α-Ni(OH)$_2$/PEI NANOCOMPOSITE FOR HEAVY METAL ION SENSING

M.Tech. Thesis

By

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DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE

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A THESIS

Submitted in partial fulfillment of the

requirements for the award of the degree

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **α-Ni(OH)$_2$/PEI NANOCOMPOSITE FOR HEAVY METAL ION SENSING** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore,** is an authentic record of my own work carried out during the period from July 2018 to June 2020 under the supervision of Dr. Dhirendra Kumar Rai, Assistant Professor IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

June 25, 2020

Signature of the student with date

ANKIT SOLANKI

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

June 30, 2020

Signature of the Supervisor (with date)

Dr. Dhirendra Kumar Rai

ANKIT SOLANKI has successfully given his M.Tech. Oral Examination held on …25/06/2020…

Signature of Supervisor of M.Tech.thesis
Date:

M. Duly 30/06/2020

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Date:

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ABSTRACT

Most of the heavy metals are highly toxic and detrimental to human health due to their non-biodegradable nature, even at very low concentrations. Heavy metal contamination as a consequence of industrialization and urbanization is one of the most serious environmental problems which leads to harmful effects on the entire ecosystem. Therefore, it is extremely important and necessary to design new materials, which exhibit ultrasensitivity in the detection of heavy metal ions. In this work, three-dimensional (3D) hierarchical flower-like α-$Ni(OH)_2$ nanocrystals have been successfully synthesized by intercalating anionic surfactants between the layers using a simple hydrothermal method. α-$Ni(OH)_2$/PEI nanohybrid was further prepared by the functionalization of polyethyleneimine (PEI) on the surface of 2D α-$Ni(OH)_2$ nanosheets through exfoliation-reassembling synthetic strategy. The as-prepared α-$Ni(OH)_2$ and α-$Ni(OH)_2$/PEI nanomaterials were characterized by powder XRD, FT-IR spectroscopy, and field-emission scanning electron microscopy. Multiple physical characterizations have confirmed that the PEI molecules are successfully immobilized on the surface of exfoliated nanosheets due to strong electrostatic interactions between the nitrogen atom and nickel nanosheets. The resulting nanocomposite has been explored for the selective and sensitive detection of heavy metal ions, as it exhibits superior electrochemical properties due to its large specific surface area, effective charge transfer efficiency, the high adsorption capacity of hierarchical α-$Ni(OH)_2$, and excellent affinity of heavy metals ions on PEI. The electrochemical performance and stripping response for Pb(II) detection were studied using square wave anodic stripping voltammetry (SWASV). Operational parameters, including the pH value of supporting electrolyte, deposition time, and deposition potential, were also optimized. The α-Ni(OH)$_2$/PEI modified electrode exhibits a low detection limit of 0.072 μM and high repeatability with 0.916% of relative standard deviation, which is well below the standard permissible values. The result shows that hybrid materials modified electrode possesses high sensitivity, good selectivity, stability, and low limit of detection. Therefore, the proposed hybrid electrode can be a promising material for the ultrasensitive detection of heavy metals.

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LIST OF ABBREVIATIONS

SDBS	Sodium dodecyl benzenesulfonate
HMT	Hexamethylenetetramine
XRD	X-ray Diffraction
AFM	Atomic Force Microscopy
WHO	World Health Organization
ISI	Indian Standard Institution
CPCB	Central Pollution Control Board
EPA	Environmental Protection Agency
ICMR	Indian Council of Medical Research
PEI	Polyethyleneimine
IHME	Institute for Health Metrics and Evaluation
CDC	Center for Diseases Control
FAO	Food and Agricultural Organization
LOD	Limit of Detection
GCE	Glassy Carbon Electrode
RSD	Relative Standard Deviation
SWASV	Square Wave AnodicSrippingVoltamettry

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NOMENCLATURE

S. No.	Symbol	Meaning
1.	α	Alpha
2.	β	Beta
3.	σ	Standard deviation
4.	µ	Micro
5.	M	Molar
6.	θ	Bragg's angle
7.	Pb	Lead
8.	Zn	Zinc
9.	Cd	Cadmium
10.	Hg	Mercury
11.	Cr	Chromium
12.	Cu	Copper
13.	Ni	Nickel
14.	As	Arsenic
15.	Fe	Iron

Chapter 1

Introduction

1.1 Introduction to Heavy Metals

The large scale anthropogenic environmental pollution has become a major source of concern that undermines global sustainability and harmfully affects life. Environmental pollution is the introduction of undesirable substances directly or indirectly into the water, air, or soil, resulting in detrimental effects on living organisms, a hindrance to environmental activities, and deleterious to human health. The heavy metal contamination with the development of industrial and agricultural manufacturers is one of the most serious environmental problems. The excessive level of heavy metal ions would lead to a greater risk to human health and the environment as these ions are highly toxic and non-biodegradable. Heavy metals are the metallic elements with relatively high density and higher atomic weight, such as mercury, chromium, arsenic, lead, zinc, copper and cadmium, etc.

1.1.1 Sources of heavy metals

Industrially discharged metal-contaminated wastewater, vehicle emissions, textile dyes, paints, lead-acid batteries, mining and smelting, agricultural pesticides, food processing, and pharmaceutical waste disposal are the major sources of heavy metal ions[1]. The presence of these toxic heavy metal ions in drinking water may cause several health illnesses such as lung cancer, skin lesions, bladder cancer, kidney, and neurological disorders, etc. Various natural and anthropogenic activities contributing to the discharge of heavy metals in the environment are presented in Figure 1.1.

Natural Sources of Heavy Metals

1. **MAGMATIC ROCKS:** Rocks and soils are the primary sources of heavy metals contamination in the environment. The molten rocks found under the surface of the earth are called magma, which can be transported to the surface by volcano eruption or other geological processes. Heavy metal ores, such as chromite, ilmenite (titanium oxide), and magnetite, are concentrated by magmatic processes. During the isomorphic substitution and crystallization of magma, a large number of heavy metals are formed which come out in the environment and cause environmental pollution.

2. **SEDIMENTARY ROCKS:** Sedimentary particles are transported to the environment through physical or chemical weathering by disintegrating the rock into particles or ions. Sedimentary rocks contain ore deposits of several chemical elements, which can be considered as the major sources of heavy metals[2].

3. **AEROSOLS FORMATION OVERSEAS:** The rapid movement of heavy metal contaminated air leads to the formation of aerosols which is one of the major sources of environmental pollution. Aerosols are liquid droplets or minute solid particles suspended in the surrounding. Aerosols over the seas are the natural sources of heavy metals as they mostly consist of mineral particles of landsoil.

Heavy metals are found in the form of sulfides, oxides, hydroxides, phosphates, silicates, sulfates, and organic compounds. Several environmental activities such as volcano eruption, rock weathering, sea salt spray, emission of aerosols, and forest fires are the natural processes of heavy metal contaminations in air, water, and soil (Figure 1.1).

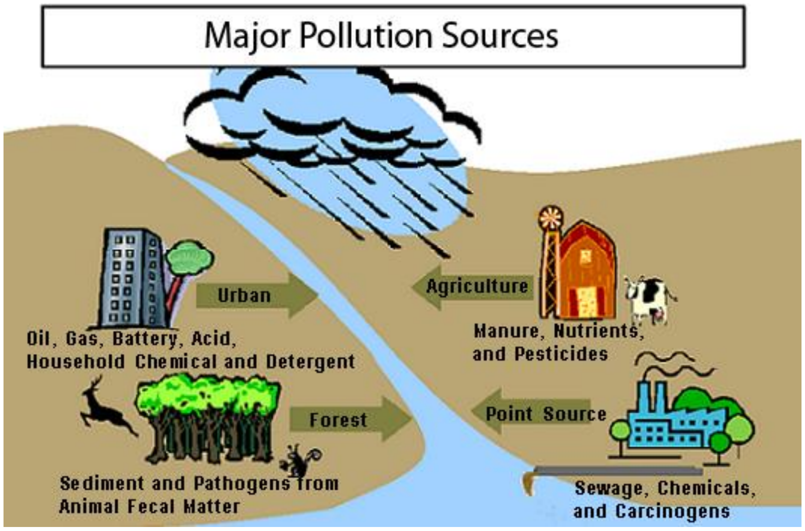

Figure1.1 Various Sources of heavy metal contamination[3]

Anthropogenic Sources of Heavy Metals

1. **INDUSTRIAL ACTIVITIES:** The industrial processes have been noted as the most important activities to release heavy metals in the surrounding. The coal and petroleum combustion, solid waste disposal, and mining are the principal anthropogenic sources of heavy metals. The combustion of fossil fuels contributes heavily to release heavy metals in the environment.

2. **PHOSPHATIC FERTILIZERS:** The fertilizers produced by the parent rocks contain a small amount of Cd, As, Ni, Pb, Zn, and

other heavy metals[4]. With repeated fertilizer applications, heavy metals accumulate in soil and degrade the quality of the soil. These heavy metals then enter into the food chain, which is very harmful to all living organisms.

3. **AGRICULTURAL PESTICIDES:** Pesticides are the chemical compounds that are used to control insects, fungi, rodents, and unwanted weeds for high agricultural production. Metal-based pesticides mainly contain Pb, As, and Hg, which are highly toxic and may increase the risk to human health.

4. **BIOSOLIDS:** Biosolids are the major byproduct derived from wastewater sludge, municipal solid wastes, and animal manure. Disposal of these biosolids has the potential to enter into the food chain, which can adversely affect human health and the environment. The commonly found toxic heavy metals in biosolids include Pb, Hg, Cr, Mo, Se, Cu, and Zn.

The anthropogenic sources have been considered to contribute more to environmental pollution through heavy metal contamination due to everyday industrial production in order to meet the demand of a large population[4].

1.1.2 Impact of heavy metals contamination

Heavy metals are considered as major sources of environmental pollution. The heavy metal contamination in the environment poses potential threats to human health, and it is often the root cause of severe health diseases. Heavy metals can bind to cellular components of human, plant, and animal tissues, such as nucleic acid, structural proteins, and enzymes, resulting in the interruption of their functioning. The introduction of toxic elements in the human body along the food chain is highly responsible for disabilities associated with malnutrition, weak immune system, and upper gastrointestinal cancer, which is represented in Figure 1.2.

