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Nickel sulfide-based composite as electrodes in electrochemical sensors: A review

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ABSTRACT

Nickel sulfide (NiS) is an extremely a transition metal sulfide with great potential use as a sensor material because of its exceptional conductivity and stability. Herein, we present first, the all of synthesis of NiS into sensor and biosensor. Electrochemical sensor, Due to the fact that disposal to electrolyte during electrochemical impact can rapidly deform NiS, lowering its electroactivity and measurement repeatability, a method for effectively integrating NiS into sensors is crucial. Then, the main focus of this review is the recent advancements in sensor systems that utilize NiS and its composites. The article discusses the correlation between sensing performance and electrode construction strategies, and identifies shortcomings and limitations in the current applications of these sensors. Based on this analysis, the authors suggest potential future directions and areas for further research in the development of NiS-based sensors. This study focused on developments in NiS-based sensor systems and their composites throughout the past articles. The article investigates the correlation between the way electrodes are made and the effectiveness of the sensors they produce. On this basis, we discuss the scope for future of NiS-based sensors and offer additional directions.

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1. Introduction

Electrochemical sensors are devices that use electrochemical reactions to detect and quantify the concentration of target analytes in a sample solution [1]. These sensors find broad usage in numerous fields, including biomedical, environmental, and manufacturing monitoring, as well as food safety and clinical diagnostics. Several methods have been used to fabricate electrochemical sensors, including photolithog-

raphy, ink-jet printing, and screen-printing. Among these techniques, screen-printing has gained popularity since the 1990s due to its ability to produce low-cost, highly reproducible, and reliable sensors on a large scale, making use of the technology was derived from the microelectronics sector [2, 3]. In recent decades, there has been a growing inclination towards making chemical and biological sensors smaller and incorporating them into compact sample analysis systems and pre-processing [4]. These devices have numerous benefits such as the capability to examine quicker analysis speed ,small amounts of samples, appropriateness for

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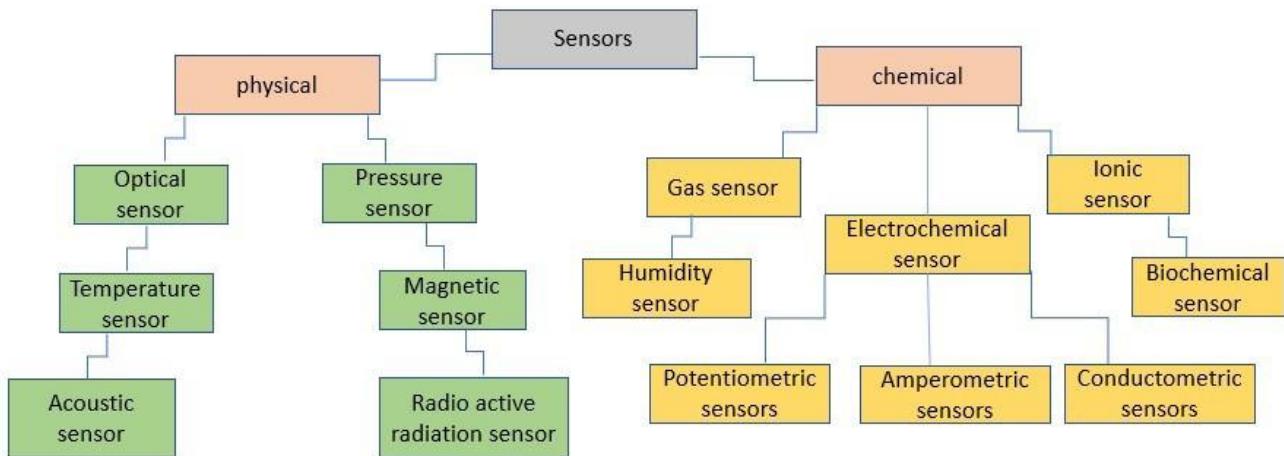


Fig. 1. Classification of sensors

mechanized processes, and enhanced consistency and dependability [5]. Lately, a considerable amount of research has been directed towards creating electrochemical sensors in a compact form factor suitable for measuring extracellular fluid, conducting clinical diagnoses, and performing micro total analysis using microscale or submicroscale devices [6, 7]. The methods used for electrochemical detection are rapid, affordable, and straightforward to carry out, allowing for accurate quantification of a diverse array of compounds present in a wide spectrum of sample [8]. At the core of every electrochemical sensor is a working electrode, which generates an electrical signal through an electrochemical process and acts as a transduction element. In more advanced biosensors, the working electrode may be coated with a sensing and biorecognition layer. The progress made in the advancement of electrochemical sensors is discussed in the review article [9].

Recently, electrochemical sensors have been created using nanomaterials consisting of different metal oxides, metal sulfides, and metal hydroxides due to their electrocatalytic features [10]. Electrodes that are enhanced with nanocomposites offer attractive electrochemical and physicochemical features, including chemical durability, excellent mechanical stability/surface area of large, biocompatibility and fast electron transfer kinetics. Besides metal oxides, metal chalcogenides (like metal sulfides) have become increasingly important in non-enzymatic electrochemical sensors due to their exceptional physical and chemical characteristics, including low cost, easy accessibility, and high catalytic activity [11, 12].

Metal sulfide nanostructures have garnered significant attention in research. Because of their possible uses in a range of areas, such as energy storage and conversion devices, light-emitting diodes, sensors, photocatalytic and electrocatalytic reactions, memory devices, and thermoelectric devices, they are considered to have significant potential. Numerous studies have extensively investigated these nanostructures. [13-15].

NiS, a compound known for its high electronic conductivity, affordability, and ease of production, it has found widespread applications in a range of fields. Examples of the mentioned items include photocatalysts, electrocatalysts [16], lithium-ion batteries [17], supercapacitors [18], and dye-sensitized solar cells. Researchers have synthesized various NiS compounds with diverse morphologies, including including, nanosheets, nanoflake arrays, nanorods, core-shell structures, hollow spheres, nanoframes, and urchin-like micro/nano-structures, that have been successfully produced and studied in previous research [19-22]. However, the creation of hierarchical flower-shaped NiS has not been widely achieved. It is worth mentioning that NiS has a distinct feature in which it tends to create intricate coordination. This means that the atoms

in the material have a tendency to arrange themselves in a complicated and well-organized manner [23, 24].

The donation of electrons from sulphide to nickel metal atoms leads to an increase in electron density on nickel, facilitating the interaction and formation of a complex with suitable moieties. Nevertheless, electrochemical reactions cause instability in pristine NiS due to variations in electronic and volume conductivity [25]. The researchers used a hybrid material called NiS/S-g-C₃N₄, which contained nickel sulfide and sulfur-doped graphitic carbon nitride, as an interface for detecting glucose without using enzymes in an alkaline solution. The modified electrode made of NiS/S-g-C₃N₄ was able to detect glucose at an applied potential of 0.55 V vs. Ag/AgCl, with a low detection limit of 1.5 μ M (S/N = 3), high sensitivity of 80 μ A $mM^{-1} cm^{-2}$, and fast response time of 5 seconds. The sensing process was not affected by various inorganic ions and organic substances. This nanohybrid material could be applied to real sample analysis and has potential for various applications in electrochemical glucose sensing [26].

