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A Highly Promising Flower-Shaped WO_2I_2/Poly(1H-Pyrrole) Nanocomposite Thin Film as a Potentiometric Sensor for the Detection of Cd^{2+} Ions in Water

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Abstract: Because of the expensive nature of sensors used to detect heavy metals and the severe health risks associated with certain heavy metals, there is a pressing need to develop cost-effective materials that are highly efficient in detecting these metals. A flower-shaped WO_2I_2-Poly(1H-pyrrole) (WO_2I_2/P1HP) nanocomposite thin film is synthesized through the oxidation of 1-H pyrrole using iodine and subsequent reaction with Na_2WO_4. The nanocomposite exhibits a distinctive flower-like morphology with an average size of 20 nm. Elemental composition and chemical structure are confirmed via X-ray photoelectron spectroscopy (XPS) analyses, while X-Ray diffraction analysis (XRD) and Fourier-transform infrared spectroscopy (FTIR) analyses provide further evidence of crystalline peaks and functional groups within the composite. The potential of the nanocomposite as a sensor for Cd^{2+} ions is determined using two approaches: simple potentiometric (two-electrode cell) and cyclic voltammetric (three-electrode cell) methods, over a concentration range spanning from 10^{-6} to 10^{-1} M. From the simple potentiometric method, the sensor showcases strong sensing capabilities in the concentration span of 10^{-4} to 10^{-1} M, displaying a Nernstian slope of 29.7 mV/decade. With a detection limit of 5×10^{-5} M, the sensor proves adept at precise and sensitive detection of low Cd^{2+} ion concentrations. While using the cyclic voltammetric method, the sensor's selectivity for Cd^{2+} ions, demonstrated through cyclic voltammetry, reveals a sensitivity of 1.0×10^{-5} A/M and the ability to distinguish Cd^{2+} ions from other ions like Zn^{2+}, Ni^{2+}, Ca^{2+}, K^{+}, Al^{3+}, and Mg^{2+}. This selectivity underscores its utility in complex sample matrices and diverse environments. Furthermore, the sensor's successful detection of Cd^{2+} ions from real samples solidifies its practical viability. Its reliable performance in real-world scenarios positions it as a valuable tool for Cd^{2+} ion detection across industries and environmental monitoring applications. These findings advocate for its utilization in commercial settings, highlighting its significance in Cd^{2+} ion detection.

Keywords: potentiometric sensor; Cd^{2+} ions; flower-shape; WO_2I_2-Poly(1H-pyrrole); cyclic voltammetry; nanocomposite thin film

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1. Introduction

The toxic nature of heavy metals such as nickel, mercury, and cadmium, and their industrial applications made this analysis very important, with the emission of these ions present in the liquid waste [1]. Cd^{2+} ions are an essential metal in many consumer products, household and industrial appliances, batteries, and mobile phones. Low levels of it are very useful for living organisms and are involved in vital processes. Excessive levels of Cd^{2+} may cause disease, toxic effects, and central nervous system disorders [1,2]. These vapors are absorbed with ease and accumulate in the body via food chains. Given the importance of the elements and their role in human life and daily life, it is very necessary to know their forms, compounds and quantities, and thus estimate the Cd^{2+} ions present.

This is because of their development in the application of mechanics and electrons and the establishment of high-tech laboratories, through which very few concentrations were determined and calculated in nanograms [3–5]. Among the modern techniques used for the determination of Cd^{2+} ions in environmental and biological samples are atomic fluorescence spectrometer (AFS), atomic absorption spectrometer (AAS), X-ray spectroscopy, neutron analysis, inductively coupled plasma mass spectrometry (ICP-MS), and ion selective membrane electrodes [6–8]. However, most spectrometers are expensive, complex, and have a very long analysis time. Recently, after the emergence and development of applications of voltage measurement sensors, they have become of great importance to academics and researchers due to their simplicity, low cost, the possibility of experiments in living organisms, and environmental, industrial, and medical analysis [9–11]. The application of voltammetry has been used for long periods, but the continuous development in the distinctive electrodes of ions made them good and powerful alternatives to other techniques. Applications of membrane voltage sensors are classified according to their structural structure into two categories, symmetric polarity characteristic ions and asymmetric polarity characteristic ions [12–14]. These electrodes are an analytical tool widely used in various chemical analyses. There are membranes composed of PVC polymers that are selective as a result of the incorporation of conductors. The challenge in this technique is the production of different ionophores [12–14]. It is composed of a polyvinyl chloride film with thiophene, with the addition of nafion to form a membrane sensor. However, this kind of sensor has disadvantages related to its nonuniform thickness, instability, and shrinking with time [15,16].