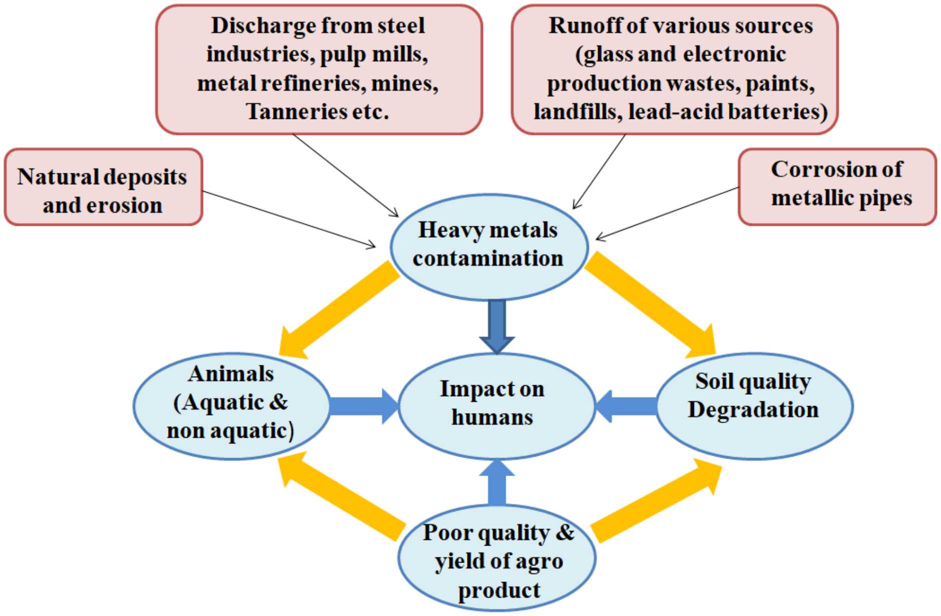

Figure 1.2 Impact of heavy metal contamination on living organisms[5]

Heavy metals contamination of soil through the disposal of industrial wastes, chemicals, and agricultural pesticides, leaded gasoline, and paints, is also the main cause of soil pollution. The heavy metals exert toxic effects on the microorganism present in the soil, which leads to a loss of soil fertility and declines the quality of the soil. Soils have been considered as the major sinks for toxic elements that are released by anthropogenic activities. The heavy metals contaminated soil is destroying the entire ecosystem due to the uptake of these heavy metal ions by plants, animals, and other living organisms along the food chain[5]. Heavy metals contamination in water as a consequence of industrialization and urbanization is becoming a serious issue around the world. Heavy metals discharged in water bodies from different sources lead to a greater risk to human health and the aquatic ecosystem. The most common heavy metal pollutants present in drinking water are copper, nickel, lead, mercury, and arsenic, which increase toxicity and decline the quality of water.

The standard guidelines of heavy metal concentrations by the World Health Organization (WHO), United States Environmental Protection Agency (USEPA), Indian Standard Institution (ISI), Indian Council of Medical Research (ICMR), and Central Pollution Control Board (CPCB) are shown in Table1.

Table 1. Permissible limits of heavy metals in drinking water[6]

S. No.	**Heavy Metals**	**Permissible limit (mg/L)**				
		WHO	USEPA	ISI	CPCB	ICMR
1.	Lead	0.05	---	0.10	---	0.05
2.	Arsenic	0.05	0.05	0.05	---	0.05
3.	Copper	1.0	1.3	0.05	1.5	1.5
4.	Mercury	0.001	0.002	0.001	---	0.001
5.	Iron	0.1	---	0.3	1.0	1.0
6.	Chromium	0.1	---	0.05	---	---
7.	Zinc	5.0	---	5.0	15.0	0.10
8.	Cadmium	0.1	---	0.05	---	---

To mitigate environmental pollution, due to the excessive level of heavy metal ions, it is necessary to detect the accurate concentration of these ions. Neutron activation analysis (NAA), atomic absorption spectroscopy (ASS), plasma mass spectroscopy (PMS), and X-ray fluorescence spectrometry (XRF) are the conventional methods to analyze heavy metal ions concentration. The neutron activation analysis is a powerful nuclear analytical technique for the detection of chemical elements. NAA is based on the most basic nuclear reaction, neutron scattering reactions, and thermal neutron capture[7]. The atomic absorption spectroscopy evaluates the concentration of heavy metal elements, quantitatively, and qualitatively. It is also an important technique for the determination of heavy metal ions due to its fast response[8]. Apart from these methods, Inductive coupled plasma mass spectroscopy has been a commercially available technology that is being used for the detection of heavy metals from a variety of solutions. Though these methods are extremely sensitive, they often require relatively complex and expensive instruments, along with the complicated operational procedure and long detection times. Nowadays, the electrochemical method for heavy metal ion detection has been gaining sustainable attention from researchers because it is a portable, low-cost, accurate, rapid, and environment-friendly technique. The simple instrumentation and user-friendly nature make electrochemical technique superior to spectroscopic techniques[9].

The electrochemical response of electrode materials is a key factor that affects both selectivity and sensitivity of the heavy metal ion sensing. Nowadays, nanomaterial-based electrodes have been gaining the sustainable interest of researchers because of their extraordinary quantum mechanical properties. In this context, inorganic-organic hybrid materials are considered as highly promising materials because they combine typical properties of organic materials (mass transport, gas diffusivity, chemical reactivity) as well as inorganic materials (conductivity, mechanical stability, surface area, electrical and optical properties) and resulting in high metal ion adsorption capacity and strong binding affinities towards selected heavy metal ions. At present, transition-metal based electrodes, including sulfides, hydroxides, selenides, phosphides, are receiving substantial attention. In particular, nickel hydroxide based nanohybrid materials are the most promising electrode materials because of their inherent properties such as high surface area, layered structure, rapid electron transport capacity, and highly exposed active sites[10].

In this work, a polyethyleneimine (PEI) functionalized α-nickel hydroxide nanosheets have been proposed as an efficient material for heavy metal ion sensing. It is well known that nickel hydroxide exists two polymorphs such as α and β-Phases. Both phases have similar morphology but different chemistries in between the brucite layers. The positively charged layers of α-$Ni(OH)_2$ are randomly oriented with intercalated anions to form turbostratic structure while β-$Ni(OH)_2$ possesses well oriented, perfectly stacked brucite layers along the c-axis to form crystalline structure[11]. Generally, α-$Ni(OH)_2$ exhibits superior electrochemical properties compared with β-phase due to the disordered and opened structure. The nitrogen-containing polymer exhibits high selectivity towards the heavy metal ion sensing. Polyethyleneimine is a very commonly used chelating polymer for the determination of heavy metal ions because of the presence of electron-rich amine groups. Functionalization of α-$Ni(OH)_2$ with polyethyleneimine (PEI) not only improves the surface properties but also enhances the affinity towards the metal cations[12].

α-$Ni(OH)_2$ and polyethyleneimine nanohybrid (α-$Ni(OH)_2$/PEI) obtained by exfoliation reassembling technique can be efficiently and effectively used as a promising electrode material for heavy metal ion sensing.

1.2 Motivation

Environmental pollution is the most serious problem that has adverse effects on humans and other living organisms. The global environmental pollution, including water pollution, soil degradation, greenhouse gas emissions, air pollution, as well as waste management, must be taken seriously as it is very harmful to life on the earth. The excess amount of heavy metal ions is also poisonous for human beings and the entire ecosystem. The heavy metals such as mercury, chromium, arsenic, and lead are the common water pollutants emitted from various industrial processes. Contamination of heavy metal ions is becoming a more serious issue around the world as it affects all the spheres of the environment, lithosphere, atmosphere, hydrosphere, and biosphere. Fertilizers, industrial waste, petrochemicals, pesticides, and biosolids (sewage, sludge) are the major sources of heavy metal ions[13]. Several international organizations like FAO, CDC, EPA, and WHO have considered heavy metal ions as the priority substances to be monitored.

The heavy metals are generally present in water at trace level, therefore, detection and removal of these ions are quite challenging. Hence, it is essential to develop a simple, accurate, highly sensitive, and environment-friendly approach to asses environmental pollution and reduce the degradation of soil and water resources. Conventional methods of heavy metal ions detection such as plasma mass spectroscopy and atomic absorption spectroscopy are complex, expensive, and time-consuming. The fast, accurate, and sensitive detection of heavy metals (e.g. mercury, lead, zinc, cadmium) is highly desirable as they become poisonous at higher concentrations. In recent years electrochemical heavy metal ion sensing has been observed as a most practical approach for the selective detection of heavy metal ion sensing.

Over the last decades, nanotechnology has emerged in all the fields of science and technologies. In recent times, nanomaterials and nanostructures have attracted great attention owing to their compatibility, good chemical stability, selectivity, reproducibility, low cost, and more number of adsorption active sites for heavy metals. The aforementioned challenges and their respective solutions motivated me to work in the field of electrochemical detection of heavy metal ions. However, to meet these objectives, I have explicitly focused on a novel inorganic-organic hybrid material that has been developed as an excellent electrode material for heavy metal ion sensing.

1.3 Thesis Objective and Scope

The electrochemical heavy metal ion sensing has received considerable interest because of its high sensitivity and fast response. In this connection, the objective of my thesis is to develop a highly efficient nanohybrid as an electrode material that can boost the sensitivity and stripping response of the electrode system for the rapid detection of heavy metal ions.

The main goal of this thesis can be stated as:-

a) To develop a high-performance Inorganic-organic hybrid material for the electrochemical sensing of heavy metal ions.
b) Characterization of as-prepared hybrid material using various physical and electrochemical techniques.
c) Assessment of the performance of as-synthesized Inorganic-organic hybrid material for the electrochemical heavy metal ion sensing.

To achieve these ultimate objectives, a list of sub-goals has been laid down to complete the proposed work:-

- Synthesis of surfactants intercalated α-phase of nickel hydroxide {α-$Ni(OH)_2$} by hydrothermal technique.
- Exfoliation of as-prepared α-$Ni(OH)_2$ by chemical assisted technique.
- Selection of organic moiety and the functionalization of the same on the as-prepared exfoliated layers of α-$Ni(OH)_2$.
- Reassembling of polymer functionalized delaminated α-$Ni(OH)_2$ layers to form hybrid material.

