-Au electrode) (a). Bar diagram of R_{ct} values at different electrode system, (b) Five times measurement $(n = 5)$ were taken 103
- Fig. 6.8. Cyclic voltammogram of 10 μ M DA (a) and 10 μ M EP (b) in 0.1 M PBS (pH 7.0) at bare, PCA and AgNPs-PCA modified gold electrodes 104
- Fig. 6.9. Nyquist plot of 10 µM DA in 0.1 M PBS at pH 7.0 using bare Au, PCA-Au and AgNPs-PCA-Au electrode (a). Bar diagram of R_{ct} values at different *e*lectrode system (b), Five times measurement ($n = 5$) were taken 105
- Fig. 6.10. Nyquist plot of 10 μ M EP in 0.1 M PBS at pH 7.0 using bare Au, PCA-Au and AgNPs-PCA-Au electrode (a). Bar diagram of R_{ct} values at different *e*lectrode system (b), Five times measurement ($n = 5$) were taken 106
- Fig. 6.11. Cyclic voltammogram of 10 μ M DA (a) and 10 μ M EP (c) in 0.1 M PBS (pH 7.0) at AgNPs (4 nm)-PCA (red curve), AgNPs (10 nm) -PCA (black curve) and AgNPs (20 nm) -PCA (green curve) modified gold electrodes 106
- Fig. 6.12. Chronoamperograms of 10 μ M DA (a) and 10 μ M EP (b) in 0.1 M PBS (pH 7.0) at $+$ 0.22 V and $+$ 0.18 V *versus* Ag/AgCl, respectively using AgNPs (4 nm)- PCA (red curve), AgNPs (10 nm) -PCA (black curve) and AgNPs (20 nm) -PCA (green curve) modified gold electrodes 107
- Fig. 6.13. Chronoamperograms with increasing concentration of DA (0.1 to 100.0 mM) in 0.1 M PBS (pH 7.0) using AgNPs-PCA-Au electrode at + 0.22 V *versus* Ag/AgCl, LOD = 0.2 nM (S/N = 3) (a). Plot of resulting current in chronoamperometry at 30 seconds *versus* concentration of DA (b), Five times measurement were taken $(n = 5)$ 108
- Fig. 6.14. Chronoamperograms with increasing concentration of EP (0.1 to 100.0 mM) in 0.1 M PBS (pH 7.0) using AgNPs-PCA-Au electrode at + 0.18 V *versus* 108

xxvi

Ag/AgCl, LOD = 0.5 nM (S/N = 3) (a). Plot of resulting current in chronoamperometry at 30 seconds *versus* concentration of EP (b), Five times measurement were taken $(n = 5)$