The industrial sector traditionally relies on fluorescence or atomic absorption spectrometry techniques for Cd^{2+} ion detection. However, due to the substantial cost associated with these methods [17], researchers and scientists have made concerted efforts to introduce electrochemical and potentiometric techniques into industrial applications. Encouraging studies, like our present research, serve as a catalyst for these initiatives, offering opportunities for further exploration in this direction.

Herein, a flower-shaped WO_2I_2/P1HP nanocomposite thin film is successfully prepared by oxidizing 1-H pyrrole using iodine and subsequently reacting it with Na_2WO_4. This nanocomposite exhibits a promising flower-like morphology with an average size of 20 nm. To understand its elemental composition and chemical structure, XPS analyses are employed. The potentiometric sensing of the WO_2I_2/P1HP nanocomposite is then tested specifically for Cd^{2+} ions in a concentration range of 10^{-6} to 10^{-1} M. Additionally, the electroanalytical technique of cyclic voltammetry is employed to evaluate the sensor's sensitivity and selectivity. In the potentiometric sensing test, the nanocomposite demonstrates its capability to detect Cd^{2+} ions over a wide concentration range, providing valuable insights into its detection capabilities for this specific ion. In the electroanalytical test using cyclic voltammetry, the sensor's sensitivity is assessed, demonstrating its ability to detect small changes in Cd^{2+} ion concentrations with high precision. Furthermore, the test evaluates the sensor's selectivity, ensuring that it accurately detects Cd^{2+} ions even in the presence of other potentially interfering ions. Moreover, natural sample testing is conducted to assess the sensor's performance in real-world scenarios, providing evidence of its practical applicability in detecting Cd^{2+} ions in complex environmental samples.

2. Experimental Section

2.1. Materials

Pyrrole and DMF are sourced from USA through Across and Saint Louis, MO, Sigma Aldrich, company, correspondingly. Na_2WO_4 and $Cd(NO_3)_2$ are sourced from London, UK and Cairo, Egypt, Win lab and Pio-Chem, company, Respectively. HCl is sourced from Merck Company, Rahway, NJ, USA.

2.2. WO_2I_2/P1HP Thin Film Sensor Preparation

1-H pyrrole is the monomer used as a source of P1HP, in which the 0.15 M iodine oxidant is added suddenly under vigorous stirring. Both monomer and oxidant are prepared separately before this addition. Through the polymerization reaction, I-P1HP nanomaterial is obtained. Through the reaction with Na_2WO_4 (0.05 M), this led to the WO_2I_2 dopant being inserted as filler in the P1HP matrix thin film nanocomposite. The resulting sensor is carefully treated and applied for detecting Cd^{2+} ions. Various conditions are tested to optimize the sensor's performance and sensitivity in Cd^{2+} ion sensing. The nanocomposite sensor's ability to detect Cd^{2+} ions under different conditions is thoroughly evaluated to ensure its reliability and applicability in practical applications.

2.3. The Potentiometric Sensing

The WO_2I_2/P1HP nanocomposite thin film is utilized as a sensor for detecting Cd^{2+} ions in aqueous solutions. The concentration of Cd^{2+} ions is determined by analyzing the calibration curve using the Nernst equation. The calibration curve is obtained through the simple potentiometric method, involving two electrodes: the WO_2I_2/P1HP thin film sensor and the calomel electrode.

The sensitivity of the WO_2I_2/P1HP nanocomposite thin film to Cd^{2+} ions is further assessed using cyclic voltammetry. The study also investigates the impact of interfering ions. To analyze the behavior of the sensor in natural samples, testing is conducted using cyclic voltammetry in a standard three-electrode cell, with the WO_2I_2/P1HP thin film sensor serving as the working electrode.

