Studies of Palladium Nanoparticles and their Bimetallic Composite for Electrochemical Sensing Application

Thesis submitted in partial fulfilment for the
Award of Degree

DOCTOR OF PHILOSOPHY

By

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6.1 Summary

Sensors play a decisive role in improving the life of mankind with their extensive applications in the field of medical diagnostics, energy sources like fuel cells, batteries, and solar power, environmental monitoring, and exploring space. In the present thesis entitled "Studies of Palladium Nanoparticles and their Bimetallic Composite for Electrochemical Sensing Application" focused on electrochemical sensors since they are associated with a large number of advantages such as excellent sensitivity, high selectivity, great reproducibility, high stability and portability, and they are easy to operate and economical. Nanotechnology in the field of sensors has played a pivotal role in designing advanced sensors with a low detection limit for the analytes as they have a large surface area that provides ease of functionalization and better biocompatibility, selectivity, and sensitivity. The thesis is divided in to six chapters including bibliography at the end of each chapter.

Chapter 1 covers fundamental concepts about sensors, including their components, types, and importance, as well as the use of transition metal nanoparticles and their bimetallic composites in various electrochemical sensing applications, the need to develop the sensor for biomolecules or drugs related to harmful diseases and abnormalities. At last, it also includes the literature survey based on the proposed research topic.

Chapter 2 describes different experimental techniques which have been used for the characterization of synthesized materials. The main techniques which have been employed in characterizations are X-ray Diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), Field Emission Scanning Electron Microscope (FESEM), Energy Dispersive Spectroscopy (EDX), High Resolution Transmission Electron Microscope (HRTEM), Atomic Force Microscopy (AFM) used for the morphological and structural investigation. Cyclic voltammetry (CV), impedimetric technique (EIS), differential pulse voltammetry (DPV) and amperometry setup has been used for electrochemical characterization and sensing of the analytes.

Chapter 3 In this work, we present an electrochemical sensor assembled with Palladium nanoparticles for the detection of ascorbic acid through differential pulse voltammetry (DPV), amperometry it curves and electrochemical impedance spectroscopy (EIS). Palladium nanoparticles has been synthesized through wet chemical reduction pathways and has been characterized using X-Ray Diffraction technique (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive Spectroscopy (EDS), and High-Resolution Transmission electron microscopy (HRTEM). The carbon paste electrode was modified with palladium nanoparticles and Fc/Fcmc. Ferrocene (Fc) and ferrocene monocarboxylic acid (Fcmc) was used as a redox couple to sense the respective changes in current and charge transfer resistance (R_{ct}) in phosphate buffer solution of pH 7.0 under similar condition. The fabricated sensor shows a good electrocatalytic response for the sensing of ascorbic acid with a linear range from 10 μM to 500 μM and a detection limit of 5 μM.

Chapter 4 presents an electrochemical sensor based on cobalt N doped carbon with palladium nanoparticles (Co-NC/Pd) modified carbon paste electrode for the detection of NADH through amperometry, CV and EIS. Dimethyl ferrocene (Dmfc) was used as a redox mediator to sense the respective changes in current and charge transfer resistance. Co-NC/Pd has been synthesized through hydrothermal synthesis and characterized by XRD, XPS, FESEM, EDX, and HRTEM. NADH was determined in PBS at ambient temperature under similar condition. The developed sensor demonstrates an extensively wide linear range (5-1250 μM) and a low limit of detection 2μM. The developed sensor shows excellent stability, sensitivity, and good selectivity at pH 7. The achieved analytical parameters are found to be comparable to or better than previously reported NADH sensors.

Chapter 5 presents an electrochemical sensor based on Ni Palladium nanoparticle decorated on functionalized multi-walled carbon nanotube (Ni-Pd/f-MWCNT) for the determination of dopamine (DA) through amperometry, DPV, and EIS. The Ni-Pd/f-MWCNT was synthesized through chemical reduction approach and characterized by XRD, XPS, HRSEM, EDX, TEM, and AFM. Ferrocene monocarboxylic acid was used as redox couple to find the respective changes in current and charge transfer resistance (R_{ct}). DA sensing was validated in phosphate buffer and commercially available dopamine hydrochloride injection under similar condition. The fabricated electrochemical sensor shows a wide concentration range (2-400 µM) and a low limit of detection (0.05 µM) and offers a fascinating sensitivity, selectivity, stability, and reproducibility at pH 7. The analytical parameters obtained are found to be comparable to or better than previously reported DA sensors.

Overall, the Pd NPs and the combination of Co-NC/Pd, Ni-Pd/f-MWCNT can lead to lower detection limits, faster response times, and better performance in biosensing and point-of-care diagnostics. The LOD for biomolecules using these sensors is typically in the low micromolar range, sometimes even lower depending on the specific design and target analyte. For instance, the LOD for detecting dopamine might be as low as 0.05 µM, reflecting the sensor's high sensitivity.

Novelty and Significance

The novelty of using modified carbon paste electrodes with Pd NPs, Pd/Co-NC, and Ni-Pd/f-MWCNT in electrochemical sensing lies in the unique combination of the high surface area and tunable structure of Co-NC and Ni/f-MWCNT with the catalytic activity of Pd NPs. This approach offers several key advantages: Enhanced sensitivity was achieved through the high surface area of N doped carbon and f-MWCNT, enabling greater Pd NP loading and more active sites, resulting in improved sensitivity and a lower LOD. Improved selectivity is attained by tailoring the tunable pore size and functionalized MWCNT to sense the specific analyte, minimizing interference. Stability and reusability were enhanced by the protective role of bimetallic nanoparticles, preventing Pd NP agglomeration and degradation. Additionally, this fabrication of CPE is cost effective and can be applied to various biomolecules sensing, including NADH, dopamine, and ascorbic acid.

6.2 Scope for the future work

In the current thesis, we have synthesized Pd nanoparticles and their bimetallic composites with enhanced electrochemical properties. Due to the synergy between the individual components, the conductivity and the electrocatalyst activity of the resulting material improved. The fabricated electrochemical sensors based on these nanocomposites enabled the determination of different biomolecules. Nowadays, mankind is greatly affected by a large number of life-threatening diseases such as various kinds of abnormalities, kidney, liver and heart diseases, and hence undergoes treatment through a large number of therapeutic drugs. Further, there is a huge amount of scope for exploiting the striking properties MOF for the sensing application. So, our target will be to fabricate MOF supported Palladium nanoparticles and its modifications for the fabrication of high-performance electrochemical and fluorescence sensor for point-of-care detection drugs or biomolecules in the blood serum samples, individually as well as simultaneous detection of some drugs which are administered in combination. MOFs provide a large surface area, tunable porosity, and a high degree of structural flexibility, which can enhance the dispersion and stability of Pd NPs. These characteristics improve the overall sensitivity and selectivity of the sensor. Pd NPs, known for their excellent catalytic activity and electrical conductivity, can facilitate rapid electron transfer during electrochemical reactions, making them effective for detecting biomolecules like glucose, dopamine, and hydrogen peroxide.

We will also make efforts to explore the potential of these nanomaterials for designing trace level sensors for environmental pollutants since day by day we are increasingly surrounded by a large number of hazardous pollutants in our environment, our atmosphere we breathe in, and our water resources on which we depend for our daily needs. Further, in comparison to the traditional solid-state electrodes such as CPE and GCE, the screen-printed electrode (SPE) exhibits the merits of easier integration, portability, versatility, smaller sizes and mass-produce. So, we will work for the preparation of rapid and portable SPE-based electrochemical sensors with a promising potential for introduction into the commercial market.