Nanomaterials modified sensors for drug sensing

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Doctor of Philosophy

By

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Summary and Future Work

6.1 Summary

In the present scenario, nanomaterials play a pivotal role in various practical applications in our day-to-day life. They are also capable of significantly enhancing the performance of the sensors with respect to their catalytic activity and sensitivity. The present thesis reports the synthesis of different 2D functionalized nanomaterials, for instance, reduced graphene oxide, MoS_2 nanosheets, and their nanocomposites with quantum dots (WS_2 QDs), conducting polymer (CPIn) and metal nanostructures (GNR) for improving their stability, catalytic and electrochemical properties. The synthesized nanomaterials were investigated by different characterization tools such as UV-vis spectroscopy, FTIR spectroscopy, XRD, SEM, TEM, CV, EIS and DPV. Further, the developed nanomaterials were exploited for the electrochemical sensing of some antimalarial and immunosuppressive drugs like CQ, PQ and Azp since these drugs may produce some serious side effects in the body if present more than the amount desired for the treatment of patients. The current thesis is compiled on the basis of designing the 2D materials, their composites, and their implementation and relevance in the field of electrochemical sensing of some therapeutic drugs. The chapter-wise summary of the thesis is described as follows:

Chapter 1 covers the general introduction of sensors, different components of sensors, types of sensors, electrochemical sensors - types, significance and advantages, nanomaterials and their beneficial properties, nanocomposites of 2D nanomaterials, and their application in electrochemical sensing of drugs. The literature survey demonstrates the relevant information related to the research topic.

Chapter 2 explains the various experimental techniques and instrumentation that were employed for the characterization of designed nanomaterials and composites. The major techniques among those include Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared (FTIR) Spectroscopy which were utilized for the structural and morphological investigation. UV-Visible spectroscopy has been employed for spectroscopic characterizations. For electrochemical characterization and sensing of analytes, Cyclic Voltammetry (CV) Differential Pulse Voltammetry (DPV) and Electrochemical Impedance Spectroscopy (EIS) were utilized.

Chapter 3 describes a highly efficient electrochemical sensor for an antimalarial drug CQ based on tungsten disulfide quantum dots decorated reduced graphene oxide sheets (rGO@ WS_2 QDs) modified GCE. The developed nanocomposite displayed a high catalytic property, excellent electro-activity and fast electron transfer kinetics. CV and DPV were employed for the quantitative determination of CQ in PBS, human blood serum and commercially available CQ tablet. The synergistic effects of rGO and WS_2 QDs enhanced the performance of the fabricated sensor which rendered it to deliver such a CQ sensing performance that was comparable to or better than the previously reported CQ sensors. The fabricated sensor exhibited a better performance through DPV in comparison to CV and displayed a linear response in the concentration range of 0.5-82 µM. The LoD was found to be 40 nM. The studies suggest that the fabricated sensor is extremely sensitive, stable, reproducible, and selective for CQ detection, and possesses a significant potential for real-time CQ detection in malarial patients.

Chapter 4 deals with a high-performance electrochemical sensor for an immunosuppressive drug Azp based on MoS_2 nanosheets modified with CPIn (MoS_2-

CPIn) through DPV over GCE. We have demonstrated the successful synthesis of MoS_2 nanosheets through hydrothermal technique and well-characterized by several characterization techniques such as XRD, TEM, SEM, EDS, XPS and FTIR. Further, CPIn chains were grown over the MoS_2 nanosheets to obtain the MoS_2-CPIn composite. Azp was determined in the PBS as well as human blood serum at room temperature. The developed sensor demonstrates an extensively wide linear concentration range of 3.49-284.44 µM for Azp estimation and the limit of detection was found to be 74.65. The developed voltammetric sensor shows excellent stability, sensitivity, and good selectivity at physiological pH. The achieved analytical parameters are found to be comparable to or better than previously reported Azp sensors.

Chapter 5 presents the easy voltammetric technique for the quantification of an antimalarial drug PQ in PBS, human blood serum and pharmaceutical formulations. We have demonstrated the synthesis of GNR through a seed-mediated growth methodology followed by the decoration of MoS_2 nanosheets with GNR. The developed nanocomposite (MoS_2-GNR) was investigated by various characterization tools like XRD, TEM, EDS, XPS and FTIR. The proposed composite exhibits an excellent electro-activity, high catalytic property and rapid electron transfer kinetics. The fabricated electrochemical sensor using a GCE was examined by DPV for the determination of PQ and the results show a wide linear concentration range of 1-150 µM. The LoD was found to be 90.2 nM. The developed sensor offers a fascinating sensitivity, selectivity, stability and reproducibility at physiological pH conditions and possesses a great potential to be used as a detection tool in diagnostic centers. The analytical parameters obtained are found to be comparable to or better than previously reported PQ sensors.

6.2 Future Work

In the current thesis, we have synthesized 2D nanomaterials and their composites with enhanced electrochemical properties. We have attempted to work out the problem regarding the aggregation of the 2D layered nanomaterials by developing their nanocomposite with other nanomaterials. The conductivity and electrocatalytic activity of the resulting material was improved due to the synergistic effects of the individual constituents. The fabricated electrochemical sensors based on these nanocomposites enabled the quantitative estimation of different therapeutic drugs. Nowadays, mankind is greatly affected by a large number of life-threatening diseases such as various kinds of cancer, 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 TMDs for the sensing application. So, our target will be to fabricate new single layer 2D TMDs and its modifications for the fabrication of high-performance electrochemical and fluorescence sensor for point-of-care detection of these drugs in the whole blood samples, individually as well as simultaneous detection of some drugs which are administered in combination.

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 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.