Reduced graphene oxide (rGO) is being used as a supportive material to effectively stabilize NiS the redox reactions of in order to resolve the problem of instability. The HER activity of catalysts Blending a conductive carbon nanomaterial with a compound of Ni-S. has not been systematically studied in research on nickel sulfide-based electrodes [27]. To address this gap, a nanocomposite of Ni₃S₂ and MWCNTs (Ni₃S₂/MWCNT-NC) was The glucose-assisted hydrothermal method was employed to synthesize it, and its kinetics and HER activity were evaluated. The study also investigated the function of MWCNTs in the catalyst and the influence of the morphology of the catalyst on HER activity to understand the origin of Ni₃S₂/MWCNT-NC's HER activity. Results demonstrated that Ni₃S₂/MWCNT-NC outperformed pure Ni₃S₂ electrodes due to its relatively small HER activation energy (E_a). Moreover, Ni₃S₂/MWCNT-NC exhibited reasonable stability during long-term operation. These findings suggest that the combination of a compound of Ni-S combined with a carbon nanomaterial that conducts electricity, can enhance catalyst performance and provide insights into the performance of the hydrogen evolution reaction (HER) of Ni₃S₂/MWCNT-NC [28].

This article intends to present a beneficial analysis of the latest research undertakings that concentrate on producing and utilizing nanostructures made of nickel sulphide. We discuss application and synthesis NiS nanostructures obtained in sensors, this comprises of various nanostructures such as nanobelts, nanotubes, nanowires, and a few distinctive nanostructures. Next, some important synthesis composite NiS with other materials are presented that it is application several sensor which include gas sensor, electrochemical sensor, biosensor, etc. The review will wrap up by providing some viewpoints and predictions about

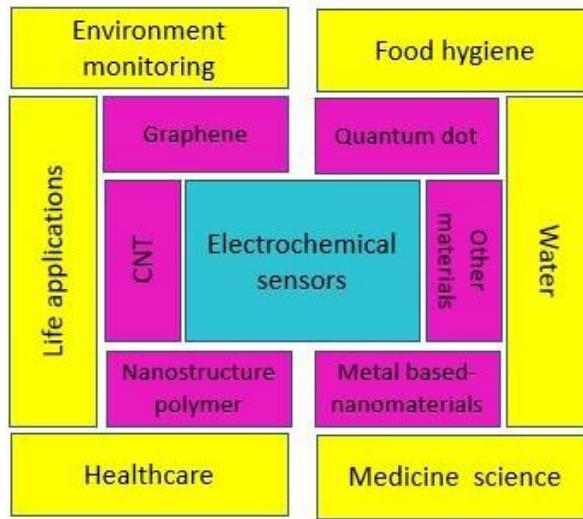


Fig. 2. Electrochemical sensors and applications.

the future advancements in the research areas related to NiS composite nanostructures.

2. Sensors

The purpose of sensors is to improve the capacity of our surroundings to detect and communicate information. They aim to make human life easier and more convenient in almost every field, including Establishing a particular ambiance or atmosphere, activating water heaters, Guaranteeing security, monitoring equipment, and etc. Sensors provide clearer visibility into processes and workflows, examine work patterns of employees and identify environmental factors across broader facilities. Through monitoring, regulation, and improving operational efficiency, sensors have the potential to enhance business management [29]. As per the Oxford English Dictionary, a sensor is an instrument that detects or gauges a specific state or characteristic, and records, indicates, or reacts to the data it receives. Therefore, sensors are accountable for transforming a stimulus into a measured signal, which may arise from various sources such as chemical, acoustic, electromagnetic, thermal, or mechanical. The measured signal is typically electrical, but other forms of signals like optical, hydraulic, or pneumatic signals may also be employed [30].

Sensors play a crucial role in the functionality of engineering devices, utilizing a wide variety of physical principles for function. With the vast selection of sensors available in the market, choosing an appropriate sensor for a new application can be an intimidating work for Design Engineers.ign Engineer [31].A sensor is typically described as a tool that can detect and react to a stimulus or signal. This description is quite all-encompassing, as it applies to a wide range of objects, from the human eye to the trigger mechanism of a gun[32].

A chemical sensor can be defined as a compact instrument that, through a chemical interaction or process between the sensor device and the gas under analysis, converts quantitative or qualitative chemical or biochemical information into a signal that can be analyzed practically [33].In recent decades, Various varieties of gas sensors have been developed using different sensing substances and conversion techniques, to create integrated multi-sensors or “electronic noses.” These electronic noses are the most advanced tools for monitoring globally.. Some important gas-sensing materials include metal oxide semiconductors, conducting and composite polymers, and other novel materials. These sensors can be combined with various transduction devices such as metal-oxide-semiconductor field-effect transistor, optical transducers, quartz crystal microbalance, surface acoustic wave, and chemo-resistive

[34]. Electrochemical sensors are a type of chemical sensor that uses electrochemical reactions to detect and quantify a target analyte. These sensors work by converting a chemical reaction into an electrical signal, which can be measured and analyzed. Electrochemical sensors are commonly used for detecting gases, such as carbon monoxide, oxygen, and hydrogen sulfide, but they can also be used for other applications, such as glucose monitoring for diabetes management. Examples of electrochemical sensors include potentiometric sensors, amperometric sensors, and conductometric sensors. Electrochemical sensors are a type of chemical sensor that measure the concentration of a specific chemical species in a sample by detecting changes in electrical properties. These sensors typically consist of an electrode and an electrolyte, and operate by converting a chemical reaction into an electrical signal.

2.1. Classification of sensors

Sensors can be categorized based on their principles of conversion (i.e., the physical or chemical effects upon which they rely), their intended use, the type of output signal they produce, the materials used, and the manufacturing technology employed. The categorization of sensors based on their method of operation is illustrated in Figure 1. They can be separated into two groups: chemical and physical sensors. Sensors that rely on physical phenomena, including magnetoelectricity, magnetostriction, photoelectricity, thermoelectricity, ionization, piezoelectricity, and others, are used to transform even the smallest variations in the measured quantity into an electrical signal. In contrast, chemical sensors translate minute modifications in the measured quantity into an electric signal via chemical adsorption, electrochemical reactions, and other chemical mechanisms [35].

Electrochemical sensors identify distinct analytes by means of electrochemical reactions and can be classified into various types based on the electroanalytical technique employed .The four main types of electrochemical sensors are conductometric, potentiometric, voltammetric, and amperometric. Amperometric sensors apply a constant potential to a sensing electrode, also known as a working electrode, causing an electrochemical reaction. The resulting current response is then measured over a period of time.

