DESIGN AND DEVELOPMENT OF ELECTROCHEMICAL SENSOR FOR SENSING ENVIRONMENTAL POLLUTANTS AND BIOMOLECULES

Synopsis

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SYNOPSIS

DESIGN AND DEVELOPMENT OF ELECTROCHEMICAL SENSOR FOR SENSING ENVIRONMENTAL POLLUTANTS AND BIOMOLECULES

The growth of ultimate electrochemical storage devices is gradually increasing to the applications in biosensor and sensors fields for the past two decades. In recent years, the electrochemical modified sensors have been fabricated based on composition of electrolyte or modification of the electrode for better performance of the different electrochemical devices, sensors (Arsenic, mercury etc.,) and biosensor (hydroquinone, L-tyrosine, Folic acid, nicotine etc.,). The present research work is proposed in this synopsis is based on the combined advantages of nanomaterial based sensors with the aim to develop sensor as stable and selectively achieving lower limit of detection and quantification of the biomolecules and heavy metal ions. Various parameters such as effect of pH, potential, scan rate, types of surfactants (cationic, anionic or non-ionic) will be optimized using various electrochemical techniques such as cyclic voltammetry, difference pulse voltammetry, amperometric method and linear sweep voltammetry. Validation of method in terms of accuracy, precision, specificity and selectivity will be done. Thus the present research work is focused on the fabrication of a sensitive and selective sensors for monitoring biomolecules and heavy metal ions. The detection of real sample analysis with acceptable recoveries is carried out for every electrolytic samples. The plausible mechanistic aspects of electrochemical determination of biomolecules and heavy metal ions using various modified electrodes are also been discussed in this present work. My thesis consists of eight chapters (I-VIII). Chapter-I deals with the review of literature which is very relevant to my research work. At the end of this chapter the scope of the present work is offered justifying the choice and significance of the work reported in the thesis. Materials, synthesis, characteracteization of electrode materials using various instrumentation techniques such as UV–vis spectroscopy, FT-IR, XRD, SEM (FE-SEM), mapping analysis, EDX, HRTEM, TGA, XPS and BET are discussed in Chapter 2. Electrochemical sensing of nicotine using $CuWO_4$ decorated reduced Graphene oxide immobilized glassy carbon electrode is discussed in Chapter 3. Chapter 4 deals with the study of electrochemical behavior and voltammetric determination of mercury (II) ion in cupric oxide/poly vinyl alcohol nanocomposite modified glassy carbon

electrode. A novel highly efficient and accurate electrochemical detection of poisonous inorganic Arsenic (III) ions in water and human blood serum samples based on $SrTiO_3$/β-cyclodextrin composite have been discussed in Chapter.5. Chapter 6 in this thesis deals with a novel electrochemical sensor for determination of hydroquinone in water using $FeWO_4/SnO_2$ nanocomposite immobilized modified glassy carbon electrode. Fabrication of Cupric oxide decorated β-cyclodextrin nanocomposite solubilized Nafion as a high performance electrochemical sensor for L-tyrosine detection is studied and presented in Chapter.8. The last chapter (Chapter.8) describes a highly sensitive and selective electrochemical sensing of folic acid (FA) using vanadium pentoxide decorated graphene carbon nitride covalently grafted polyvinyl alcohol modified GC electrode (V_2O_5/G-C_3N_4/PVA/GCE).

CHAPTER-I Introduction

The biomolecules such as (folic acid, L-tyrosine, hydroquinone and nicotine) and heavy metal ions (Arsenic (As^{3+}) and mercury (Hg^{2+})) present in the biological system are more prone to oxidize and to understand the mechanism of this important redox reaction is an intensive research work has been carried out for the past decades. The oxidation process of biomolecules and heavy metals are also related to the pathogenic conditions associated with oxidative stress, Parkinson disease, Alzheimer disease and a number of other age-related diseases. The changes in the level of biomolecules reflect the various conditions during age-related manifestation. The study of electron transfer mechanistic details of oxidation of biomolecules (folic acid, L-tyrosine, hydroquinone and nicotine) and heavy metal ions (As^{3+} and Hg^{2+}) using nanomaterial modified glassy carbon electrode is the prime aim of this research work. The modified electrode shows excellent electrocatalytic properties, such as high sensitivity, a low detection limit, good stability and resistance. Cyclic voltammetric, linear sweep voltammetry, differential pulse voltammetric and amperometric studies are useful techniques to achieve the aforesaid objectives of the present work. In addition, the present electrochemical sensor is applied to the real samples of blood serum, urine sample was collected from Rajaji hospital, Fruits and vegetables collected from simmakkal market, waters from various sources and the obtained experimental results are in accordance with the literature studies.