1.4 Organization of the Thesis

This dissertation mainly focuses on the electrochemical detection of heavy metal ions using inorganic-organic hybrid material modified electrode. Investigation in this field began with the synthesis and development of an efficient hybrid nanomaterial-based electrode modifier, which is highly capable in the detection of heavy metal ions. The entire thesis has been divided into five Chapters as detailed below:

- **Chapter 1,** describes the need for the mitigation of environmental pollution and the harmful effect of an excessive level of heavy metal ions present in the environment. This chapter also provides an overview of different techniques employed in heavy metal ions sensing.

- **Chapter 2,** provides a brief description of the important literature of past studies on the electrochemical detection of heavy metal ions. This section includes a brief discussion on electrode materials, electrolytes, analytes, and operating conditions.

- **Chapter 3,** describes experimental procedures adopted for the design and synthesis of materials, components of the electrochemical system, modification of electrode. The characterization techniques used for the analysis of synthesized electrode material have also been explained in this chapter.

- **Chapter 4,** describes the results of the electrochemical performance of as-synthesized inorganic-organic hybrid material for heavy metal ion sensing using square wave voltammetry. The selectivity and sensitivity of electrocatalyst material for the detection of heavy metal ions have also been explained in this section. This chapter also mentions the calculation for the limit of detection, relative standard deviation, and repeatability studies.

- **Chapter 5,** summarizes the work with a key conclusion. The future recommendations related to the work have also been made.

Chapter 2

Literature Survey

This chapter contains an inclusive literature survey on recent developments and current achievements in the field of electrochemical heavy metal ion sensing. Many of the researchers found the different pathways to improve the detection of heavy metals and various important parameters such as detection limit, sensitivity, selectivity, and recyclability. The electrochemical heavy metal ion sensing has been studied for many years, and several good papers and reviews have been written on the various approaches for the voltammetry analysis of heavy metals. Several reports have been published for the advancement of electrode materials in the field of heavy metal ion sensing. It is also the aim of this chapter to explore the literature on the development of novel materials that can be used for the detection of heavy metal ions.

2.1 Current State of Art in Heavy Metals

Heavy metals are the chemical elements with relatively high density and higher molecular weight known for their potential risk, toxicity to living organisms, and the environmental contexts. A more common definition of heavy metal is any metal that can cause negative health effects and capable of environmental damage. Certain heavy metals, for e.g., chromium, manganese, copper, zinc, cobalt, molybdenum, and magnesium, may be toxic but the low concentration of these chemical elements is needed to support the normal functioning of the biological system. At the same time, the excessive level of heavy metals can cause severe diseases and cellular damage. Some of the heavy metals are most toxic even at its low concentration, such as cadmium, lead, mercury, and arsenic. The toxicity of any metal depends on the oxidation state of metal and varies widely with the physical form (i.e. ionic form, complex form, or suspended form) of metal, based on the environmental condition. Unlike other elements, cadmium is not essential for the ecosystem and has been found to cause of itai-itai diseases. Mercury is also a very toxic element, and toxicity is associated with physiological stress and the central nervous system. The presence of arsenic in the groundwater, through the weathering of sediments and rocks, causes poisoning to blood, skin, and lung cancer and breathing problems. Najeeb et al. stated that lead is a highly toxic heavy metal that is capable of inhibiting the growth of plants by changing the quality of its components[14]. Societal development and a continuous increase in anthropogenic activities redistribute many toxic metals from the earth's crust to the environment which increases the probability of human exposure due to contamination of soil, groundwater, and air. World health organization has established guidelines to limit the concentration of heavy metal ions in water. Usually arsenic is usually present in water at a concentration of less than 1-2 μg/L. The permissible limit for arsenic is 1-10 μg/L, and the elimination of arsenic to a concentration below 10 μg/L is difficult in many circumstances. Chromium is an essential nutrient and widely distributed in Earth's crust. The maximum allowable limit of chromium in the drinking water is 50 μg/L[15].

Based on the IHME report 2015, lead exposure accounts for the loss of 9.3 million disability-adjusted life years (DALYs) and 494,550 deaths. According to USEPA, 40-60% of infants and 10-20% of adults are exposed to lead contamination via drinking water[16]. Research published in Nigeria revealed the acute and immediate consequences of lead poisoning in young children through the contamination of lead in water, soil, and food[17]. Poisoning and severe toxic effects by heavy metal ions to aquatic bodies require better treatment techniques. Several techniques, such as electrochemical sensing, plasma mass spectroscopy, neutron activation analysis, and atomic absorption spectroscopy, are being used for the sensing of heavy metal ions due to their high selectivity and sensitivity.

2.2 Heavy Metals Ion Detection Techniques

Heavy metal ion sensing is mainly performed using spectroscopic techniques because of their versatility and high sensitivity. Ashutosh et al. have determined the concentration of heavy metals present in the soil through atomic absorption spectroscopy. The study shows the variation in the soil samples of the industrial area, urban area, river sites, and institutional area. The research revealed that the soil sample exhibits a higher concentration of Mn and Zn present as compared to Cr, Cu, and Pb. Heavy metals provide a unique fingerprint of any soil, and a large concentration of these toxic metals diminishes the quality of soil[18].

Plasma mass spectrometry is a comparatively a new technique for the detection of toxic elements. Voica et al. investigated the quality of surface waters from various water treatment plants and determined the concentration of heavy metals by inductive coupled plasma mass spectrometry. Water from various areas was quantitatively determined and the concentrations of heavy metals were calculated in the range of

0.001-25 mg/L. Mass spectroscopy with inductive-coupled plasma offers the measurement of heavy metals ions with high sensitivity, good precision, and great accuracy, which can detect parts per billion or even parts per trillion for certain metal elements.[19]. Feisal et al. determined the concentration of heavy metals in human hair by plasma mass spectrometry. The result of the study provides sufficient evidence that plasma mass spectroscopy can be used for the quantitative analysis of toxic heavy metals (Cd, Pb, Ni, As) in hair samples[20]. X-ray fluorescence spectroscopic technique has been utilized for many years for the determination of chemical elements from stardust to forensic samples. Jaiswal et al. studied the quantification and detection of heavy metals in gallstones through X-ray fluorescence spectrometry. The chemical elements, particularly Mg, Fe, Mn, Cu, Si, in gallstones have been quantified using wavelength-dispersive X-ray fluorescence spectrometry (WF-XRF). The major advantage of this technique is the ability to simultaneously determine all the metal elements in the concentration range of 1 ppm to 100 ppm[21].

The electrochemical method is also one of the most promising techniques for the detection of heavy metal ions. The electrochemical heavy metal ion sensing is superior to spectroscopic techniques because of its simple instrumentation and environment-friendly nature. Wei et al. have designed a novel electrochemical sensor using Ln-MOF for the determination of trace heavy metal ions. In this research, the electrochemical sensor has shown excellent selectivity and sensitivity for the detection of lead and cadmium ions in aqueous solutions, which can be attributed to excellent conductivity and high adsorption capacity[22]. In heavy metal ion sensing, the electrode surface is improved by some superior materials aiming to obtain the detection limit in the ppb range.

2.3 Advancement of Materials

The performance of electrochemical heavy metal ion sensing strongly depends on the properties of the working electrode. The limit of detections obtained by modifying the working electrode by several materials is given in Table 2. Mainly such materials are metal oxides, metal nanoparticles, carbonaceous materials, and their nanocomposite. At present, nanomaterials have attracted sustainable attention as suitable electrode materials in the field of electrochemical sensing. The nanomaterials are the most suitable materials for heavy metal ion sensing because of their superior properties such as high adsorption capacity, large surface area, and strong affinity towards heavy metal ions.

Table 2. Materials for the modification of electrode and their limit of detection

Electrodemodifier	**Analyte**	**Detection limit**	**Ref.**
Graphene oxide (GO)	Pb^{2+} Cd^{2+}	0.41 µg/L 2.13 µg/L	[23]
Carbon nanotubes (CNTs)	Cu^{2+} Cd^{2+} Pb^{2+}	15 ppb 0.41 µg/L 0.30 µg/L	[24]
Zeolite	As^{3+} Hg^{2+}	0.9 ppb 0.8 ppb	[25]
CNT/Nafion/GCE	Cu^{2+} Fe^{3+}	0.051µg/L 0.71 µg/L	[26]
G/PANI/ SPE	Pb^{2+} Cd^{2+} Zn^{2+}	1.0 µg/L 0.1 µg/L 1.0 µg/L	[27]

Graphene/Au electrode	Cu^{2+} Pb^{2+}	1.5 nM 0.4 nM	[28]
Ti/TiO_2/GCE	Cu^{2+} Pb^{2+} Cd^{2+}	0.10 µM 0.14 µM 0.16 µM	[29]

To improve the performance of electrochemical heavy metal ion sensing, several efforts have been made to explore the advanced materials with a well-defined structure. Layer double hydroxides (LDHs) are excellent materials for the electrochemical heavy metal ion sensing owing to their inherent properties such as tunable compositions and ion-exchangeability. Yu et al. have demonstrated MgFe-layered double hydroxide for simultaneous detection of the trace of Cd^{2+} and Pb^{2+}. The good reproducibility and high repeatability of layered double hydroxide make it the most suitable material in the future practical application[30]. Metal hydroxides and metal oxides have been extensively used for electrochemical sensing. Mathew et al. have reported $Ni(OH)_2$ modified electrode for highly sensitive electrochemical sensing of glucose[31]. Nickel hydroxide based nanomaterials possess superior electrochemical properties such as flexible ion-exchangeability, layered structure, high surface area, and a large number of active sites so that it can be effectively used for the determination of heavy metal ions. The functionalization and surface modification of electrode materials with organic polymer also boost the electrochemical activity. Hu et al. have studied polyethyleneimine functionalized rGO nanohybrid for the selective detection of trace Cu^{2+} ion. PEI is a very commonly used chelating polymer for the determination of heavy metals because of the excellent affinity of electron-rich amine groups towards metal cation[32].

Numerous research has been done on inorganic materials, organic materials, and their composites for the detection of heavy metals. Advancement in the process of heavy metal ion sensing still finite, and enough work has to be done for the development of materials.

Chapter 3

Experimental Section

3.1 Materials

All the chemicals used in the experiments were of analytical grade and used as received without any further purification. These chemicals include copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), cadmium nitrate tetrahydrate ($Cd(NO_3)_2.4H_2O$), and lead nitrate ($Pb(NO_3)_2$) were obtained from SRL chemicals. Hexamethylenetetramine ($C_6H_{12}N_4$), sodium dodecylbenzene sulfonate (SDBS), and formamide ($HCONH_2$) and polyethyleneimine (PEI) with a molecular weight of 600 were purchased from TCI chemicals. By mixing stock solutions of 0.1 M sodium acetate (NaAc) and acetic acid (HAc), a buffer solution of pH 5 was prepared. Milli-Q Deionized water was used in all the experimental process.