Voltammetric sensors utilize a variety of potentials applied to the working electrode concerning a reference electrode. The resulting currents are then measured for each potential. In contrast, potentiometric sensors generally determine the voltage variation between a working electrode and a reference electrode in the absence of any electric current passing through the cell. Conductometric sensors, frequently utilized for assessing the level of ionic analytes, gauge the electrochemical

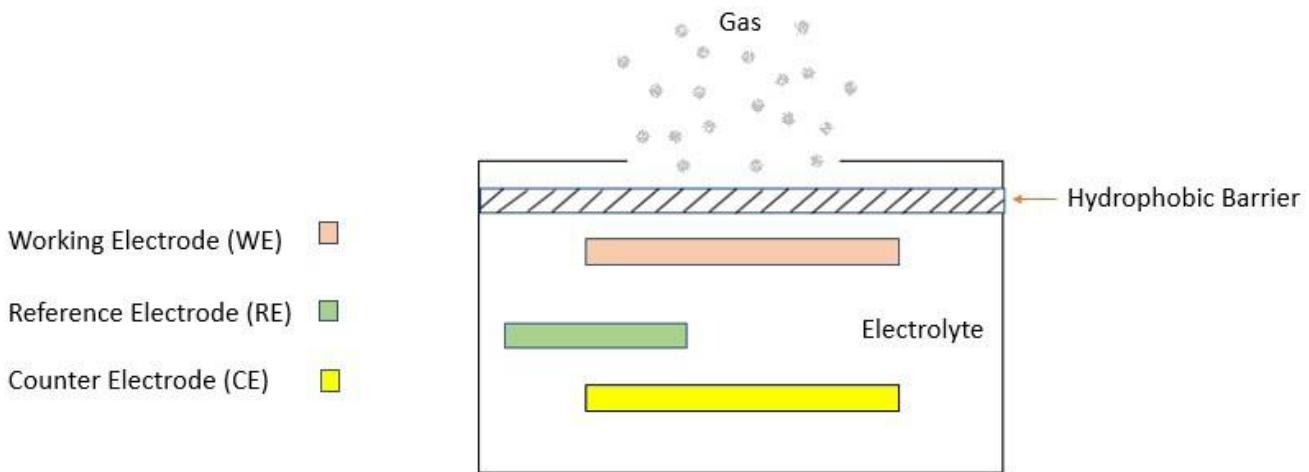


Fig. 3. Design of electrochemical sensor.

cell conductance [36, 37]. In some cases, the production of a signal can result from a sequence or chain of reactions. Electrochemical sensors have found widespread application in various domains over the past few decades, such as environmental monitoring, pathogen detection, healthcare, automotive industry, food industry, engineering, and various commercial applications[38] . There are several types of electrochemical sensors, including:

- Potentiometric sensors: These sensors measure the potential difference between an indicator electrode and a reference electrode, and are commonly used to measure pH and ion concentration.
- Amperometric sensors: These sensors measure the current produced by an electrochemical reaction, and are commonly used to measure gases such as oxygen and carbon dioxide.
- Conductometric sensors: These sensors measure changes in electrical conductivity that occur as a result of a chemical reaction, and are commonly used to detect gases such as ammonia and chlorine.
- Electrochemical sensors are widely used in a variety of applications, including environmental monitoring, medical diagnostics, and industrial process control.

2.2. Applications electrochemical sensors

Electrochemical (bio) sensors exhibit remarkable analytical advantages over conventional methods. Because of their distinct characteristics, such as being easily transportable, capable of being made smaller in size, simplicity, self-containment, affordability, exceptional sensitivity, and impressive selectivity [39, 40]. Furthermore, these powerful analytical tools can be efficiently controlled through sustainable methods that involve simple preparations of samples and the application of reagents. There is a widespread recognition that the development of electrochemical sensing platforms that can detect target molecules using various analytical principles depends greatly on the quality of electrode materials [41]. The employment of different bio-ingredients in various biological analyses is a distinct attribute of electrochemical technology. Maintaining the biological activity and orientation of biomolecules during immobilization is critical because inadequate fixation can lead to decreased specificity, loss of activity, and poor biocompatibility. The latest trend in the immobilization of various biomolecules involves the use of functionalized nanomaterials. This is because they increase the electrode's surface area, which leads to more stable immobilized biomolecules and improved electrochemical analysis performance [3]. Several published reviews [42, 43] in the field of electrochemical biosensors

have provided an up-to-date overview of the literature. The remarkable specificity of biological recognition events has resulted in the creation of electrochemical biosensors with exceptionally high selectivity. Among these biosensors, enzyme electrodes that rely on either potentiometric or amperometric methods to track variations resulting from biocatalytic processes have a long-standing tradition. In situ electrochemical monitoring of contaminants can achieve enhanced specificity by incorporating these devices with remotely deployed probes. However, while adapting enzyme electrodes for in situ operation, it is crucial to account for the effects of field conditions, including salinity, pH, and temperature, on biocatalytic activity [44]. Research on metal sulfides has primarily focused on their use in electrochemical usages. For instance, copper sulfide has been utilized in nonenzymatic glucose sensors [45] while iron sulfide has been studied for its ability to detect hydrogen peroxide. Additionally, nickel sulfide and cobalt sulfide have been investigated for their potential in dye-sensitized solar cells [46], and molybdenum sulfide has been examined as a catalyst for hydrogen evolution. At room temperature, nickel sulfide, also referred to as Ni_3S_2 , is a metallic conductor that exhibits a low resistivity of $1.8 \times 10^{-5} \Omega$. Ni_3S_2 occurs in different shapes and structures at the nanoscale and has been researched for its potential use in supercapacitors, catalysts, and electrochemical sensors [47, 48]. Figure 2, show Electrochemical sensors and applications.

The potential applications of electrochemical technology in a range of industries have made it a leading subject of basic and applied research . Electrochemical processes are generally viewed as environmentally friendly and sustainable due to their use of electrons as “clean reagents” to initiate reactions. As a result, electrochemical technology has found extensive use in energy-related applications [49, 50], environmental monitoring [51] and biochemical sensing [52]. To this end, developing selective, sensitive, robust, and sandwich electrode devices for use in electrochemical sensors and biosensors is of critical importance. Electrochemical sensors have the potential to address various societal issues, including those related to the health of human beings and the environment [53]. The major issues faced by electrochemical sensors in detecting drug compounds are excessively high voltage and overvoltage, as well as weak signals. To address this problem, electrodes that have been altered with conductive catalysts are commonly utilized. Among the various catalysts employed in designing novel electrochemical sensors, nanomaterials are a crucial type [54].