- Fig. 6.15. Overlaid DPVs for each increment of 0.1 μ M DA at AgNPs-PCA-Au electrode in 0.1 M PBS solution at pH 7.0 (a). A plot of oxidation peak current *versus* increasing concentration of DA (b), Five times measurement were taken $(n = 5)$ 109
- Fig. 6.16. Overlaid DPVs for each increment of 0.1 μ M EP at AgNPs-PCA-Au electrode in 0.1 M PBS solution at pH 7.0 (a). A plot of oxidation peak current *versus* increasing concentration of EP (b), Five times measurement were taken $(n = 5)$ 109
- Fig. 6.17. Overlaid differential pulse voltammogram for each increment of $0.2 \mu M$ DA to $0.2 \mu M$ EP at AgNPs-PCA-Au electrode in 0.1 M PBS buffer solution at pH 7.0 (a). A plot of reduction peak current *versus* increasing concentration of DA (b), Five times measurement were taken $(n = 5)$ 110
- Fig. 6.18. Overlaid differential pulse voltammogram for each increment of 0.2 μ M EP to 0.2 μ M DA at AgNPs-PCA-Au electrode in 0.1 M PBS buffer solution at pH 7.0 (a). A plot of reduction peak current *versus* increasing concentration of EP (b), Five times measurement were taken $(n = 5)$ 110
- Fig. 6.19. Overlaid DPV for simultaneous increase of concentration of DA and EP in 0.1 M PBS at AgNPs-PCA-Au electrode (a). Plot of current as a function of concentration of DA and EP with linear trend line (b) 111
- Fig. 6.20. DPVs of 0.2 μ M DA and 0.2 μ M EP and in presence of 1000 times higher concentration of AA and UA 111
- Fig. 6.21. Overlaid differential pulse voltammogram for simultaneous increment of DA, EP, AA and UA at AgNPs-PCA-Au electrode in 0.1 M PBS buffer solution at pH 7.0 (a). Plot of reduction peak current *versus* increasing concentration of DA, EP, AA and UA (b and c), Five times measurement were taken in each case $(n = 5)$ 112
- Fig. 6.22. Overlaid DPV for simultaneous increment of DA, EP, AA and UA at AgNPs-PCA-Au electrode in 0.1 M PBS buffer solution at pH 7.0 (a). Plot of oxidation peak current *versus* increasing concentration of DA, EP, AA and UA (b and c), Five times measurement were taken in each case $(n = 5)$ 112
- Fig. 6.23. Cyclic voltammograms of 10 µM DA in 0.1 M PBS (pH 7.0) at different scan rate using AgNPs-PCA modified gold electrode (a). Plot of oxidation peak current *versus* square root of scan rate (b), Five times measurement were taken $(n = 5)$ 115
- Fig. 6.24 Cyclic voltammograms of 10 μ M EP in 0.1 M PBS (pH 7.0) at different scan rate using AgNPs-PCA-Au electrode (a). Plot of oxidation peak current *versus* square root of scan rate (b), Five times measurement were taken $(n = 5)$ 115
- Fig. 6.25. DPVs of 0.6 µM DA in 0.1 M PBS at different pH using AgNPs-PCA modified gold electrode (a), Plot of anodic peak current of 0.6 µM DA *versus* pH(b), Plot of oxidation peak potential of 0.6 µM DA *versus* $pH(c)$, Five times measurement were taken (n = 5) 117
- Fig. 6.26. DPVs of 0.6 μ M EP in 0.1 M PBS at different pH (5.0 117

- 9.0) using AgNPs-PCA modified gold electrode (a), Plot of anodic peak current of 0.6 µM EP *versus* pH(b), Plot of oxidation peak potential of 0.6 μ M EP *versus* pH(c), Five times measurement were taken (n $= 5$)

- Fig. 6.27. Amperometric response at AgNPs-PCA-Au with an applied potential of $+ 0.22$ V on subsequent addition of 0.01 μ M DA, 1.0 μ M AA, 1.0 μ M UA, 1.0 μ M Cys, 1.0 µM CA, 1.0 µM Glu, 1.0 µM NaCl, 1.0 µM KCl under stirring condition (a). Amperometric response at AgNPs-PCA-Au electrode with an applied potential of $+$ 0.18 V on subsequent addition of 0.01 μM EP, 1.0 μM AA, 1.0 μM UA, 1.0 μM Cys, 1.0 μM CA, $1.0 \mu M$ Glu, $1.0 \mu M$ NaCl, $1.0 \mu M$ KCl under stirring condition (b) (Supporting electrolyte: 0.1 M PBS, pH 7.0) 119
- Fig. 6.28. Overlaid DPV of human blood sample solution and after addition of standard DA and EP (a). Overlaid DPVs of human blood sample solution and after addition of standard UA and AA solution in blood sample solution (b). [Green arrow shows scan direction] 120

List of Tables

Symbols

D diffusion coefficient

87687 SERIAL NO.: AUE/SEM/12

ASSAM UNIVERSITY: SILCHAR

Consequent upon Arrear/Betterment

30595

INTEGRATED PRE PH.D. COURSE WORK EXAMINATION, 2013

MARK SHEET

The following are the marks obtained by **EXALL RESOUSHIK BARMAN**

Son/Daughter of HARI NARAYAN BARMAN and MAMATA BARMAN

Department of Chemistry σ

bearing Registration Number 24402326 of 2009-2010 and Roll 011311 No 00210097 $\frac{1}{2}$ INTEGRATED PRE PH.D.

COURSE WORK Examination, held in May 2013

CONTROLLER OF EXAMINATIONS