3. Results and Discussion

3.1. Analyses

The chemical behavior of the WO_2I_2/P1HP nanocomposite is assessed through the analysis of bond vibrations and the excitation of crystalline internal electrons, which are examined using FTIR and XRD analyses, respectively. In Figure 1a,b, FTIR and XRD spectra are presented, respectively, to study the effects of incorporating WO_2I_2 into the P1HP polymer matrix.

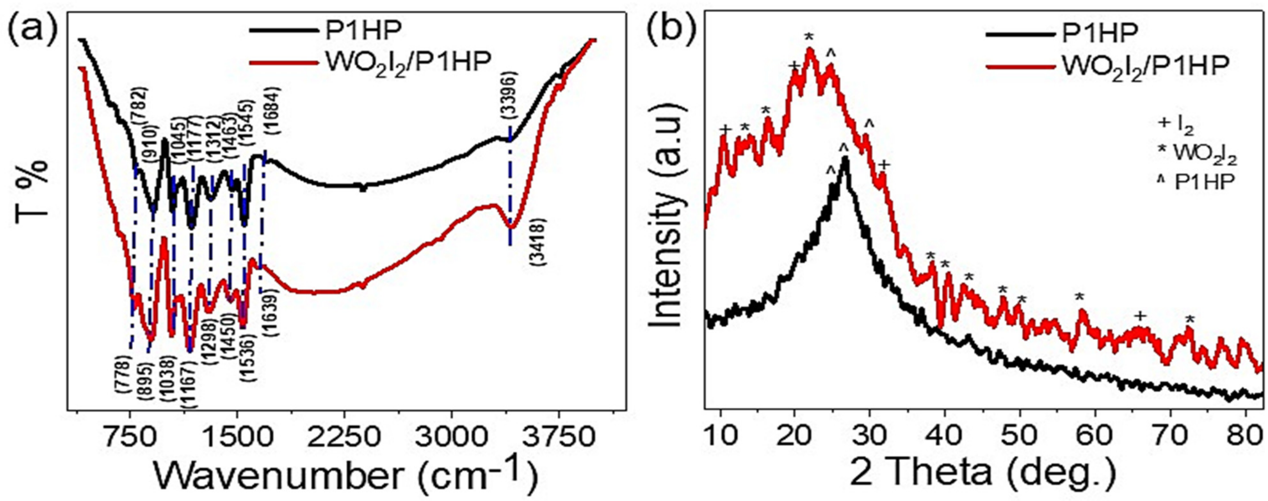

Figure 1. The WO_2I_2/P1HP nanocomposite chemical estimation by (**a**) FTIR spectroscopy and (**b**) XRD pattern.

Through FTIR analysis (Figure 1a), the changes in bond vibrations are observed, indicating the interactions between the inorganic WO_2I_2 and the polymer matrix [18,19]. The insertion of WO_2I_2 leads to small shifts in the bands of certain functional groups, such as C-N, C-H, and C=C of benzene or quinone. The majority of bands in the nanocomposite are almost identical to those of the pure P1HP polymer. Table 1 provides a concise summary of the band positions before and after the composite formation, facilitating a clear comparison of the changes induced by WO_2I_2 incorporation.

Table 1. The summary of the band positions before and after the composite formation.

Band Position (cm^{-1})		Function Group
WO_2I_2/P1HP	P1HP	
1639 and 1536	1684 and 1545	P1HP ring
1450 and 1298	1463 and1312	C-N [20]
1298	1304	C-N
1167	1177	C-H [21]
778	782	Para ring [22]

In addition to FTIR, XRD analysis (Figure 1b) also sheds light on the chemical behavior of the nanocomposite. It allows for the examination of crystalline internal electrons, providing insights into the structural changes induced by the inclusion of WO_2I_2. The XRD patterns illustrate the crystallinity of the nanocomposite and help identify any shifts or new peaks resulting from the presence of WO_2I_2 within the P1HP matrix.