2.3. Components of sensors

hydrophilic membranes called wetting filters separated these electrodes , which are designed to be hydrophilic so that they can facilitate

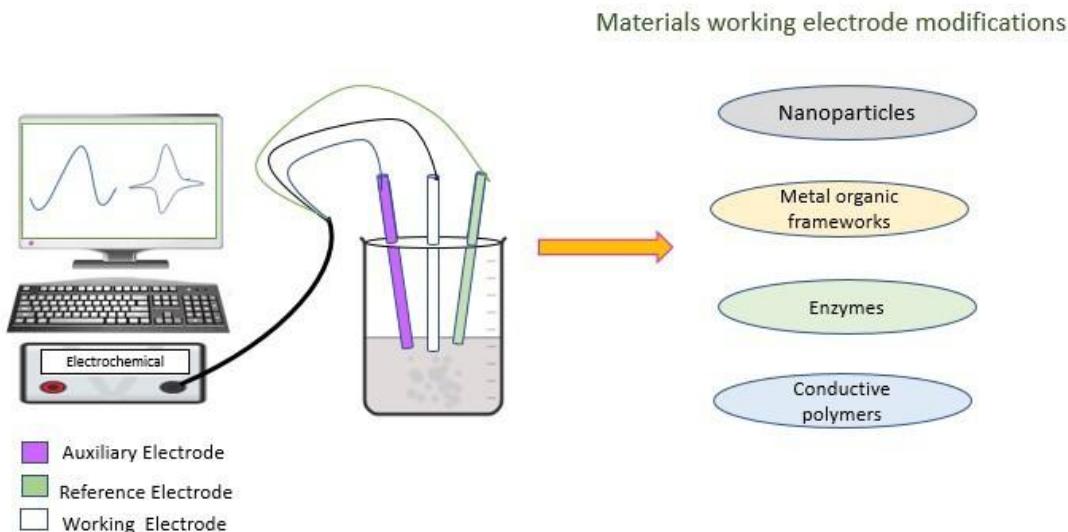


Fig. 4. Materials working electrode modifications in electrochemical sensors.

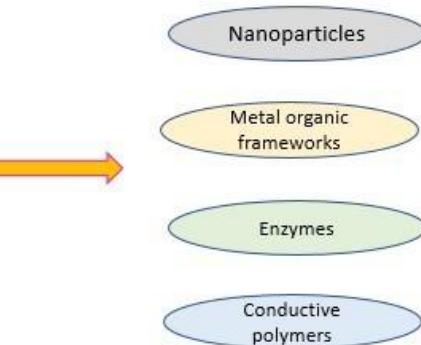
the transport of electrolyte among the adjacent electrodes. This enables ions to move in and out of the electrodes (see Figure 3) [55]. Electrochemical sensors are systems that incorporate an electrochemical transducer that may transform the response received from the interaction of the target analyte and the element that senses into a quantifiable signal that corresponds to the analyte concentration. The traditional electrochemical sensor, as shown in Fig. 1, is made up of three electrodes: the working electrode (WE), the counter electrode (CE), and the reference electrode (RE). WE is the site of the electrocatalytic reaction and is changed with various nanomaterials to improve the electrocatalytic reaction. CE completes the circuit, continuing the flow of electrons, while RE guarantees that the WE potential is applied correctly [56]. The equilibrium procedures enable the three-electrode configuration to preserve its sensor sensitivity and consistency for most of its lifespan. A gas permeable membrane is typically used to allow gases into the system. Its hydrophobic membrane effectively separates water from gases and controls the gas quantity that can access the working electrode's surface and simultaneously obstructs any liquid leakage from the sensor's interior [57].

The location where either reduction or oxidation takes place depends on the interaction of the gas species under observation with the system at the working electrode. To each reaction that occurs on the exterior of the working electrode's area, there will be a corresponding feedback from the counter electrode, which acts as a balancing pole. When the system is activated, the counter electrode works to equilibrium the potential change resulting from the response of the working electrode to the gases being detected. The primary measurement for an amperometric electrochemical sensor is the monitoring of the balancing current in a dynamic manner. To maintain the system, the potential on the reference electrode is necessary to secure the working electrode [58].

3. Electrodes Materials

Electrochemical sensors rely heavily on electrodes as they are essential in transforming chemical reactions into electrical signals. Typically, an electrochemical sensor is consisting of a pair of electrodes, namely a reference electrode and a working electrode. The working electrode serves the purpose of identifying the target analyte and generating a signal, whereas the reference electrode maintains a steady electric potential that permits the measurement of the potential of the working electrode. A variety of electrodes are employed in electrochemical sensors, including metal electrodes, carbon electrodes, and conductive polymer electrodes [49]. Metal electrodes, such as gold and platinum, are frequently

Materials working electrode modifications



used as working electrodes owing to their high stability and conductivity. Carbon electrodes, like glassy carbon and carbon nanotubes [59], are also widely used due to their large surface area and low background current [60]. The use of conductive polymer electrodes, such as polypyrrole and polyaniline, is on the rise because of their potential to identify particular analytes selectively [61]. Electrochemical sensors may incorporate a counter electrode along with the working and reference electrodes, to ensure the smooth flow of electrons through the electrical circuit. A non-reactive metal such as platinum or stainless steel is often utilized for the counter electrode. Other types of electrodes used in electrochemical sensors include pseudo-reference electrodes, working electrodes, and reference electrodes [49].

Metal-based materials, including metal nanoparticles, oxides, and hydroxides [62-65], are often employed as electrodemodifiers due to their excellent electrocatalytic properties [66]. These materials can effectively reduce interference and lower the overpotential needed for analyte detection. While noble metals such as Pt, Au, and Ag [62] are well-known for their electrocatalytic potential, cheaper metals like Cu, Co, and Ni [65] have demonstrated similarly promising results. Of these, nickel has garnered significant attention as a surface modifier for electrodes, particularly in the form of oxides or hydroxides, owing to its superior stability in air or solution when compared to pure metallic particles [67].

The choice of the suitable electrode type relies on factors such as the properties of the analyte, the sensitivity required, and the cost constraints. Below are the types of electrodes:

Platinum (Pt) electrode: Pt is a commonly used electrode material due to its high electrical conductivity, stability, and low reactivity with most chemicals. It is commonly used in electrochemical sensors for gas detection, oxygen measurement, and pH sensing [68].

Gold (Au) electrode: Au is also a popular electrode material due to its high conductivity, biocompatibility, and stability. It is commonly used in biosensors for the detection of biological molecules, like to proteins, DNA, and viruses [69].

Carbon-based electrodes: Carbon-based materials [70], such as glassy carbon [71], graphen [71, 72], and carbon nanotubes [73, 74], are commonly used in electrochemical sensors because of their extensive surface area, low cost, and ease of modification. They are used in a variety of electrochemical sensing applications, including glucose sensing, DNA sequencing, and detection of environmental pollutants.

Metal oxide electrodes: Metal oxide materials, such as tin oxide, zinc oxide, and titanium oxide, are used in gas sensors for the recognition of gases, including carbon monoxide, methane, and hydrogen, through detection methods. They are also used in electrochemical sensors for the

detection of environmental pollutants [75, 76].

Nickel sulfide (NiS) electrode: NiS is a versatile electrode material that has been used in electrochemical sensors for the detection of various analytes, such as glucose, hydrogen peroxide, and dopamine. Biosensors for detecting specific biological molecules can be developed by modifying NiS electrodes with various biomolecules [77, 78].