3.2 Synthesis of Surfactant Intercalated α-$Ni(OH)_2$

Figure 3.1 shows the schematic representation of the overall synthesis procedure. In a typical experimental procedure, dodecyl sulfonate (DS) intercalated layered nickel (II) hydroxide was prepared by precipitation of an aqueous solution of nickel (II) nitrate and SDBS through hydrolysis of hexamethylenetetramine(HMT). Three types of aqueous solutions of 1 M

HMT, 0.25 M SDBS, and 0.5 M $Ni(NO_3)_2.6H_2O$ were prepared. The HMT (12 mL), SDBS (40 mL), and divalent nickel (4 mL), solutions were mixed with 44 mL of deionized water by magnetic stirring. The as-prepared solution was transferred into a Teflon vessel, and the mixed solution was heated at 120 °C for 24 hrs under airtight condition. After hydrothermal treatment, the green precipitate obtained was centrifuged, washed several times thoroughly with DI water and ethanol. Finally, it was dried at 40 °C for 24 h in a vacuum oven to obtain a sheet-like product of α-$Ni(OH)_2$[33].

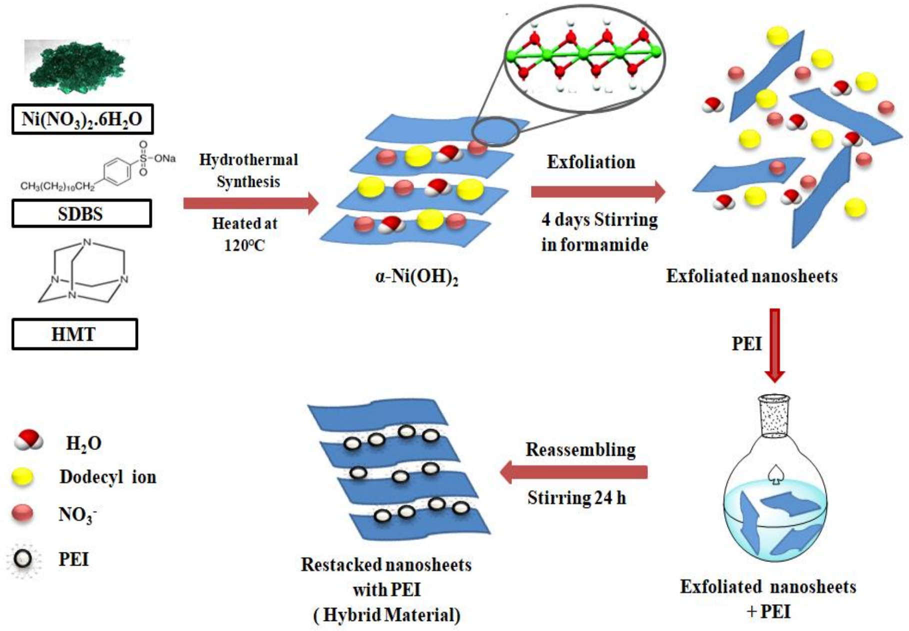

Figure 3.1 Schematic representation of the synthesis of hybrid material

3.3 Exfoliation of α-$Ni(OH)_2$

To prepare the exfoliated $Ni(OH)_2$ nanosheets, 50 mg of precipitate was dispersed in 50 ml of formamide (99% of purity) in 100 cm^3 conical flask, which was covered by an airtight cap. Then, the mixture was stirred at

200 rpm with 35x9 mm magnetic stir bar for seven days. The resultant translucent colloidal suspension was centrifuged at 2000 rpm for 10 minutes to remove unexfoliated particles. Subsequently, the supernatants nanosheet solution was centrifuged at 10000 rpm for 30 min, and the precipitate was washed with DI water for three times and finally dried in a vacuum oven at RT for two days[34]. The dried product can be used as solid nanosheets for further treatment.

3.4 Synthesis of α-$Ni(OH)_2$/PEI Hybrid Material

The α-$Ni(OH)_2$/PEI composite was synthesized by the mechanical mixing of α-$Ni(OH)_2$ nanosheets and polyethyleneimine (Figure 3.1). Two suspensions were prepared by dispersing 10 mg of as-obtained exfoliated $Ni(OH)_2$ nanosheets and 5 mL of polyethyleneimine in methanol. PEI solution (1mg/mL) was then added dropwise to the $Ni(OH)_2$ suspension under stirring at 300 rpm for 24 h. After centrifugation, the resultant precipitate was dried at 80 °C to obtained reassembled α-$Ni(OH)_2$/PEI nanohybrid.

3.5 Instrument and Characterization

All the samples were characterized by various physical and electrochemical characterizations. The compositions and crystallographic structures of as-synthesized materials were characterized by P-XRD analyses, which were collected on Rigaku automated multipurpose X-ray diffractometer with monochromatic Cu Kα radiation(λ=0.154 nm) at a scanning rate of 2°/min. The morphologies of the prepared sample were studied by field emission scanning electron microscopy (FE-SEM, Supra55 Zeiss, extremely wide operating range, from 0.02-30kV). The Fourier transform infrared (FTIR) spectra were recorded by FT-IR TENSOR 27, BRUKER. Atomic force microscopy (AFM) images were taken under ambient conditions using Park systems in AC mode. Sample for AFM was prepared by re-dispersing the nanosheets powder in ethanol and drop-casting of 60 µl of this dispersion onto a fresh silica substrate.

3.6 Preparation of α-$Ni(OH)_2$ and Nanohybrid Modified Electrode

The working electrode was modified by as-prepared α-$Ni(OH)_2$/PEI, to examine the electrochemical sensitivity of hybrid material. Prior to the modification, the bare GCE was polished with 0.3 µm alumina powder slurry to a shiny glass surface. Then, the electrode was rinsed and sonicated with distilled water and ethanol for 1 min. to remove any adsorbed particles on the electrode surface. The cleaned surface of the electrode was dried at room temperature. After that, α-$Ni(OH)_2$ and α-$Ni(OH)_2$/PEI suspensions were prepared by dissolving 4 mg of material in 1 mL of ethanol, then these suspensions were sonicated for at least 20 min. to get a homogenous dispersion of materials. Finally, 10 µl of sonicated dispersion was dropcast onto the surface of polished clean electrodes; then, the electrodes were air-dried at room temperature. Before the next measurement, the electrode surface was regenerated after polishing and sonication.

3.7 Electrochemical Measurements

All electrochemical measurements were carried out at RT using AUTOLAB 204 computer-controlled electrochemical potentiostat with NOVA 2.1.4 version software. All the experiments were performed in a three-electrode system with a bare or hybrid material modified GCE as a working electrode, platinum wire as a counter electrode, and an Ag/AgCl as a reference electrode. Figure 3.2 shows the electrochemical experimental setup for heavy metal ion sensing.

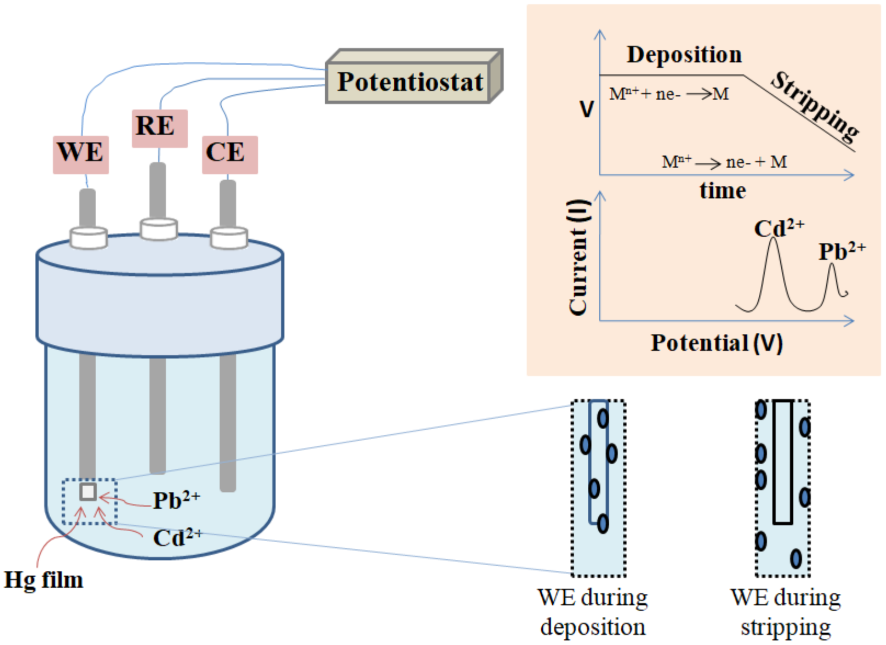

Figure 3.2. Electrochemical Experimental setup and measurement

For heavy metal ions sensing experiments, 0.1 M buffer solution of acetic acid and sodium acetate (HAc-NaAc) at pH 5 was used as an electrolyte solution. The electrochemical performance of the modified electrodes was investigated by SWASV. The square wave voltammogram was recorded for heavy metal ion sensing under the following optimized condition: frequency of 15 Hz, pulse height of 8 mV, pulse amplitude of

50 mV. A similar process and parameters were applied in the selectivity and stability studies.

Chapter 4

Result and Discussion

4.1 Structural Characterization

4.1.1 P-XRD pattern of materials

Crystal structures and phase purity of all the materials were determined by powder X-ray diffraction patterns. P-XRD patterns of surfactant intercalated α-$Ni(OH)_2$, partially and completely exfoliated nanosheets, and α-$Ni(OH)_2$/PEI nanohybrid powder samples are shown in Figure 4.1. The formation of dodecylbenzene sulfonate (DBS) intercalated α-$Ni(OH)_2$, synthesized by hydrothermal technique, was confirmed by the P-XRD pattern. All the diffraction peaks (Table 3) are corresponding to the rhombohedral phase of α-$Ni(OH)_2$ (JCPDS 38-0715) shown in Figure 4.1(a), which indicates the high purity of as-prepared DBS intercalated α-$Ni(OH)_2$ in the system. Several (00n) reflections, observed (where n=4,5,6) at a lower angle, indicate the large interlayer spacing along c-direction resulting from the intercalation of DBS anions. α-$Ni(OH)_2$ has a layered structure made up of brucite layers of $Ni(OH)_{2-x}$, in which nickel is octahedrally surrounded by hydroxyl groups. These two-dimensional sheets, with structural defects as a consequence of the absence of hydroxyl groups, are stacked by the intercalation of anions[35].