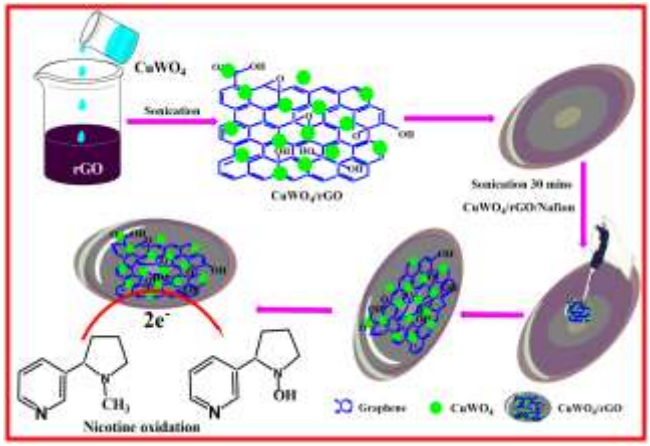
CHAPTER-II Materials and methods

Chemicals detail, methods of synthesis of nanomaterials, fabrication of modified electrodes, characterization of nanomaterials and the details of instrumentation techniques such as UV–vis, FT-IR, XRD, SEM (FE-SEM), mapping analysis, EDX, HRTEM, TGA, XPS and BET are discussed in this chapter.

CHAPTER-III

Electrochemical sensing of nicotine using $CuWO_4$ decorated reduced graphene oxide immobilized glassy carbon electrode

In this work, we successfully synthesized copper tungstate decorated reduced graphene oxide nanocomposite using sonication method and well characterized using powder X-ray diffraction analysis, FTIR, scanning electron microscope, EDX analysis, High-resolution Transmission electron microscope and Raman spectra. The catalyzing activity of the $CuWO_4$/rGO nanocomposite modified electrode was effectively studied using various electrochemical techniques for the determination of nicotine. The fabrication of $CuWO_4$/rGO immobilized glassy carbon electrode ($CuWO_4$/rGO/Nf modified GCE) was performed suspiciously. Furthermore, the $CuWO_4$/rGO/Nf modified GCE exhibits superior electrocatalytic activity by means of higher cathodic peak current towards the detection of Nicotine. The fashioned electrode attained two wide linear response ranges (0.1 µM to 0.9 µM) with a lower detection limit of about 0.035 µM (S/N=3) correspondingly. Furthermore, the fabricated sensor displayed brilliant sensitivity of 1.348 $\mu A \mu M^{-1} cm^{-2}$ and good selectivity for nicotine sensing yet in the survival of related interfering compounds and biomolecules. Beside with that, the premeditated sensor executed conspicuous reproducibility, repeatability, and stable stability. The schematic representation of electrochemical sensing of nicotine using $CuWO_4$ decorated reduced graphene oxide immobilized glassy carbon electrode is shown in **Scheme.1**

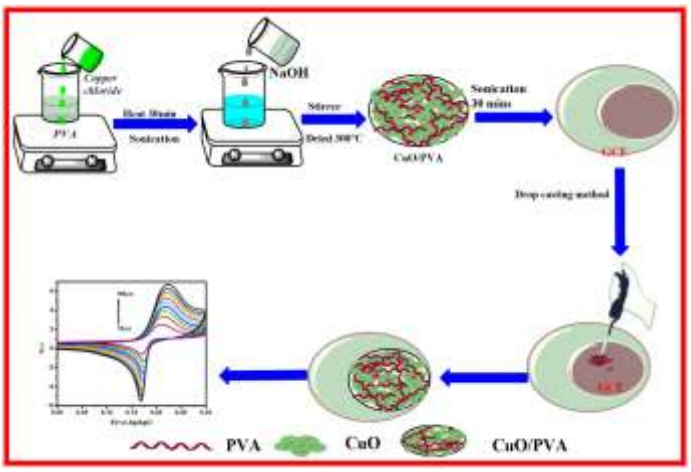


Scheme.1 Stepwise fabrication of $CuWO_4$/rGO modified glassy carbon electrode for nicotine sensor.