By combining both FTIR and XRD analyses, a comprehensive understanding of the chemical behavior of the WO_2I_2/P1HP nanocomposite is achieved, offering valuable insights into the interactions between the inorganic material and the polymer matrix. This knowledge is essential for optimizing the properties and performance of the nanocomposite for various applications.

By the same manner, the influence of WO_2I_2 on the P1HP appears well through the XRD pattern through the changing of the behavior of the XRD pattern. The P1HP appear to be amorphous; this behavior is not a drawback in the polymer material, but sometimes it has advantages related to the military applications of these semiconductor materials for aircrafts or some weapons designs. Thus, the amorphous nature of P1HP is proved through estimation of the broad peaks at 24.6° after the interaction of WO_2I_2, the XRD pattern changes, in which WO_2I_2 cause the exhibition of additional peaks at 22.1°, 38.3°, 40.3°, 42.5°, 47.6°, 50.0°, 58.2°, and 72.5° [23]. Other peaks illustrate the I_2 present in this nanocomposite: 10.2°, 20.0°, 65.9° [24].

The elemental composition and chemical state of the WO_2I_2/P1HP nanocomposite are analyzed using X-ray photoelectron spectroscopy (XPS), as shown in Figure 2a. In this technique, the sample surface is bombarded with X-rays, leading to the emission of photoelectrons from the atoms in the material. By measuring the kinetic energy of these emitted photoelectrons, valuable information about the elemental composition and chemical environment of the atoms is obtained.

In the XPS survey, the characteristic peaks corresponding to the elements in the nanocomposite are identified. The P1HP ring is estimated by monitoring the carbon (C) and nitrogen (N) elements at binding energies of 286 eV and 401 eV, respectively.

For the WO_2I_2 elements, the characteristic peaks are observed at $W4f_{5/2}$ and $W4f_{7/2}$ with doublet peaks located at 38 eV and 35.8 eV, respectively, related to the W^{6+}. The presence of the iodine (I) element is also confirmed through peaks at 619 eV and 630 eV, indicating the formation of WO_2I_2 within the polymer matrix, leading to the formation of the WO_2I_2/P1HP nanocomposite.

The XPS analysis provides crucial evidence of the successful incorporation of WO_2I_2 into the polymer matrix and the formation of the nanocomposite, validating the material's composition and chemical states. These insights are valuable for understanding the structural properties of the nanocomposite and its potential applications in various fields.

The topographic of the WO_2I_2/P1HP nanocomposite is an essential property for the sensing behavior of this nanocomposite. With increasing the surface area, the sensing efficiency increases by a large percentage; this is related to increasing the sites of sensing to the estimated heavy metal. The topography of the pure polymer reflects well on the synthesized nanocomposite through the promising morphologies of the synthesized

WO_2I_2/P1HP nanocomposite. The P1HP surface area consists of wrinkle nanoparticles that combine well for forming large particles (300 nm) that are similar to wrinkle brain, as observed in Figure 3a. The WO_2I_2/P1HP nanocomposite exhibits distinct and well-defined particles, each with an average size of approximately 20 nm. This uniformity in particle size and shape is clearly demonstrated in the simulated theoretical image presented in Figure 3b. The image illustrates the highly consistent and small particles that constitute the nanocomposite material.