Table 3. XRD planes and corresponding diffraction angles

S. No.	**2θ (degree)**	**(hkl)**
1.	12.4	(004)
2.	15.6	(005)
3.	18.7	(006)
4.	33.8	(101)
5.	60	(110)

The first three diffraction peaks at 12.4°, 15.6°, and 18.7° could be indexed as (004), (005), and (006), respectively. These reflections at a low angle ($2\theta<20°$) are providing clear evidence of layered structure. The interlayer spacing (D) is related to (00n) reflections by the relationship D = 1x d(001) = 2x d(002)=3x d(003)……..nx d(00n)[36].

From this relation, the calculated interlayer spacing of DBS intercalated α-$Ni(OH)_2$ is 2.7 nm, which is almost equal to the sum of the length of DBS ion (about 2.2 nm) and thickness of brucite-layer (4.6Å).

The broad and asymmetric peaks at high value of diffraction angles are corresponding to non-basal planes. The asymmetric reflection of (101) plane at $2\theta=33.8°$ corresponds to the turbostratic character of α-$Ni(OH)_2$, which has been observed in most of the layered metal hydroxides. The turbostratic disorder is usually related to the random orientation of brucite layers, which are parallel and equidistant along the c-axis but twisted relative to each other[37]. The diffraction peak at $2\theta=60°$ could be assigned as (110) related to the non-basal atomic plane. From this peak, the in-plane Ni-Ni interatomic distance has been calculated, which is equal to $2.d_{110}$(where d_{110}= 1.56Å).

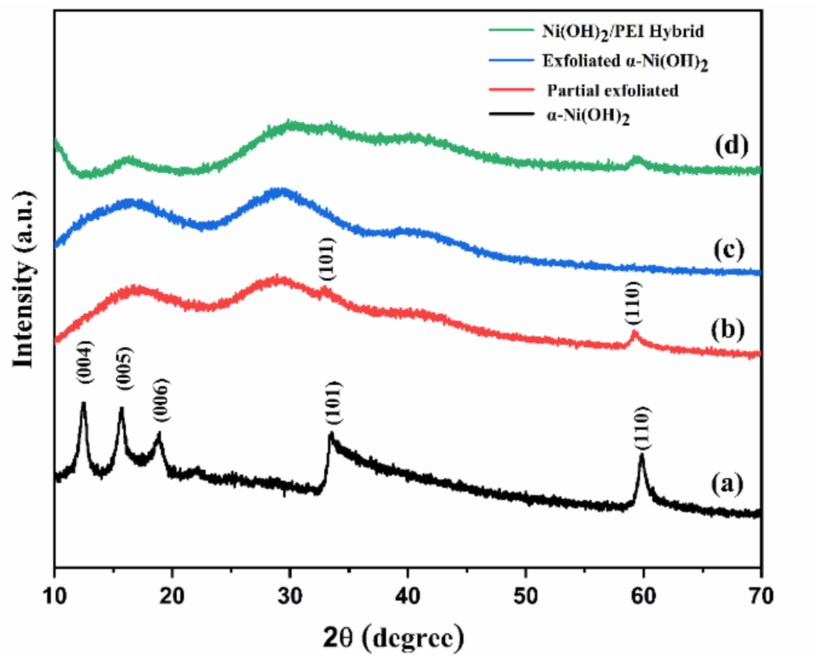

Figure 4.1. P-XRD patterns of (a) α-Ni(OH)$_2$, (b) Partially exfoliated nanosheets, (c) Exfoliated nanosheets, (d) α-Ni(OH)/PEI nanohybrid.

The XRD patterns of partially and completely exfoliated DBS intercalated α-Ni(OH)$_2$ has been shown in Figure 4.1(b) and (c), respectively. During the exfoliation, brucite layers of α-Ni(OH)$_2$ comes apart because of the removal of anions present in the interlayer gallery space. After the exfoliation process, the amorphous nature of the XRD pattern indicates that there is a reduction in the crystallinity of DBS intercalated α-Ni(OH)$_2$. In Figure 4.1(b), reduced intensity and shifting of diffraction peaks can be observed because of the high degree of interlayer expansion. The disappearance of sharp basal reflections in the P-XRD pattern of completely exfoliated nanosheets indicates that the host layers are no longer parallel, which also confirms the exfoliation of as-prepared material. The broad amorphous-like halos observed at a low diffraction angle corresponds to the diffraction of individual nanosheets[38].

The XRD pattern of α-Ni(OH)/PEI nanocomposite is shown in Figure 4.1(d). The lack of crystallinity and reduced basal spacing in the XRD pattern indicates the presence of polyethyleneimine in the hybrid material. The reappearance of diffraction peak (110) at 2θ=60° confirms the reassembling of polyethyleneimine functionalized α-$Ni(OH)_2$ nanosheets[39].

4.1.2 FT-IR spectra of α-$Ni(OH)_2$ and hybrid materials

The FT-IR spectroscopy experiments were conducted to examine the functional groups present in the materials. FT-IR spectra of α-$Ni(OH)_2$, and α-$Ni(OH)_2$/PEI nanocomposite samples have been shown in Figure 4.2. A broad absorption at 3439 cm^{-1} corresponds to the O-H stretching vibration ν_s(O-H) of the water molecules and H-bonded OH groups, occupying the interlamellar space of α-$Ni(OH)_2$. A narrow absorption band at 3652 cm^{-1} is attributed to the O-H stretching vibration of the free hydroxyl group present in the brucite like structure. The observed major bands in Figure 4.2 are assigned to the various groups of DBS ligands. The bands at 2950 $cm^{-1}$and 2861 cm^{-1} are corresponding to the stretching mode of -(C-H) vibration of CH_2 groups. The vibration band at 1632 cm^{-1} is characterized by the bending mode of intercalated water molecules. The band at 1410 cm^{-1} is attribute to the vibration of NO_3^- ions, which are present in the interlamellar space of brucite like sheets of α-$Ni(OH)_2$.

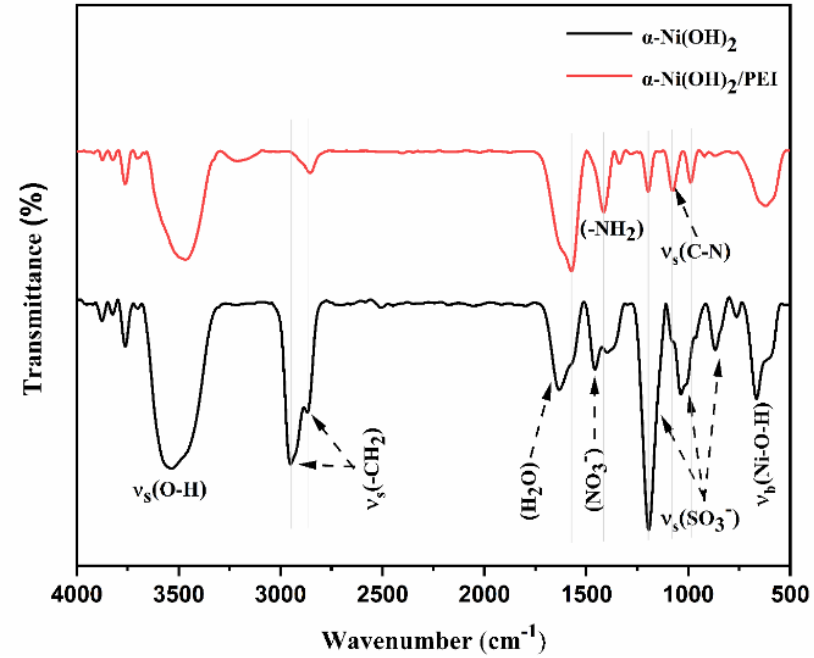

Figure 4.2 FT-IR spectrum of α-Ni$(OH)_2$ and α-Ni$(OH)_2$/PEI hybrid

The intercalation of SDBS in the interlayer spacing of α-Ni$(OH)_2$ is confirmed by the vibration bands of sulfonate group (-SO_3) at 1192, 1031, and 861 cm^{-1}. The absorption band at 660 cm^{-1} is related to the Ni-O bending vibration of Ni-O-H[40].

Two additional bands can be observed in the FT-IR spectrum of α-Ni$(OH)_2$/PEI, which confirms the functionalization of polyethyleneimine on α-Ni$(OH)_2$ nanosheets. The absorption band at 1071 cm^{-1} is related to the C-N stretching vibration of amine groups. The characteristic peak of PEI at 1409 cm^{-1} is corresponding to the N-H bending vibration of primary amines. These peaks evidence the successful bonding of PEI with exfoliated nanosheets[41].

4.2 Morphological Studies

4.2.1 SEM images of materials

The morphologies of as-prepared DBS intercalated α-$Ni(OH)_2$, exfoliated nanosheets, and α-$Ni(OH)_2$/PEI nanohybrid were investigated by SEM images, which reveal the nanoparticles, nanosheets, and nanopetals morphologies of the materials, respectively. The low magnification SEM image of α-$Ni(OH)_2$ samples can be clearly seen in Figure 4.3(a), which shows that α-$Ni(OH)_2$ is a layered material mainly composed of uniform nanoflower like architectures. The high magnification SEM images (Figure 4.3(b)) show the well ordered and highly uniform hierarchical structure mostly consists of dozens of aggregated nanosheets and nanopetals with an average thickness of about 10 nm. Moreover, a closer observation demonstrates that the flower-like α-$Ni(OH)_2$ exhibits a large number of pores between the nanopetals and thin nanosheets.

The SEM images of exfoliated nanosheets of α-$Ni(OH)_2$ are shown in Figure 4.3(c) and (d). After the chemical exfoliation of DBS intercalated α-$Ni(OH)_2$ in the formamide solution, the aggregated nanopetals and nanoflakes were transformed into thinner nanosheets. During the exfoliation process, a high degree of swollen phase is observed because of the diffusion of a large amount of formamide into the interlayer gallery space. The increased interlayer spacing due to the removal of intercalated anions is also evidence of the successful exfoliation of α-$Ni(OH)_2$[42]. It can be clearly observed in Figure 4.3(d) that a large scale two-dimensional ultrathin nanosheets were obtained. These nanosheets are irregular in shape, which is because of the fracture or breakage during the delamination process[43].