Selecting the right electrode materials is extremely important because the harmful nature of Hg can cause risks to both human health and the environment. Over the past few decades, a range of electrochemical sensors for heavy metal detection have been developed based bismuth electrodes [79]. The deposition of these materials on the electrode is a well-established fact, and they tend to easily amalgamate with heavy metal ions at negative potentials. The use of anodic stripping voltammetry (ASV) produces electric currents that correspond to a particular heavy metal ion when it undergoes oxidation at a specific anodic potential. One of the most sensitive, affordable, easy-to-use, and safe techniques for analyzing heavy metals in water is Square wave anodic stripping voltammetry (SWASV), which is widely recognized and commonly used [80].

Carbon plays an essential role in electroanalysis and electrocatalysis for sensing purposes is possibly the most extensively utilized material. Among carbon-based nanomaterials, graphene and CNTs are highly sought-after for electrode design in the bioanalytical field because they offer a combination of desirable properties, including good electrical conductivity, acceptable biocompatibility, high surface area, and electrochemical or chemical durability [81]. Owing to their small size and high conductivity, carbon nanotubes (CNTs) are appropriate for use as single nanoscale electrodes. Numerous studies have demonstrated that these individual nanoelectrodes possess electric properties that can effectively enhance electron-transfer reactions [82]. However, integrating CNTs into biosensing electrodes has proven to be challenging. They are typically used as intermediaries linking enzymes to electrodes composed of glassy carbon, Au, Pt. A binder is utilized to produce a CNT paste that can be used to obtain arbitrary distributions of carbon nanotubes on electrodes made of glassy carbon, Au, Pt.

The two-dimensional plane of graphene grants it a vast specific surface area, which makes it ideal for immobilizing substantial quantities of various substances, including metals, nanoparticles, and biomolecules [83]. Due to the fact that every single atom in graphene is considered a surface atom, the interaction between molecules and the transportation of electrons through graphene can be highly sensitive to any molecules that are absorbed. Due to its properties, graphene can aid in the transfer of electrons during its use as an electrode. This makes it a cost-effective replacement for carbon nanotubes [84]. Unlike the curled configuration of graphene, carbon nanotubes are a planar sheet with an uncovered structure. As a result, both sides of the graphene sheet can be used for catalysis support [85]. As a result, it is regarded as a more favorable catalyst carrier. Until now, graphene sheets have been utilized in the production of electrochemical sensors for hydrogen peroxide, ascorbic acid, hydrazine, and biosensors. Conversely, materials based on copper oxide and copper have been extensively studied for the electro-oxidation of glucose over an extended period [86, 87].

Thin films of metal chalcogenides are attractive materials for the production of various devices including photodiode arrays covering a wide area, coatings that selectively absorb solar energy, cells that convert sunlight into electricity, sensors, and photoconductors [88]. Among the VIII-VI group of compound semiconductors, Nickel sulphide is a compound of a transition metal that displays interesting characteristics. By doping or in response to temperature and pressure changes, nickel sulphide displays a metal-insulator transition. The compound demonstrates antiferromagnetic semiconductor properties in its low temperature phase, and paramagnetic properties in its high temperature phase.

Owing to these unique properties, nickel sulphide thin films are utilized

in several applications such as solar selective coatings. The authors, SURESH et al, opted for the chemical bath deposition (CBD) method due to its multiple benefits such as easy instrumental operation, low cost, large area production, and low elaboration temperature. The objective of their study is to synthesize NiS thin films produced through the use of the CBD technique. The micrographs of the NiS thin films demonstrated that they were homogenous, finely-grained, and thoroughly coated onto the substrate, with some particle overgrowth. These NiS thin films are applicable in a range of devices such as storage electrodes in photoelectrochemical storage devices, IR detectors, and solar selective coatings [89]. Figure 4, show Materials working electrode modifications in electrochemical sensors.

Luo et al. [90] have reported that in an alkaline solution, glucose shows a positive response at a nickel electrode. A $\text{Ni}^{2+}/\text{3}^+$ ion pair present on the Ni surface that has undergone oxidation was suggested as the possible mechanism for this response. Ni-NDC (Nickel nanoparticles distributed in erratic graphite-like carbon) were analyzed by T. You et al [91] to study their reaction to sugars.

According to their findings, They revealed that the sensitivity of Ni-NDC towards sugars is enhanced by at least one level, and it shows a relative standard deviation of 1.75% for 40 successive detections in comparison to bulk Ni. Prabhu and Baldwin, on the other hand, used amperometric detection of glucose at a constant potential in basic solution with CuO plated on glassy carbon [92]. The $\text{Cu}^{2+}/\text{3}^+$ redox pair mediated the electrocatalysis for glucose oxidation in the same way that the Ni-electrode did.

Among the accomplishments made possible by the use of nanomaterials in electrode modification are the following [93]:

- Improved surface kinetics
- Increased electrochemical processes due to increased electroactive surface area.
- Nanomaterials, also offer a robust foundation as well as highly active integration sites that enhance electrode selectivity.

4. Synthesis and properties of nanomaterials nickel sulfide

There are several types of nickel sulfide, including:

- Nickel monosulfide (NiS): a binary compound of nickel and sulfur, with the chemical formula NiS.
- Nickel disulfide (NiS₂): a binary compound of nickel and sulfur, with the chemical formula NiS₂.
- Nickel subsulfide (Ni₃S₂): a ternary compound of nickel and sulfur, with the chemical formula Ni₃S₂.
- β -Nickel sulfide (β -NiS): a transitional stage of nickel sulfide, which is the most commonly studied form of nickel sulfide in electrochemical sensors.

The properties and applications of these nickel sulfide compounds can vary depending on their structure and composition. For example, β -NiS has shown promise as a sensing material in electrochemical sensors because its the distinctive characteristics like excellent conductivity and good catalytic activity. Nickel sulfide is a potential nanomaterial that has various uses in the fields of energy conversion, catalysis, and electronics. The synthesis of NiS nanoparticles has been widely investigated using various methods such as chemical precipitation, hydrothermal synthesis, and solvothermal synthesis. These approaches provide a significant level of mastery in regulating the dimensions, structure, and crystal morphology of the nanoparticles obtained. A solvothermal technique was employed to produce NiS with a flower-like structure, which was found to exhibit remarkable catalytic performance towards the electrochemical oxidation of H₂O₂ on a carbon paste electrode under alkaline conditions. The resulting material displayed high

catalytic activity for MOR.

According to a study conducted by Jingchao Zhang et al [94], they found that the H_2O_2 sensor had remarkable consistency, a broad range of detection 0.5 μM to 1.37 mM, and strong electrocatalytic capabilities. Furthermore, the NiS with a flower-shaped hierarchical structure demonstrated excellent electrocatalytic activity in an alkaline medium for the methanol oxidation reaction (MOR) and displayed significant tolerance towards the catalyst-poisoning species produced during the reaction. The process of MOR was observed to occur by directly electro-oxidizing methanol on the surface layer of oxidized NiS. This was attributed to the redox reactions of Ni (II)/Ni (III).