CHAPTER-IV

Electrochemical behaviour and voltammetric determination of mercury (II) ion in cupric oxide/poly vinyl alcohol nanocomposite modified glassy carbon electrode

A novel and selective electrochemical sensing of mercury (II) ions is studied using poly vinyl alcohol supported cupric oxide nanocomposite (CuO/PVA) modified glassy carbon electrode (GCE). The CuO/PVA nanocomposite is synthesized using sonication method and characterized by UV-DRS, XRD, FT-IR, SEM, EDX, SAED, HR-TEM, Raman techniques. The CuO/PVA nanocomposite modified GCE (CuO/PVA/GCE) shows superior electrocatalytic response for the detection of mercury (II) ions as compared to bare GCE. A better selectivity and sensitivity is achieved using CuO/PVA/GCE to detect 0.10 µM mercury (II) ions in the presence of 100-fold excess concentrations of different interferents. The present $CuWO_4$/rGO/Nf immobilized GCE electrochemical sensor exhibits an ample range of sensing from 10–70 µM and the low detection limit is found to be 0.42 nM (S/N=3). Comparable results are achieved for the determination of nicotine in various real samples such as river and tap water and obtained improved recoveries. The schematic representation of voltammetric determination of mercury (II) ion in cupric oxide/poly vinyl alcohol nanocomposite modified glassy carbon electrode in presented in **Scheme.2.**

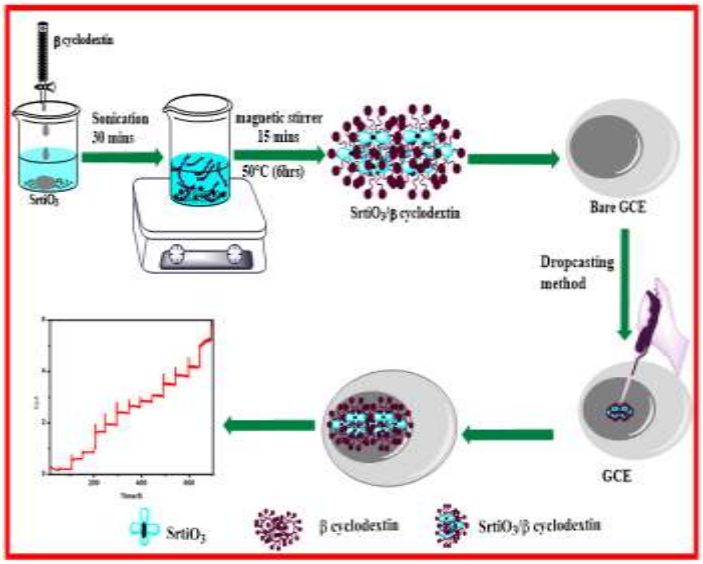


Scheme.2. schematic representation of Fabrication of CuO/PVA modified glassy carbon electrode for Hg^{2+} sensing.

CHAPTER-V

A novel highly efficient and accurate electrochemical detection of poisonous inorganic Arsenic (III) ions in water and human blood serum samples based on $SrTiO_3$/β-cyclodextrin composite

A novel Strontiumtitaniumtrioxide ($SrTiO_3$) decorated β-cyclodextrin (β-CD) nanocomposite modified glassy carbon electrode ($SrTiO_3$/β-CD/GCE) was developed for the determination of venomous Arsenic (III) ions. The synthesized $SrTiO_3$/β-CD nanocomposite was successfully characterized by physicochemical method. The present $SrTiO_3$/β-CD nanocomposite modified GC electrode was provided an excellent electrochemical performance due to higher surface area, comparable to glassy carbon electrode with $SrTiO_3$ and β-CD separately. Besides, the electrochemical studies of the prepared nanocomposite were characterized by the CV, DPV and Amperometric technique. The oxidation peak current of Arsenic (III) was obtained by Amperometric, studies displayed the linearity response of the proposed sensor range between 10-140 µM and the detection limit was found to be 0.02 µM. The present $SrTiO_3$/β-CD/GC electrode was also showed better stability, good sensitivity and reproducibility. In addition, the real sample analysis exhibited appreciable recovery towards the determination of detection of Arsenic (III) in water and serum samples. The electrochemical detection of poisonous inorganic Arsenic (III) ions in water and human blood serum samples based on $SrTiO_3$/β-cyclodextrin composite is shown in **Scheme.3.**