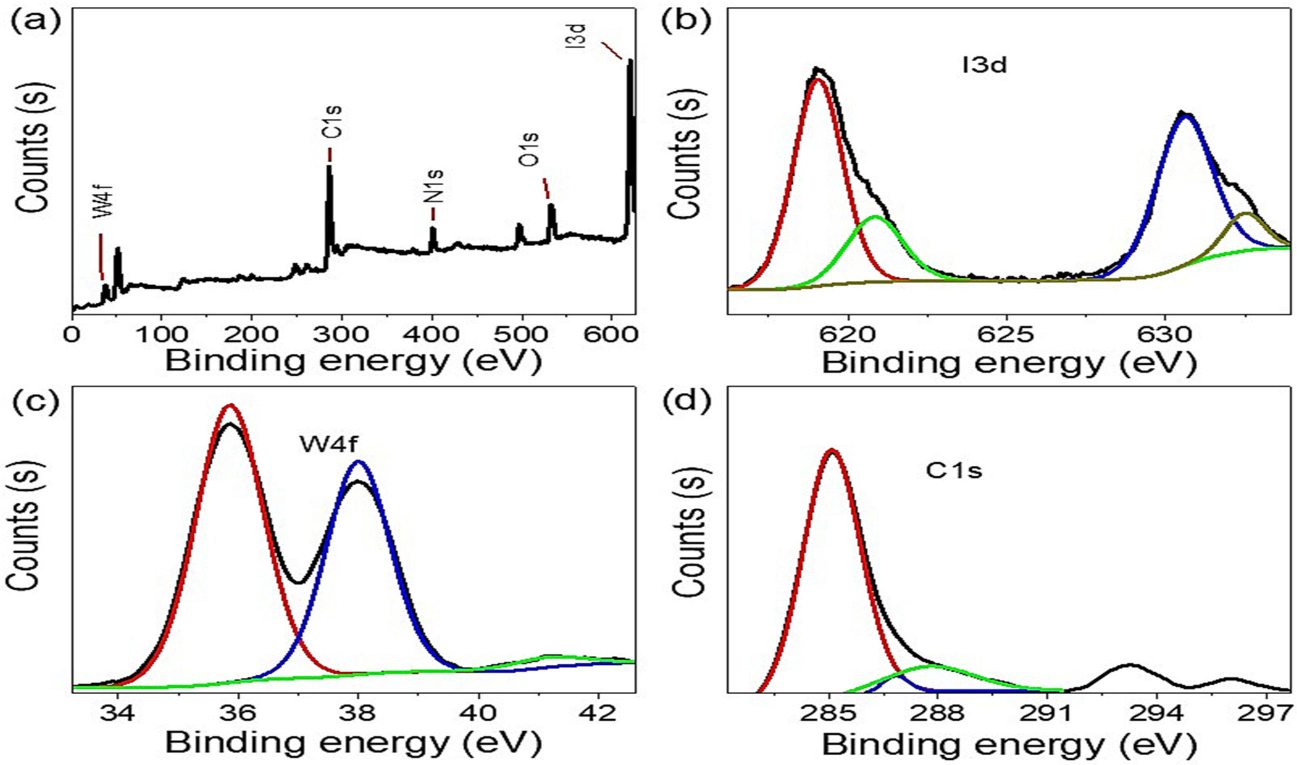

Figure 2. WO_2I_2/P1HP nanocomposite XPS for elemental estimation, these analyses include (**a**) survey, (**b**) I, (**c**) W, and (**d**) C elements.

The controlled synthesis process of the nanocomposite results in the formation of nanoparticles with precise dimensions, leading to the observed uniform morphology. This uniformity is of significant importance in sensing applications, as it ensures consistent and reliable performance when detecting heavy metals or other target analytes [25,26]. The small particle size also contributes to the high surface area of the nanocomposite, as mentioned earlier, enhancing its sensing efficiency by providing more active sites for interactions with the analytes. This property is essential for achieving accurate and sensitive detection of heavy metals, making the WO_2I_2/P1HP nanocomposite a promising candidate for various sensing and environmental monitoring applications.

The morphological properties of the WO_2I_2/P1HP nanocomposite are further demonstrated through SEM images in Figure 3c,d. These images reveal the presence of small and porous particles in the nanocomposite material. The inorganic WO_2I_2 component is clearly visible as shiny dots, which are coated with the gray-colored polymer materials. The small size of the particles is consistent with the previously-mentioned average size of approximately 20 nm, further confirming the uniformity in particle dimensions. The porous nature of the particles is evident from the observed texture, indicating the presence of numerous void spaces within the nanocomposite. The combination of small size and porosity in the WO_2I_2/P1HP nanocomposite enhances its surface area and promotes more efficient interactions with target analytes, such as heavy metal ions. The presence of the inorganic WO_2I_2 within the polymer matrix contributes to the overall structural integrity of the nanocomposite and plays a crucial role in its sensing capabilities [18,27].