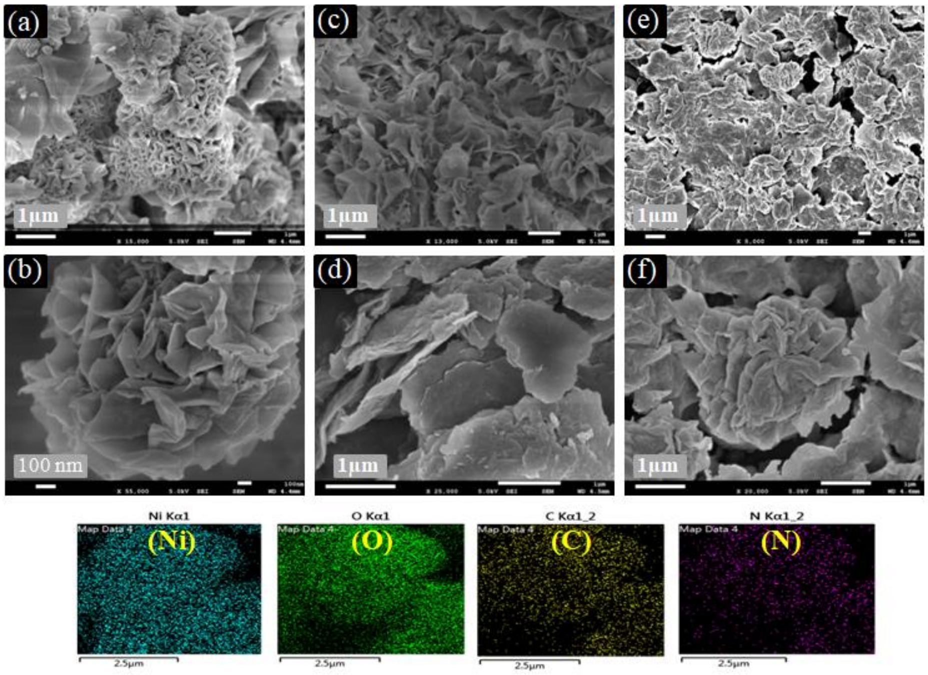

Figure 4.3 SEM images of (a) α-Ni$(OH)_2$, (b) exfoliated nanosheets, (c) α-Ni$(OH)_2$/PEI nanohybrid, and elemental distribution of N, C, O, and Ni.

The morphology of PEI functionalized reassembled α-Ni$(OH)_2$ nanosheets can be observed in Figure 4.3 (e-f), which suggests that the surface of α-Ni$(OH)_2$ nanosheets are uniformly modified by polyethyleneimine. After the functionalization of PEI, the α-Ni$(OH)_2$ nanosheets are restacked to form hybrid material. The driving factor for such reassembly may be the interaction between the lone pairs of nitrogen atoms in the –NH_2 polar group of PEI and the positively charged nickel nanosheets[44]. The reassembling of nanosheets has reduced the overall crystallinity of finally obtained α-Ni$(OH)_2$/PEI hybrid material.

The elemental mapping analysis of α-Ni$(OH)_2$/PEI nanohybrid is presented in Figure 4.3. It can easily be seen that the elements nickel (Ni), oxygen (O), carbon(C), and nitrogen(N) are uniformly distributed in the as-prepared hybrid material. The homogenous distribution of nitrogen atom also confirms the uniform functionalization of polyethyleneimine on the exfoliated nanosheets of α-Ni$(OH)_2$.

4.2.2 Formation mechanism of hierarchical α-Ni(OH)₂ nanostructure

The nucleation and growth mechanism for the formation of a three-dimensional hierarchical structure of α-Ni(OH)₂ has been proposed in Figure 4.4.

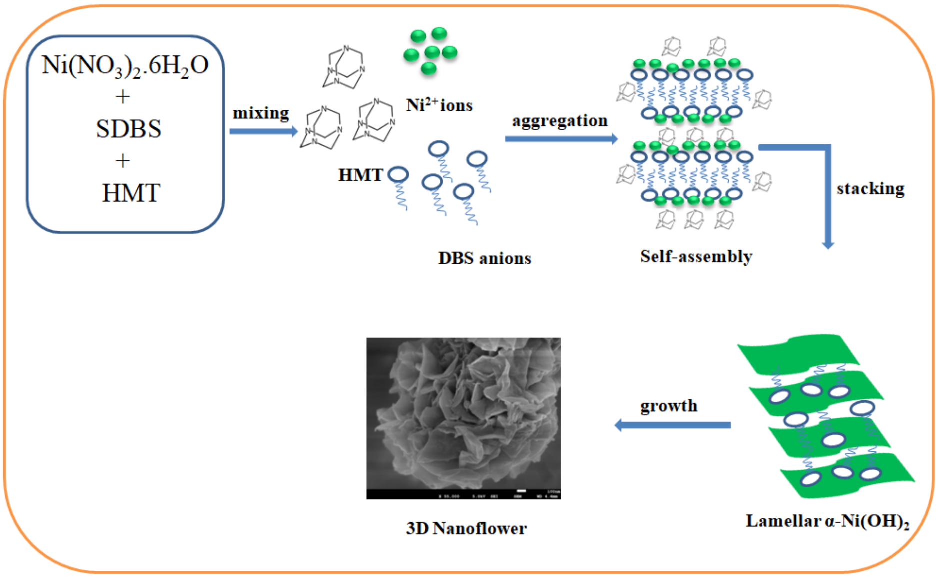

Figure4.4. Schematic representation of the formation mechanism of the 3D flower-like α-Ni(OH)₂ nanostructure

The precursors used in the synthesis of flower-like structure of α-Ni(OH)₂ are nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), sodium dodecylbenzene sulfonate (SDBS) and hexamethylenetetramine (HMT). The SDBS is an anionic surfactant which has been widely used for the surface modification in the synthesis of three-dimensional flower-like structure. The morphology of surfactant intercalated α-Ni(OH)₂ varies with the concentration of SDBS and HMT[45]. Initially,bilayer-like micelles are formed by the SDBS molecules, which play an important role in the formation of the hierarchical structure of α-$Ni(OH)_2$. At this moment, nickel nitrate is dissolved in the aqueous solution, which generates Ni^{2+} ions. Ni(II) clusters occupy the head groups region of DBS micelles via electrostatic interactions. These ions further react with a hydroxyl group (OH^-) obtained by the hydrolysis reaction of HMT $\{(CH_2)_6N_4\}$ in order to produce numerous tiny crystals of α-$Ni(OH)_2$. After that, the growth of $Ni(OH)_2$ nuclei takes place in the form of ultrathin nanosheets. The two dimensional thinner nanosheets stacked with several brucite layers aggregate to form nanopetals, which further transform into a hierarchical flower-like α-$Ni(OH)_2$ with the intercalation of anions[46].

The relevant chemical reaction involved in the formation of the flower-like architecture of α-$Ni(OH)_2$ can be written in the following equations[47]:

$$6H_2O + (CH_2)_6N_4 \longrightarrow 4NH_3 + 6HCHO \qquad (1)$$

$$NH_3 + H_2O \longrightarrow NH_4OH \qquad (2)$$

Nickel ions react with ammonium hydroxide and form a complex compound, which finally converts into thin sheets of nickel hydroxide :

$$NiNO_3 + NH_4OH \longrightarrow 2NH_4NO_3 + Ni(OH)_2 \qquad (3)$$

The morphology of surfactant intercalated nanomaterials mostly varies with the concentration of SDBS, which provides an approach to obtain different morphologies of such materials.

4.2.3 AFM images of α-Ni(OH)$_2$ and exfoliated nanosheets

The two-dimensional atomic force microscopy (AFM) images of bulk α-Ni(OH)$_2$ and exfoliated nanosheets of α-Ni(OH)$_2$ have been shown in Figure 4.5(a-b). The AFM images were used to characterize the thickness of nanosheets to confirm the delamination of α-Ni(OH)$_2$. AFM images of obtained materials were taken by directly dropping the colloidal suspension onto a piece of freshly cleaved Si-wafer.

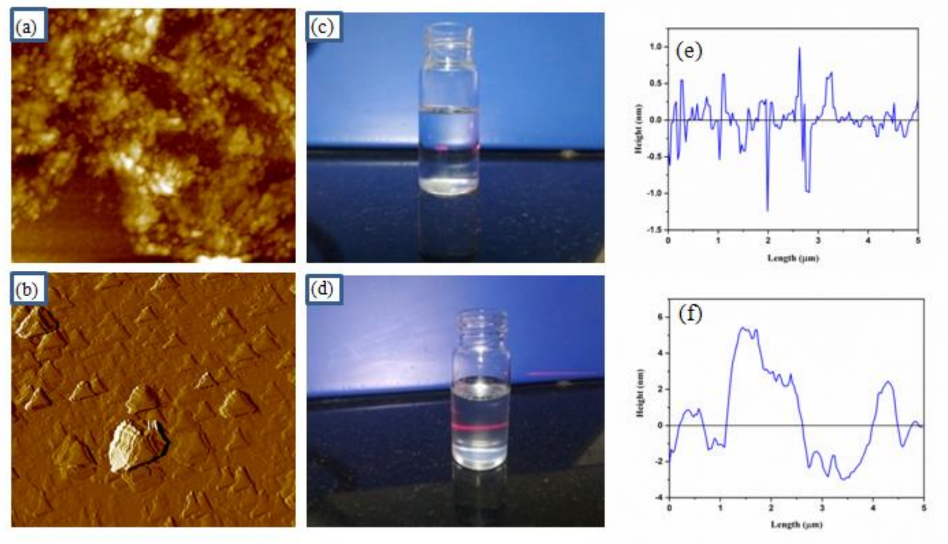

Figure 4.5. Tapping mode AFM images (a-b), Tyndall effect (c-d), and height profile (e-f) of Bulk α-Ni(OH)$_2$ and Exfoliated nanosheets.

The AFM image of exfoliated nanosheets is improper in shape due to the fracture or breakage of nanosheets during the exfoliation process[48]. The exfoliated nanosheets have the lateral size in the range of a few hundreds of nanometers to a micrometer.