As far as we know, this study represents the first documented instance of creating a distinctive hierarchical flower-shaped NiS material using a solvothermal technique for the purpose of detecting H_2O_2 through an electrochemical method. Furthermore, the material showed strong catalytic activity for the MOR in an alkaline setting when applied to a carbon paste electrode. The strong electrocatalytic capabilities displayed by the NiS nanostructures for the MOR in an alkaline environment implies potential new applications for them as effective electrocatalysts in DM-FCs. Wenqin Wu et al [95] reported in their study that they synthesized Ni7S6 particles using a one-pot hydrothermal method, with $\text{NiC}_{12}\cdot6\text{H}_2\text{O}$ and thiourea as the precursors. To elaborate, they first dissolved 454.46 mg $\text{NiC}_{12}\cdot6\text{H}_2\text{O}$ in 6 mL of distilled water, and so added 24 mL of EA and 114.18 mg of thiourea to the solution. The solution was stirred for approximately 25 minutes and introduced into an autoclave composed of stainless steel that is lined with Teflon and has a volume of 50 mL. It was subsequently heated at 180°C for a duration of 12 hours. Following this, the sulphide was collected and washed multiple times with ethanol and

deionized water, before being dried under vacuum. The structure and morphology of the synthesized Ni_7S_6 were then examined through SEM analysis, revealing that it had a flower-like appearance with multiple nanoplates featuring sharp tips that extended from the core. The particle size was estimated to be roughly 1 μm .

Ongoing research is dedicated to improving the performance of non-enzymatic glucose sensors using Ni_3S_2 as a material. The promising properties of Ni_3S_2 make it an attractive candidate for glucose monitoring applications. Recent research by Soochan Kim et al. involved the development of Ni_3S_2 with diverse morphologies on Ni foam through adjustments to solvent composition.

The structure and morphology of the resulting products can be significantly influenced by the polarity and coordination of the reaction medium, which in turn can have a notable impact on the reactivity and diffusion of the reactants. Nevertheless, no research has been reported yet on the confinement of the Ni_3S_2 structure's morphology with the help of a solvent. Several different structures of Ni_3S_2 were created on Ni foam by means of a hydrothermal technique in a environmentally friendly solution of water and ethanol, with the aim of filling this void [96]. By controlling the reaction medium, a hierarchical structure of Ni_3S_2 was produced, and its electrochemical properties were investigated with regards to its morphology. The prepared Ni_3S_2 electrode with a hierarchical structure was then employed to detect glucose, demonstrating excellent selectivity, sensitivity, and repeatability [97]. Ni_3S_2 nanosheet arrays were synthesized via a simple one-step hydrothermal process on Ni foam substrate, and directly utilized as an electrode for a high-performance supercapacitor and non-enzymatic glucose sensor. The resulting electrode demonstrated both high energy density and ex-

Table 1.

Nickel sulfide-based composite as electrodes in electrochemical sensors.

Composite based NiS	Method	Linear range (μM)	Limit of detection (μM)	Scan rate (mV/s)	Sensitivity	Potential (V)	Properties & application	Ref.
CLFW@Ni-NiS/MIV	solution of vitrimer by dip coating method	-	-	100	-	high values of 0.79	Variable, shape-memory, self-healing supercapacitors, catalysis and sensors	[102]
NiS/GO/MGCE	hydrothermal method	0.1–1.0 mM	3.79 μM	50	-	3.39 (5.4 μA) and 0.15 (2.7 μA)	A non-enzymatic urea sensor	[107]
b-NiS@rGO/AuNS/GCE	single-step hydrothermal	1 mM to 1 mM, 2 mM to 1 mM	682 nM, 1.3 mM and 6 nM	10–100	-	0.18, 0.15, and 0.33	Biosensors and energy storage devices	[108]
Au/N-GOQDs/NiS _x /BC/MIP/GCE	differential pulse voltammetry	DA (0.05–8 μM and 8–40 μM)	CPZ 0.005–2 μM	100	-	-	Electrochemical sensor	[109]
rGO/NiS/AuNCs	simple single-step hydro- thermal	34.4–269.2	0.09 $\mu\text{g}\cdot\text{L}^{-1}$	-	3.38 \times 10 ⁻⁸ A per $\mu\text{g}\text{L}^{-1}$	-0.5	Electrochemical sensing	[11]
NiS@NiO/TiO ₂	a simple hydrothermal method.	0.001 to 45 ng mL ⁻¹	1.67 \times 10 ⁻⁴ ng mL ⁻¹ (S/N = 3)	0.1	-	+0.6 to -0.2	Photoelectrochemical biosensor	[110]
ZnS-NiS	a simple ion-exchange reaction	-	(0.125 mm)	50	48.5 $\mu\text{A}\text{mm}^{-1}$	-0.60 to 1.00	Nonenzymatic Electrochemical Glucose Sensors	[111]
β -NiS/Ppy	hydrothermally	10 nM to 900 μM , 20 nM to 1 mM	1 nM and 5 nM	50	-	0.42 to 1.04	Biosensing applications	[112]
ZnS/NiS@ZnS	via a water-soluble route	0.1 to 300 $\mu\text{M}(\text{HQ}), 0.5$ to 400 $\mu\text{M}(\text{CC})$	24nM for HQ, 71nM for CC	10 to 300	8.0 * 10 ⁶ Acm^{-2} , -1.0 * 10 ⁴ Acm^{-2}	-59 mV pH ⁻¹	Electrochemical sensor	[113]

Table 1.