The unique morphological properties of the WO_2I_2/P1HP nanocomposite, as revealed by SEM, highlight its potential for various applications, including heavy metal sensing and environmental remediation. The well-defined particles with their distinctive features make the nanocomposite a promising material for achieving high-performance sensors and catalysts.

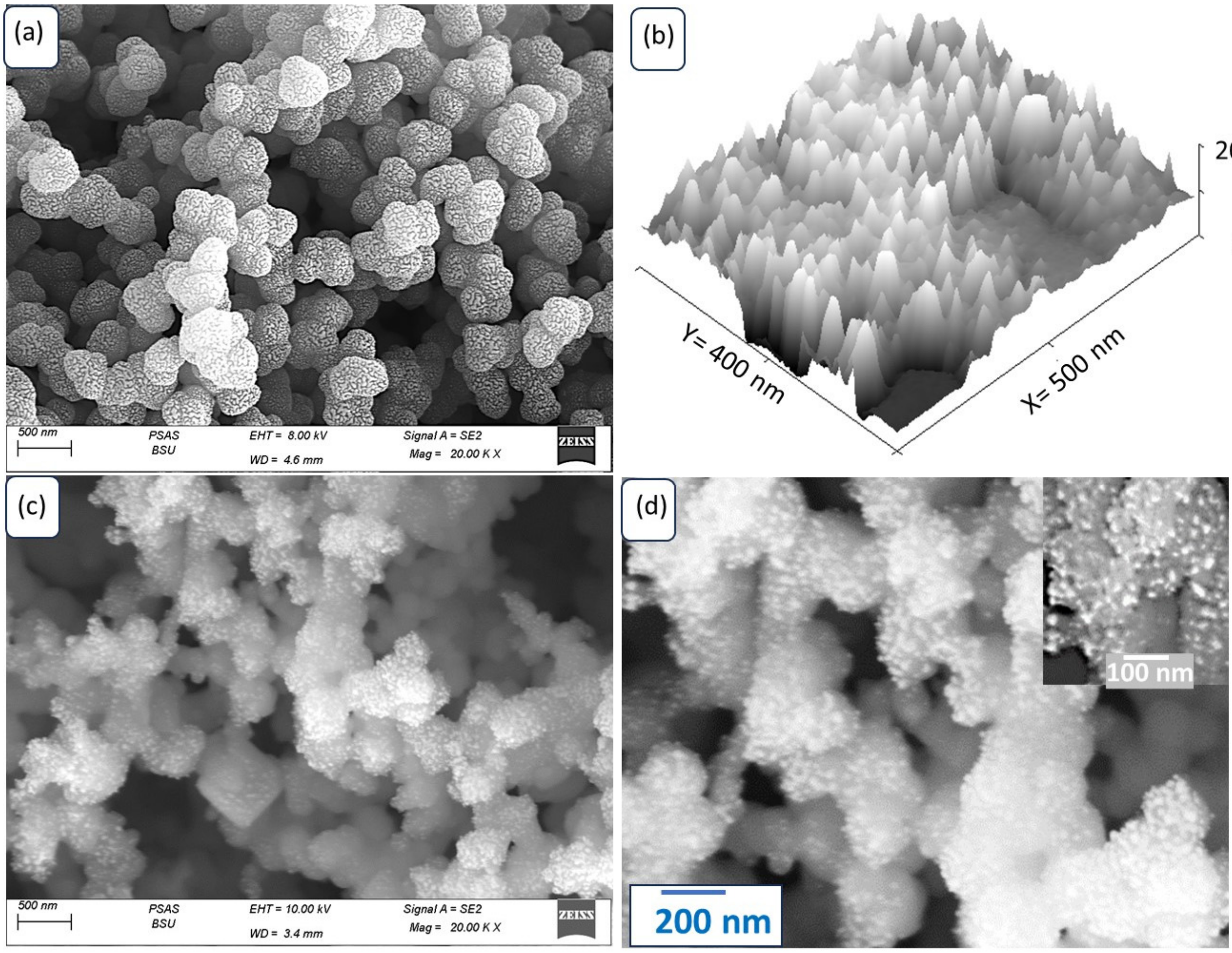

Figure 3. (**a**) SEM of P2ABT. (**b**) TEM image and (**c**,**d**) SEM images (different scale bar) of WO_2I_2/P1HP nanocomposite.