The corresponding height profiles of bulk α-$Ni(OH)_2$ and exfoliated nanosheets are shown in Figure 4.5 (e-f). The height profile of exfoliated nanosheets suggests that the average thickness of nanosheets is about 2 nm. The thickness of nanosheets falls in the range between the hydroxide sheet thickness and interlayer spacing derived from X-ray diffraction (XRD) pattern. The AFM images and their corresponding height profile provide evidence of successful exfoliation of bulk α-$Ni(OH)_2$ into thin nanosheets.

The colloidal suspension of $Ni(OH)_2$ nanosheets were obtained through the exfoliation of DBS intercalated nickel hydroxide in formamide. Figures 4.5(c-d) show the bulk α-$Ni(OH)_2$ suspension and translucent colloid of exfoliated nanosheets. The as-prepared colloidal suspension of exfoliated nanosheets in ethanol was very stable at room temperature for several days. A clear scattering of light (Tyndall effect) was observed (Figure 4.5(d)), indicating the presence of exfoliated nanosheets in the translucent colloidal suspension while in case of bulk α-$Ni(OH)_2$ suspension the dispersed material settled down, and no Tyndall effect was observed[49].

4.3 Optimization of Experimental Conditions

The experimental conditions are optimized to obtain the best electrochemical performance for the detection of heavy metal ions using inorganic-organic hybrid material modified GCE. The experimental parameters and operating conditions for the electrochemical detection of heavy metal ions have been given in Table 4. It is well-known that SWASW is considered to be the most effective analytical technique because of its low background noise and high sensitivity. The square wave voltammetry is developed based on the square wave polarography and alternating current voltammetry. The electron scanning potential diagram and AC signals obtained through SWASW are called square wave voltammogram, which is used for the detection of heavy metal ions. The experimental parameters such as deposition time, pH value of supporting electrolyte, and deposition potential are needed to be optimized when an electrode is chemically modified for the heavy metal ion sensing. The simultaneous detection of heavy metal ions is quite challenging because the redox peaks of various heavy metals may overlap due to identical values of potential.

4.3.1 pH value of electrolyte

It was found that the pH value of supporting electrolyte has a considerable effect in the determination of heavy metal ions. The accumulation of these ions varies with the pH of supporting electrolyte solution. The heavy metal ions are tended to hydrolyze if the pH value is too high, resulting in the reduction of accumulating ions. The stripping current and accumulation of heavy metal ions may also decrease at low pH value of electrolyte because of the competition between metal ions and protons for binding with the donating atom on the electrode surface. Usually, low pH of buffer leads to the generation of more H^+ ions in the electrolyte that increases the H_2 evolution, and at the high pH buffer solution there is the formation of OH^- ions, both the low and high pH can hinder the oxidation of heavy metals[50]. So the optimization of buffer solution pH is important. Therefore 0.1M sodium acetate and acetic acid (HAc-NaAc) buffer solution of pH-5 has been used as the electrolyte solution for heavy metal ion sensing (Table 4).

Table 4. Experimental parameters and operating conditions in the electrochemical detection of heavy metal ions:

S.No.	**Experimental Parameters**	**Operating Conditions**
1.	Deposition Potential	-1 Volt
2.	pH value	5
3.	Deposition time	120 sec
4.	Pulse Amplitude	50 mV
5.	Pulse Frequency	15 Hz
6.	Pulse Height	8 mV

4.3.2 Deposition potential

Anodic stripping voltammetry is a two-step process: (a) preconcentration and (b) stripping. During the preconcentration step, analytes are deposited on the surface of the working electrode, and then the accumulated ions are oxidized during the stripping step. The preconcentration conditions have a significant effect on the stripping current of the heavy metal ions. When the applied deposition potential is too high, the incomplete reduction reaction takes place, which reduces the deposition of cations on the top of the electrode. On the contrary, more negative deposition potential results in the formation of hydrogen bubbles, which might damage the material deposited on the surface of electrode[51]. It has been identified that the deposition potential of -1.0 volt is sufficient to reduce Pb^{2+}, Cd^{2+}, Hg^{2+}, and Cu^{2+} ions to Pb, Cd, Hg, and Cu metals[52]. The influence of deposition potential on the stripping current is studied in most of the voltammetry analysis.

4.3.3 Deposition time

Deposition time is an important parameter and might affect the sensitivity and the limit of detection of the stripping analysis of heavy metal ions. The stripping peak current increases with increasing deposition time up to a certain value after that it levels off until it reached a constant value. The electrochemical sensing experiment has been performed with the deposition time of 120 sec.

Some of the parameters have also been considered in the development of the materials for the modification of electrode such as the number of active sites available on the electrode surface, stripping response, conductivity of the material, and the potential value corresponding to the metal ion under consideration.

4.4 Electrochemical Response of Different Modified Electrodes

To examine the stripping response, electrodes were modified by different materials. The bare GCE, α-$Ni(OH)_2$ modified GCE {α-$Ni(OH)_2$/GCE} and PEI/α-$Ni(OH)_2$ modified GCE {α-$Ni(OH)_2$/PEI/GCE} were used to detect lead ion (Pb^{2+}) in 0.1M of NaAc-HAc buffer solution of pH 5 containing 20 μM of Pb^{2+}. The square wave voltammograms of different modified electrodes are shown in Figure 4.6. A sharp stripping peak at -0.55 V corresponding to Pb^{2+} was observed with all the three electrodes. As shown in Figure 4.6(a), the prominent peak indicates the stripping of

Pb to Pb^{2+} on the surface of bare GCE. The stripping response for the detection of Pb^{2+} through α-$Ni(OH)_2$/GCE can be clearly observed in Figure 4.6(b). The observed peak current corresponding to the stripping of Pb^{2+} on α-$Ni(OH)_2$/GCE has increased by 9 μA as compared to bare GCE. This demonstrates the better electrochemical activity of α-$Ni(OH)_2$ towards heavy metal ion sensing.

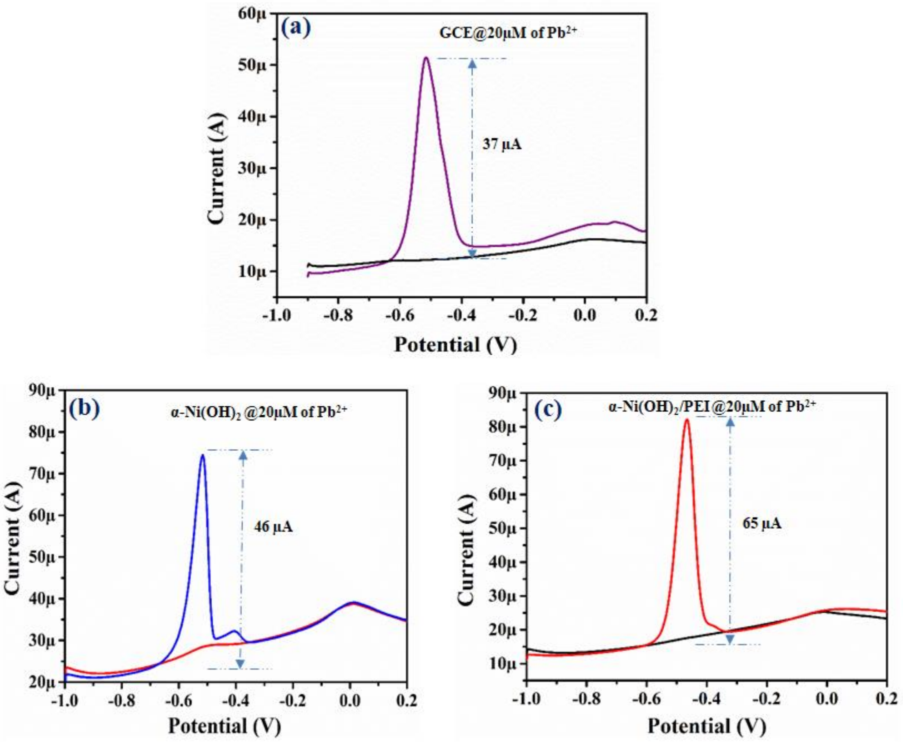

Figure 4.6 Stripping response of Pb^{2+}on the bare GCE, α-$Ni(OH)_2$/GCE, and α-$Ni(OH)_2$/PEI/GCE in 0.1M buffer solution of pH 5.

The electrochemical stripping response towards Pb^{2+} ions on the surface of α-$Ni(OH)_2$/PEI/GCE is given in Figure 4.6(c); the peak current further increases, which indicates the excellent electrochemical sensitivity of hybrid material towards the detection of Pb^{2+}. Therefore, α-$Ni(OH)_2$/PEI nanohybrid modified electrode was selected for further studies. This high performance can be ascribed to the synergistic effect of α-$Ni(OH)_2$ layered structure and chelating ability of PEI with metal ions.

4.5 Selectivity Studies

The selectivity and interference studies of α-$Ni(OH)_2$/PEI/GCE were performed by testing the anodic stripping voltammetry behavior in the buffer solution containing four different heavy metal ions Pb^{2+}, Cu^{2+}, Hg^{2+}, and Cd^{2+}. **Figure 4.7** displays the sensitivity towards heavy metal ions (Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}) on the α-$Ni(OH)_2$/PEI modified electrode.

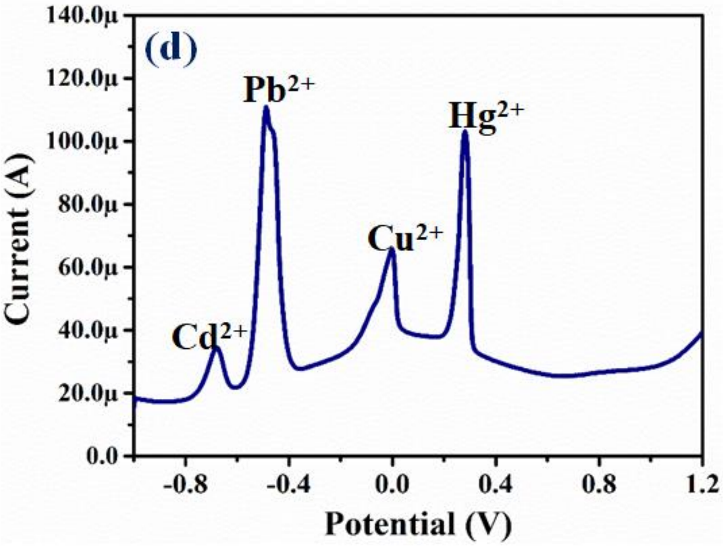

Figure 4.7 Selectivity studies towards heavy metal ions on α-$Ni(OH)_2$/PEI modified electrode

The result showed that the sensitivity of Pb^{2+} on α-$Ni(OH)_2$/PEI/GCE is much higher than the sensitivities of Cd^{2+} and Cu^{2+}. In addition, the stripping peak current of Hg^{2+} on the hybrid material modified electrode is almost comparable with Pb^{2+}. The selectivity studies towards different heavy metal ions clearly demonstrate that the as-synthesized α-$Ni(OH)_2$/PEI nanohybrid is highly sensitive for the Pb^{2+}

and Hg^{2+} as compared to Cu^{2+} and Cd^{2+} ions. Therefore, in principle, the same material can also be extended to detect Hg(II) without any hindrance in the presence of other metal ions.