Continue

Composite based NiS	Method	Linear range (μM)	Limit of detection (μM)	Scan rate (mV/s)	Sensitivity	Potential (V)	Properties & application	Ref.
NiS/S-g-C ₃ N ₄ /GCE	Thermal	3–2000 μM	0.1 to 2.1 μM	1.5 μM (S/N = 3)	10 to 100	80 μA $\text{mM}^{-1} \text{cm}^{-2}$	0.55 vs. Ag/AgCl	Non-enzymatic glucose sensing
3D Ni ₃ S ₂ nanosheet/NF	facile one-step hydrothermal	0.005–3.0 μM to mM	0.005–3.0 μM to mM	1.2 μM	20	6,148 μA $\text{mM}^{-1} \text{cm}^{-2}$	-	Non-enzymatic sensor
Ni ₃ S ₂ /MWCNTs	using glucose-assisted hydrothermal	30 to 500 μM	30 to 500 μM	1 μM	1	μA $\text{mM}^{-1} \text{cm}^{-2}$	-	Highly sensitive and selective biosensor for glucose
NiS–rGO nanohybrid	facile one-step hydrothermal	0.005–1.7	0.005–1.7	10	50	-	-0.2 and 0.6	Sensor/glucose solution
PVP–NiS	Electrodeposition, thermal air oxidation	0.2–2.97	0.2–2.97	4.6 mM	20	82.73 mA mM^{-1}	0.5	Electrochemical sensing of glucose
MPL–NiS/rGO	hydrothermal electrodeposited	43 nM–0.26 μM	43 nM–0.26 μM	0.5 to 53 nM(BPA)	-	-	-1.0	Sensor for electrochemical measurements
f-CB/NiS	electrochemical method	0.125 to 268 μM	0.125 to 268 μM	0.02 μM	50	1223 μA $\text{mM}^{-1} \text{cm}^{-2}$	0.47	Non-Enzymatic Glucose Sensor
NiS/ITO	one-step electrodeposition method	0.32 μM	0.32 μM	5–45 μM	20	7430 μA $\text{mM}^{-1} \text{cm}^{-2}$	0.5	Non-enzymatic Glucose Sensor
α -NiS/GC	via a template-free method	0.125 μM –0.2 mM	0.125 μM –0.2 mM	0.08 μM	50	80 μA mM^{-1}	0.60	Non-enzymatic glucose sensors and water treatment, supercapacitors
NiS hollow spheres/GCE	hydrothermal	0.125 μM –2.0 mM	0.125 μM	0.125 μM	50	155 mA $\text{mM}^{-1} \text{cm}^{-2}$	0.60	Supercapacitors and Non-Enzymatic Glucose Sensors
Ni ₃ S ₂ /Nickel foam	hydrothermal method	0.5 μM –3 mM	0.5 μM –3 mM	0.82 μM	5 to 100	16,460 μA $\text{mM}^{-1} \text{cm}^{-2}$	0–0.8	Glucose sensing, other electrochemical applications
Ni ₃ S ₂ @Ni foam	chemical corrosion by sodium sulfide	1–300 μM	1–300 μM	0.045 μM	50	14674 μA $\text{mM}^{-1} \text{cm}^{-2}$	0.5	Hydrazine electrochemical sensor
Ni ₃ S ₂ /MWCNTs	one-pot hydrothermal				20	185.04 μA $\text{mM}^{-1} \text{cm}^{-2}$	0.415	Amperometric sensor for nitrite
CTAB/NiS/CS/GCE	solvothermal	0.01–200.0 μM	0.01–200.0 μM	3.35 and 2.94 nM	10 to 250	-	-0.2–1.3	Validate the Practical Application of the Present Sensor
Ni ₃ S ₂ -CNT	simple solution method	0.1 nM to 10.0 mM	0.1 nM to 10.0 mM	30.0 \pm 0.02 pM	-	632.9224 μA $\text{mM}^{-1} \text{cm}^{-2}$	0.0 to +1.5	Chemical sensor

cellent long-term stability. Furthermore, as a non-enzymatic sensor, the 3D Ni₃S₂ nanosheet array electrode exhibited exceptional electrocatalytic activity towards glucose oxidation, with a excellent sensitivity of 6148.0 mA $\text{mM}^{-1} \text{cm}^{-2}$. In addition, the Ni₃S₂ nanosheet array electrode exhibits extraordinary glucose electrocatalytic activity, including high sensitivity, excellent selectivity, a low detection limitation, and an immediate response. All of these remarkable performance metrics indicate that the Ni₃S₂ nanosheet array is a promising electrode material for glucose sensors that do not rely on enzyme [98].

Electrodeposition is another method for synthesizing nickel sulfide. In a study by Padmanathan et al., a thin film of NiS was successfully deposited via chronoamperometry onto ITO-coated glass substrates. Prior to electrodeposition, the ITO substrates were cleaned to remove surface impurities. This was done by using Ultrasonic treatment using ethanol as the solvent and then in water for a period of 10 minutes. To prepare a

solution for a NiS thin film sensor, 0.01m Ni(NO₃)₂·6H₂O and 0.1m thiourea were mixed in 100 mL of water that has been distilled twice. The NiS thin films were deposited on an ITO substrate by applying a fixed potential of 0.9 V for 500 s. The produced sensor demonstrated a low detection limit and high sensitivity, with values of 0.32 mm and 7.43 mA $\text{mM}^{-1} \text{cm}^{-2}$, respectively. Additionally, it had a response time of less than 8 seconds [78]. In a separate study conducted by Rekha Bhardwaj and colleagues [99], the process of creating mesoporous rhombohedral β -NiS involved using thiourea as the source of sulfur, and was done through a solvothermal method. By conducting a Rietveld refinement, it was verified that the formation of rhombohedral β -NiS occurred in a single phase. The optical, electro-catalytic, and morphological properties of the synthesized β -NiS nanoparticles were found to be influenced by the reaction temperature. The FESEM pictures showed that there were structures resembling cluster beans and 1-D nano-rods.

5. Composites of nickel sulfide

The composite of nickel sulfide (NiS) electrode is a commonly used material in electrochemical sensors. Electrochemical sensors are devices that measure the concentration of a specific substance in a solution by measuring the current produced by an electrochemical reaction. The composite of nickel sulfide electrode is a versatile material that can also be used in biosensors. Biosensors are instruments that employ biological substances like antibodies or enzymes for the purpose of detection, and measure the concentration of specific substances in a sample. These devices are widely used in healthcare, food safety, and environmental monitoring.

NiS-based electrodes have been used in various electrochemical sensors for the detection of different analytes such as glucose, hydrogen peroxide, and neurotransmitters. One of the main advantages of using NiS-based electrodes in electrochemical sensors is their high electrocatalytic activity, which enables the efficient conversion of analyte molecules into measurable electrical signals. The exceptional catalytic performance is credited to the distinctive configuration of NiS, which has abundant active sites and a vast surface area that helps in the transfer of electrons during reactions. Moreover, NiS-based electrodes possess excellent stability and durability, making them suitable for long-term sensing applications. They also have good biocompatibility, which makes them ideal for biosensing applications. Several methods have been reported for the fabrication of NiS-based electrodes, including chemical vapor deposition, electrodeposition, and hydrothermal synthesis. **Table 1** shows the types of nickel sulfide-based electrodes, along with their fabrication methods and applications. In the following, research about nickel sulfide composites has been discussed. Among methods, the hydrothermal method is a popular technique for synthesizing nickel sulfide composite electrodes due to its several advantages. The hydrothermal method allows for precise control over the size, shape, and composition of the synthesized nanoparticles. The reaction occurs in an aqueous solution under high pressure and temperature, which facilitates the formation of homogeneous and crystalline nanoparticles and this is a simple and cost-effective technique, which makes it suitable for large-scale production of nickel sulfide composite electrodes. The method does not require complex equipment and can be easily scaled up. Therefore, due to its precise control over nanoparticle size and shape, simplicity and cost-effectiveness, and excellent electrochemical properties, the hydrothermal method is a good method for the synthesis of nickel sulfide composite electrodes. NiS electrodes show significant promise for the advancement of electrochemical sensors due to their exceptional electrocatalytic activity, long-lasting stability, durability, and compatibility with biological systems. Further research is required to optimize the fabrication and functionalization of NiS-based electrodes for to detect a wide spectrum of analytes with high sensitivity and selectivity.