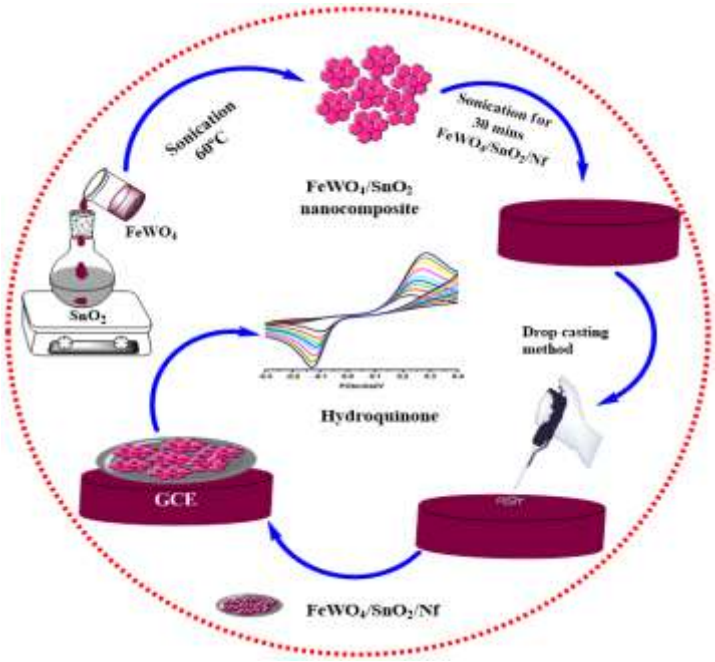
Scheme.3. Schematic diagram of fabrication of $SrTiO_3$/β-CD modified glassy carbon electrode for Arsenic (III) sensor.

CHAPTER-VI

A novel electrochemical sensor for determination of hydroquinone in water using $FeWO_4/SnO_2$ nanocomposite immobilized modified glassy carbon electrode

A selective amperometric detection of hydroquinone (HQ) sensor in biological samples was developed using iron tungstate doped tin oxide nanocomposite nafion immobilized modified glassy carbon electrode ($FeWO_4/SnO_2$/Nf). The nafion (Nf) taking an advantage of dispersing medium as well as supporting agent for selectively welcomes HQ molecule on the electrode surface. The $FeWO_4/SnO_2$/Nf was characterized by analytical (Fourier transform infrared spectroscopy (FT-IR), Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), energy dispersive X-ray analysis (EDX), Field emission scanning electron microscopy (FE-SEM) and electrochemical method (cyclic voltammetry (CV), difference pulse voltammetry (DPV) and amperometric (i-t curve) respectively. Electrochemical methods such as are used to describe the electrochemical appearance of the surface modified electrode for HQ sensing studies. The $FeWO_4/SnO_2$/Nf immobilized GCE is exhibited exceptional catalytic activity with the increasing current signal during HQ sensing. Besides, the amperometric *i-t* curves displayed a fast diffusion and wide linear response range of HQ concentrations from 0.01 µM and 50 µM µM with a detection limit

(LOD) of 0.0013 µM. Moreover, the present modified electrode shows good reproducibility and excellent anti-interference behavior. In addition, the present electrochemical sensor is applied to the real samples of collected waters from various sources and the obtained experimental results are quite satisfactory. The electrochemical determination of hydroquinone in water using $FeWO_4/SnO_2$ nanocomposite immobilized modified glassy carbon electrode is depicted in **Scheme.4.**



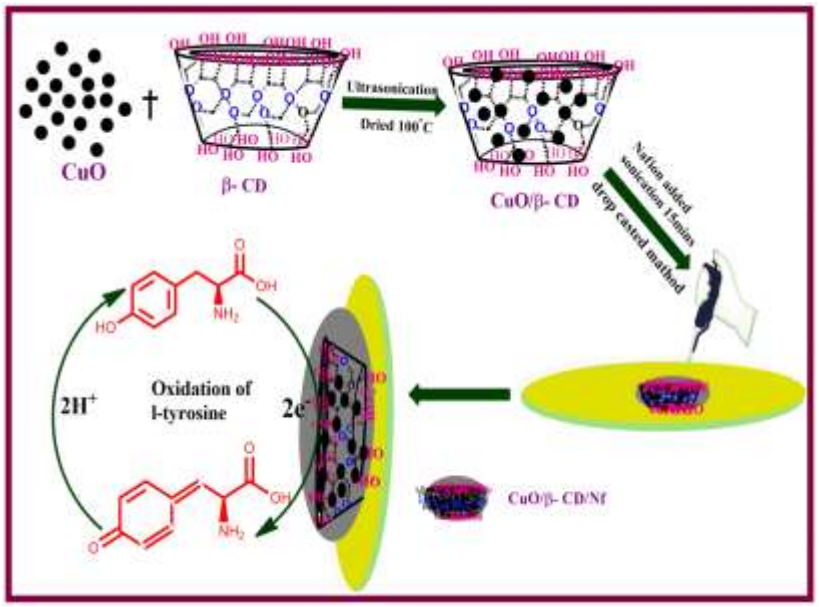
Scheme.4. Schematic representation of HQ sensing using $FeWO_4/SnO_2$/Nf immobilized modified GC electrode.