4.6 Electrochemical Detection of Pb^{2+} through SWASV

Under the optimized conditions, α-$Ni(OH)_2$/PEI modified electrode was used to carry out the electrochemical detection of Pb^{2+} through SWASV in a wide range of concentrations from 0 µM to 20 µM. The electrochemical response of Pb^{2+} on the α-$Ni(OH)_2$/PEI/GCE for varying concentration has been shown in Figure 4.8.

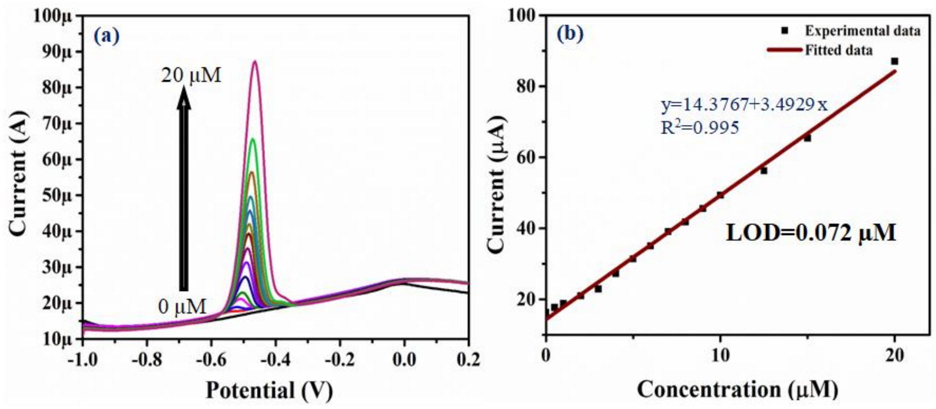

Figure 4.8(a) SWASV curves of α-$Ni(OH)_2$/PEI nanohybrid for the detection of Pb^{2+} (b) corresponding calibration plot.

The stripping peak potential for the electrochemical detection of Pb^{2+} appeared at about -0.55 V. As shown in Figure 4.8(a), the peak currents corresponding to Pb^{2+} linearly increases against the concentrations.

The calibration curve was plotted by linear fitting of peak current values in order to determine the relationship between the concentration and stripping current of heavy metal ions, as shown in Figure 4.8(b).

The linear equation can be described as:

$$I = 14.376 + 3.4929\ C,$$

Where I is the peak current value, and C is the concentration of Pb^{2+} ion. The calculated correlation coefficient $R^2 = 0.995$.

The limit of detection can be calculated by the following formula:

$$LOD = 3\sigma/S\ ,$$

Where σ is the standard deviation and S is the slope of the linear curve.

The limit of detection and sensitivity were calculated to be 0.072 μM and 17.79 $\mu A\ \mu M^{-1}\ cm^{-2}$, respectively. The lower values of the limit of detection and good sensitivity indicate the excellent electrochemical performance of α-$Ni(OH)_2$/PEI nanocomposite, which is mainly due to the functionalization of PEI on α-$Ni(OH)_2$. Besides offering numerous adsorption sites, the modification of α-$Ni(OH)_2$ nanosheets with PEI molecules also gives roughness to the electrode surface and, thus, increases the active area of the electrode surface. This eventually leads to capture Pb^{2+} even at low concentrations of Pb^{2+} effectively.

4.7 Repeatability Studies of Hybrid Material Modified Electrode

The quality of sensor materials can be measured using a repeatability test by doing the same stripping experiments for a number of times.

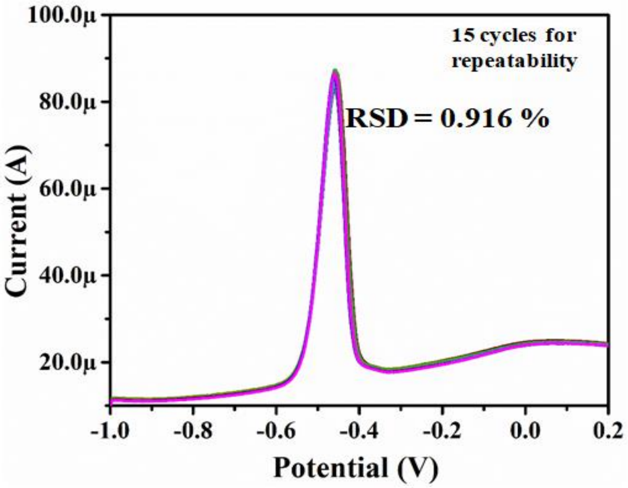

Figure 4.9 Repeatability studies of α-Ni(OH)$_2$/PEI nanohybrid for the detection of Pb^{2+} ion.

To evaluate the repeatability of as-prepared hybrid material, a series of repetitive SWASV experiment was carried out for 15 cycles under the optimized condition. The corresponding stripping current from each cycle is shown in Figure 4.9. The stripping potential in the SWASV was observed at -0.55 V in all the subsequent cycles, and distinct alternate in the peak current has not appeared. The relative standard deviation (RSD) was calculated to be 0.916%. Such high repeatability indicates that the developed α-Ni(OH)$_2$/PEI hybrid modified electrode holds a great advantage in future practical applications.

Chapter 5

Conclusion and Future Scope

5.1 Conclusion

In conclusion, a novel inorganic-organic hybrid material was successfully prepared by immobilizing polyethyleneimine on the exfoliated α-Ni(OH)$_2$ nanosheets through exfoliation reassembling synthetic strategy. The hybrid material was further utilized for the electrochemical heavy metal ion sensing. A well-defined layered structure of α-Ni(OH)$_2$ exhibits exceptional electrochemical activity owing to its tunable composition and flexible ion-exchangeability. The three-dimensional hierarchical flower-like structure of α-Ni(OH)$_2$ provides excellent channels for the adsorption of heavy metals due to the existence of a large number of mesopores. The development of inorganic-organic hybrid materials by the exfoliation reassembling technique opens up a new strategy in the field of electrochemical sensing. The modification of α-Ni(OH)$_2$ nanosheets with polyethyleneimine improves the electrochemical sensing performance because the lone pairs of electrons offered by the nitrogen atom of amine groups can be attributed to strong affinity towards metallic cation.

The results showed that PEI functionalized α-Ni(OH)$_2$ nanocomposite has achieved remarkable electrochemical performance. The electrochemical studies reveal that α-Ni(OH)$_2$/PEI hybrid exhibits enhanced electrochemical characteristics, including efficient charge-transfer capabilities, the high value of stripping current, high specific surface area as well as a large number of electrochemically active sites exposed to heavy metals as compared to single-component counterparts. α-$Ni(OH)_2$/PEI modified electrode has superior electrochemical sensing performance towards detection of trace Pb^{2+} with excellent stability, high repeatability, good selectivity, broad linear range, and low detection limit. Moreover, α-$Ni(OH)_2$/PEI modified electrode also offers high sensitivity and strong stipping current towards the electrochemical sensing of Hg^{2+}. Under optimized conditions, stripping current intensity increased linearly with increasing concentration of Pb^{2+} within a wide range, which concludes that α-$Ni(OH)_2$/PEI nanomaterial could be explicitly utilized for the accurate and selective detection of heavy metal ions.

The extraordinary analytical property of the developed sensing system has been attributed to the integrated effects of the associated components, α-$Ni(OH)_2$ and PEI. Both together offer a three-dimension hierarchical layered architecture, high specific surface area, good electrical conductivity, a large number of mesoporous channels, and strong affinity towards heavy metal ions. All these findings demonstrate a great potential of α-$Ni(OH)_2$/PEI-based electrochemical sensor for a highly sensitive and reliable determination of heavy metal ions.

5.2 Future Scope

This project work has successfully addressed the development of inorganic-organic hybrid material for the accurate detection and quantification of heavy metal species using electrochemical techniques. Many of the researchers found different pathways to improve various parameters involved in heavy metal ion sensing such as sensitivity, selectivity, stability, reproducibility, and limit of detection. During the course of this work, many concepts have immerged which have significant research potential. The developed hybrid material can be explored in the following future practical application:

1. **Biosensors:** The detection and quantification of biomolecules have great significance in many fields such as disease diagnostics, food safety inspection, and medicinal application. The integration of α-Ni(OH)/PEI nanocomposite in the development of biosensor is a novel approach.

2. **Electrochemical Reduction of CO_2:** The large scale anthropogenic greenhouse gas emission in the atmosphere is one of the major concerns over global climate change. The effective and selective conversion of CO_2 into high-value hydrocarbon chemical fuels has received considerable attention to mitigate the global climate change and energy shortage simultaneously. Carbon dioxide can be converted into value-added chemicals that include formaldehyde (HCHO), methanol (CH_3OH), formic acid (HCOOH), carbon monoxide (CO), and ethylene (C_2H_4) using various processes such as electrochemical reduction, photo-catalytic, thermo-catalytic, photosynthetic and biochemical processes. α-$Ni(OH)_2$ and polyethyleneimine nanohybrid (α-$Ni(OH)_2$/PEI) obtained by exfoliation reassembling technique can be efficiently and effectively used as a promising electrocatalyst material for the reduction of CO_2. The hierarchical structure and presence of amine in the hybrid material are expected to support the adsorption of CO_2 on the electrode material, which is the main prerequisite of CO_2 reduction.

3. **Real-time monitoring of heavy metals:** Highly toxic heavy metal ions enter the human body through drinking water and food chain. The traditional methods of heavy metal ion

detection are very complex and time-consuming because of manual sampling and laboratory analysis. The development of inorganic-organic hybrid material for the real-time monitoring of heavy metal ions is of great significance.

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