Electrode materials can be categorized into three types based on their composition: The original text refers to three types of materials inorganic polymer compound materials, metal compound materials, and non-metallic materials [100, 101]. The ability of an electrode material to store energy is influenced not only by its individual characteristics, but also by its microstructural properties. Among metal compound materials, The nanofibers made of NiS and shaped like flowers have a unique structure made of nano-sheets. This structure provides multiple pathways for the transfer of ions and electrons, which results in excellent rate performance. Additionally, these nanofibers have a high specific capacitance. Furthermore, the sensor assembled with the CLFW@Ni-NiS/V hybrid can detect even small amounts of deformation or external pressure by converting them into current signals. This sensitivity showcases the sensor's ability to detect subtle changes [102]. The exceptional properties

displayed by a hybrid that is intelligent and can perform multiple functions, such as self-healing capabilities, shape-memory, and good reshaping, make it a promising candidate for a vast array of uses, which may involve sensing, catalysis, and energy storage. These applications have been extensively studied and are of great interest to researchers [18-20]. The limited conductivity of NiS has hindered its further application. To address this issue, some researchers have combined NiS with materials that exhibit good conductivity to achieve enhanced electrochemical performance. Examples of such materials include carbon [103] and metal nanoparticles. Sunil Kumar Naik et al [104], reported on the use of graphene oxide / NiS to modify a glassy carbon electrode in order to improve the conductivity of NiS. This modified electrode was referred to as NiS/GO/MGCE. Both electrochemical and electrochemical impedance spectroscopy (EIS) modes were used to assess the detection abilities pertaining to the electrode that has been altered or adjusted in some way towards urea in water. The results suggest that the electrode modified with NiS/GO nanocomposite showed an exceptionally low level of detection and that the process of the electrode was found to be controlled by diffusion. The newly developed sensor was evaluated for its practicality, long-term stability, interference, and selectivity. Consequently, the MGCE /GO/ NiS showed impressive electrocatalytic properties when detecting urea, showcasing strong sensitivity, selectivity, and reproducibility. In research about nickel sulphide by R.M. Abdel Hameed et al [105], the process of electrospinning was employed in order to create carbon nanofibers that have nickel sulphide nanoparticles incorporated onto them. This was achieved by using a sol-gel mixture of DMF and PAN, and NiAc and NH₄S were added. The mixture was then subjected to an electrospinning process at 20 kV, afterwards, the material was subjected to calcination in an argon environment at a temperature of 900 degrees Celsius for a duration of 2 hours. The nanomaterial that was obtained showed exceptional catalytic efficiency in the electro-oxidation of urea under basic conditions, mainly due to the enhanced surface area of the metallic nanofibers and their effective dispersion. The NiS/CNFs nanocomposite exhibited higher oxidation current density values in KOH solution when the concentration of urea molecules was increased. Through an EIS examination, it was discovered that there was a better charge transfer mechanism occurring at the surface of the nanomaterial, suggesting its potential to be an efficient nanocatalyst for electrocatalytic reactions involving urea. Furthermore, The method utilized to produce the nanocomposite has the potential to be expanded for the synthesis of multiple bimetallic nanocomposites in various proportions, which can be utilized in sustainable energy system [106]. In recently study, NiS was utilized to selectively interact with analytes as it helps with electron distribution. However, neat NiS is unstable during the interaction, so stabilizing the compound is crucial. Thus, the researchers synthesized nickel sulfide/graphene oxide (NiS/GO) via the superficial hydrothermal method to stabilize the compound. They characterized the synthesized functionalized GO nanoparticles to fine-tune the size, surface area, and morphology for the specific application. The results showed that the NiS/GO nanocomposite modified electrode had a very low detection limit and that the electrode process was controlled by diffusion. Additionally, the developed NiS/GO/MGCE showed excellent electrocatalytic behavior towards urea sensing with good sensitivity, selectivity, and reproducibility in sensor.

6. Conclusion and future perspectives

Electrochemical sensors are essential tools used in various fields, such as environmental monitoring, medical diagnostics, and energy storage. The development of novel electrode materials with enhanced sensitivity, selectivity, and stability is crucial for the advancement of electrochemical sensing and energy storage technologies. Nickel sulfide (NiS)

is a promising material for use as electrodes in electrochemical sensors due to its excellent electrical conductivity, low cost, and high surface area. However, the sensitivity and selectivity of NiS-based sensors can be improved by incorporating other materials into the NiS structure to form composite electrodes. This article discussed the use of NiS-based composites as electrodes in electrochemical sensors, highlighting their potential applications and benefits. The use of NiS-based composites as electrodes in electrochemical sensors has shown significant promise for various applications. For example, NiS-carbon nanotube (CNT) composite electrodes have been shown to have high sensitivity towards glucose, making them suitable for glucose monitoring applications. The high sensitivity of this composite electrode can be attributed to the synergistic effect between NiS and CNT, which enhances the interaction between the electrode and glucose molecules. NiS-reduced graphene oxide (rGO) composite electrodes have also been explored for use in electrochemical sensing applications, such as the detection of dopamine. The NiS-rGO composite electrode showed high sensitivity and selectivity towards dopamine, making it a promising candidate for dopamine detection in biological samples. Furthermore, NiS-based composites have also been used as anodes in lithium-ion batteries due to their high theoretical specific capacity and excellent cycling stability. NiS-carbon composites have been shown to have enhanced electrochemical performance as anodes in lithium-ion batteries, making them promising candidates for energy storage applications. The use of NiS-based composites as electrodes in electrochemical sensors and energy storage devices shows great promise, but there are several challenges that need to be addressed. One of the main challenges is the stability of the composite electrode under various conditions, such as high temperatures and corrosive environments. The development of stable NiS-based composite electrodes with high performance and stability is crucial for their practical applications. Another challenge is the scalability and reproducibility of the NiS-based composite electrode fabrication process. The development of cost-effective and scalable fabrication methods is necessary for the practical application of NiS-based composite electrodes.

Future research can focus on developing new NiS-based composites with improved sensing and energy storage properties for various applications. The design and optimization of NiS-based composite electrodes can also be explored to improve their performance and stability. In addition, the integration of NiS-based composite electrodes with microfluidic systems and portable devices can further enhance their potential applications in various fields. In conclusion, the incorporation of other materials into NiS structures to form composite electrodes has shown great potential for various electrochemical sensing and energy storage applications. Future research can focus on developing new NiS-based composites with improved sensing and energy storage properties for various applications. The design and optimization of NiS-based composite electrodes can also be explored to improve their performance and stability. Overall, the use of NiS-based composites as electrodes in electrochemical sensors and energy storage devices shows great promise and is an exciting area of research for future development.

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Conflicts of Interest

The authors declare that they have no conflict of interest

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