CHAPTER-VII

Fabrication of Cupric oxide decorated β-cyclodextrin nanocomposite solubilized Nafion as a high performance electrochemical sensor for L-tyrosine detection

Cupric oxide decorated on β-cyclodextrin (CuO/β-CD) via a sonochemical method. The structure and surface morphology of the CuO/β-CD composite was characterized by Raman spectroscopy, ultra violet visible spectroscopy, and Fourier transmission infra red spectroscopy, x-ray diffraction, mapping analysis and energy dispersive X-ray spectroscopy. Fascinatingly, the CuO/β-CD nanocomposite Nafion (Nf) solubilized modified glassy carbon electrode (CuO/β-

CD/Nf/GCE) has exhibited a superior electrocatalytic activity towards the L-tyrosine, when compared to the modified β-CD, CuO, and bare GCE electrodes. Besides, the electrochemical sensing performance was revealed as an excellent amperometric i-t current response for the L-tyrosine determination with a wide linear range from 0.01 to100 µM, high sensitivity 442 µA $\mu M^{-1}cm^2$ and low detection limit (LOD) 0.0082µM. The sensor was applied to the determination of L-tyrosine (spiked) human serum and food samples, as well as in urine, where it displays good recovery and accuracy. The sensor is show better reproducibility, stability and selectivity even in the presence of other biomaterials. High performance electrochemical detection for L-tyrosine using cupric oxide decorated β-cyclodextrin nanocomposite solubilized Nafion is shown in **Scheme.5.**



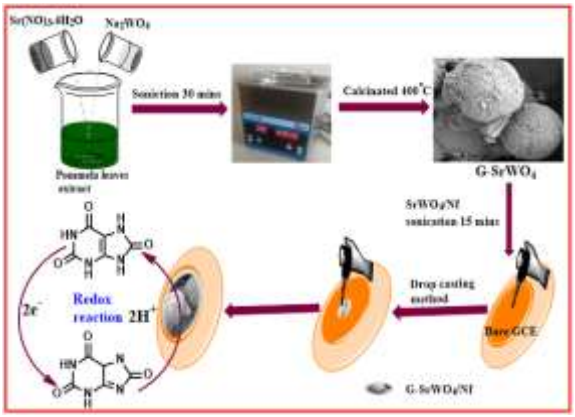
Scheme.5.Stepwise fabrication of CuO/β-CD/Nf/GCE for L-tyrosine sensor.

CHAPTER-VIII

A highly sensitive and selective electrochemical sensing of folic acid (FA) using vanadium pentoxide decorated graphene carbon nitride covalently grafted polyvinyl alcohol modified GC electrode

A highly sensitive and selective electrochemical sensing of folic acid (FA) using vanadium pentoxide decorated graphene carbon nitride covalently grafted polyvinyl alcohol modified GC electrode (V_2O_5/G-C_3N_4/PVA/GCE). The V_2O_5/G-C_3N_4/PVA nanocomposite was

synthesized by an in-situ oxidative polymerization method and characterized by various techniques such as UV-visible, Raman, FE-SEM, XRD, FT-IR, EDX, HR-TEM, SAED, and electrochemical methods. The V_2O_5/G-C_3N_4/PVA nanocomposite modified GCE showed superior electrocatalytic activity towards the FA detection. The superior electrochemical activity of the catalyst is owing to good conductivity, high surface area and enhanced electron transfer efficiency of the nanocomposite. The amperometric (i-t) studies revealed that the V_2O_5/G-C_3N_4/PVA nanocomposite modified GCE performed well by attaining a linear response of FA from 0.01-60μM with a lower detection limit 0.00174μM and the sensitivity of 19.02 $\mu A \mu M^{-1}$ cm^{-2}. Meanwhile, the V_2O_5/G-C_3N_4/PVA nanocomposite modified GCE exhibited good selectivity, rapid and stable response towards FA. The proposed method has been successfully applied for the selective determination of FA in various real samples such as apple juice, green tea and tap water with samples with good recoveries. The pictorial representation of electrochemical sensing of folic acid (FA) using vanadium pentoxide decorated graphene carbon nitride covalently grafted polyvinyl alcohol modified GC electrode in depicted in **Scheme.6.**



Scheme.6.Stepwise fabrication of G-$SrWO_4$/Nf modified GC electrode for UA sensor.