

Chapter 7

Overall conclusion and future scope of the work

7.1. Overall Conclusion

Four chapters of the thesis (**Chapters 3, 4, 5 and 6**) describe the research work. The work is focused on the sensing of some important small bio-molecules based on gold electrode chemically modified with metal complexes and nanoparticles.

In **Chapter 3**, electrochemical detection of adenine (A) and guanine (G) using the self-assembled monolayer of copper(II)-thiophenylazoimidazole modified gold electrode (Cu^{2+} -IATP-Au) is reported. The self-assembled monolayer of 4-(2'-imidazolylazo)thiophenol (IATP) on gold electrode surface was prepared by covalent immobilization of imidazole onto 4-aminothiophenol monolayer modified gold electrode by diazotization-coupling reaction. The catalyst was formed by immobilizing Cu(II) ion on the IATP modified gold electrode. The modified gold electrode was characterized by field emission scanning electron microscopy, energy dispersive X-ray analysis, infrared spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopic techniques. The Cu^{2+} -IATP-Au electrode exhibits excellent electrocatalytic activity towards the oxidation of A and G. Without separation or pre-treatment, the modified electrode can detect A and G simultaneously in a mixture and DNA sample. Presence of excess common interferents such as ascorbic acid, citric acid, cysteine, glucose, Na^+ , K^+ , Cl^- , SO_4^{2-} had no effect on the peak current of A and G. In differential pulse voltammetry measurement, the oxidation current response of A and G was increased linearly in the concentration range 10 - 60 μM and the detection limit was found to be 0.06 μM and 0.01 μM ($\text{S/N} = 3$), respectively. The proposed method was applied to determine adenine and guanine in herring sperm DNA and the result was satisfactory.

Chapter 4, describes a non-enzymatic electrochemical sensor, bis(acetylacetonato)oxovanadium(IV) complex, $[\text{VO}(\text{acac})_2]$, fabricated on a self-assembled 4-(pyridine-4'-amido)thiophenol (PATP) monolayer modified gold electrode, was developed for the detection of glucose and hydrogen peroxide (H_2O_2) at neutral pH. The modified electrode was characterized by electrochemical and microscopic techniques. The non-enzymatic sensor exhibited a remarkable catalytic performance for glucose oxidation and H_2O_2 reduction. Chronoamperometry was used for the electrochemical determination of glucose and H_2O_2 . The non-enzymatic sensing of

glucose was realized with a linear response range from 0.001 to 0.5 mM with a detection limit of 0.1 μM ($S/N = 3$). The sensor also showed a good performance with regards to the electrocatalytic reduction of H_2O_2 with a linear response range from 0.02 to 0.9 mM and a detection limit of 0.03 μM ($S/N = 3$). In addition, $[\text{VO}(\text{acac})_2]$ -PATP-Au exhibited a good selectivity for glucose and H_2O_2 detection in the presence of potential interfering agents such as ascorbic acid, uric acid, L-dopa, L-cysteine and different ions like Na^+ , K^+ , Cl^- etc. The kinetic parameters such as the electron transfer coefficient and the catalytic reaction rate constant were also determined for glucose and H_2O_2 . Finally, the modified electrode was used to achieve the quantitative detection of glucose and H_2O_2 in blood and milk, respectively for practical applications.

Chapter 5, demonstrates the electrocatalytic oxidation of ascorbic acid in phosphate buffer solution (pH 7.0) by immobilized silver nanoparticles ($\text{Ag}@$ CTAB) on L-cysteine modified gold electrode. The modified electrode was characterized electrochemically using redox couple $[\text{Fe}(\text{CN})_6]^{3-/4-}$. The electrocatalytic activity of the prepared electrodes was studied using cyclic voltammetry and electrochemical impedance spectroscopy. Electrochemical measurements show that the modified electrode ($\text{Au}/\text{L-cysteine}/\text{AgNPs}$) was highly active towards ascorbic acid oxidation. The oxidation peak of ascorbic acid at the $\text{Au}/\text{L-cysteine}/\text{AgNPs}$ electrode was highly stable upon repeated potential cycling. The oxidation current of ascorbic acid increased upon each increment (0.05–0.35 μM) in differential pulse voltammetry experiments and the oxidation current revealed a linear relationship with the concentration of ascorbic acid with a correlation coefficient of 0.996. The detection limit of ascorbic acid was found to be $2 \times 10^{-12} \text{M}$. Common physiological interferents such as glucose, tartaric acid, citric acid, and cysteine did not show any interference within the detection limit of ascorbic acid. The silver nanoparticles modified gold electrode was used to determine the amount of ascorbic acid present in fruit and vegetable juices.

Chapter 6, describes a highly selective and sensitive electrochemical sensor, AgNPs -penicillamine-Au, that was developed for the simultaneous detection of dopamine (DA) and epinephrine (EP) in presence of high concentration of ascorbic acid (AA) and uric acid (UA). Microscopic and voltammetry techniques were used for the characterization of

modified electrode. Chronoamperometry was used for the determination of DA and EP in the linear range of 0.1 to 100.0 μM with the detection limits of 0.2 nM and 0.5 nM, respectively. The simultaneous determination of DA, EP, AA and UA were achieved by using differential pulse voltammetry. The proposed sensor was successfully applied for the simultaneous determination of DA and EP in human blood sample with excellent recovery.

7.2. Future scope of the work

The described protocols can be utilized in real life sensor applications for the detection of clinically significant bio-molecules such as glucose, ascorbic acid etc. Different kinds of small portable sensors can be made based on these newly developed protocols. Another very important application of these systems will be in energy related research. One or two modified electrode systems that are used for bio-molecule sensing, will also be applicable for electrocatalytic water oxidation reactions and may serve as efficient industrial catalysts in solving energy related issues.