3.2. Sensing Properties

The estimation of Cd^{2+} ions is of significant importance due to their hazardous effects on plants, animals, and humans. To achieve this, a highly morphological polymer-based sensor, specifically the WO_2I_2/P1HP thin film sensor, is utilized. The sensor's design and unique morphological properties make it well-suited for detecting Cd^{2+} ions with high sensitivity and accuracy.

The concentration range of Cd^{2+} ions tested in this study spans from 10^{-6} to 10^{-1} M. This wide range allows for the evaluation of the sensor's performance across different concentrations, covering both low and high levels of Cd^{2+} ions.

The measurements are carried out at room temperature using advanced equipment such as the digital AVO meter and CHI608E workstation. These tools ensure precise and reliable data acquisition, contributing to the accuracy of the Cd^{2+} ion estimation.

By utilizing the WO_2I_2/P1HP thin film sensor in this study, researchers aim to provide an effective and efficient solution for detecting and quantifying Cd^{2+} ions, thus contributing to environmental monitoring and public health protection efforts. The promising results obtained from this investigation may pave the way for further applications of the sensor in various fields, such as environmental science, toxicology, and industrial safety.

The detection of Cd^{2+} ions is achieved through the electrochemical interaction between the charges of the WO_2I_2/P1HP nanocomposite and the charged Cd^{2+} ions. The inclusion of iodine in the nanocomposite enhances this electrochemical attraction through the formation of coordination bonds, resulting in increased sensitivity towards Cd^{2+} ions. The sensing performance is conducted using the WO_2I_2/P1HP thin film sensor as the primary electrode for this detection reaction. To assess the sensing behavior, both the simple potentiometric method and cyclic voltammetry techniques are employed.

In the potentiometric method, the potential difference between the reference and working electrodes is measured, providing valuable information about the Cd^{2+} ion concentration. On the other hand, cyclic voltammetry involves applying a range of voltages to the sensor and measuring the resulting current, enabling the evaluation of the sensor's response to different Cd^{2+} ion concentrations. By employing these electrochemical techniques, the WO_2I_2/P1HP thin film sensor exhibits its potential for accurate and sensitive detection of Cd^{2+} ions. This sensing capability could have significant implications in environmental monitoring, industrial applications, and public health protection, where rapid and reliable detection of Cd^{2+} ions is crucial.

In the simple potentiometric method, the sensing behavior is evaluated using only two electrodes: the main electrode (WO_2I_2/P1HP thin film) and the reference electrode (calomel electrode). By measuring the potential difference between these electrodes, the sensing efficiency of the nanocomposite towards Cd^{2+} ions is determined. As the concentration of Cd^{2+} ions increase from 10^{-6} to 10^{-1} M, the potential measured also increases, confirming the sensing capability of the nanocomposite.

The sensitivity of this sensing behavior is calculated using the Nernstian equation [28,29], which is applicable to ions with oxidation states of 2+. For Cd^{2+} ions, the theoretical slope of the Nernstian equation is 29.56 mV/decade, and the nanocomposite's actual sensitivity can be determined based on this value. On the other hand, the cyclic voltammetry technique provides further insight into the sensing behavior [30–32]. By analyzing the area and intensity of the cyclic voltammetry curves, the responsivity and sensing performance of the nanocomposite are assessed. As the concentration of Cd^{2+} ions increase from 10^{-1} to 10^{-6} M, the peak current in the cyclic voltammetry curve also increases, indicating the nanocomposite's enhanced sensing ability towards Cd^{2+} ions.

Therefore, both the potentiometric method and cyclic voltammetry technique will contribute to a holistic understanding of the WO_2I_2/P1HP nanocomposite's sensing behavior. The combination of these electrochemical techniques allows for precise quantification of the nanocomposite's sensitivity and provides valuable information for its potential application in detecting Cd^{2+} ions with high accuracy and reliability.

In Figure 4, the relationship between the pM values ($-\log [Cd^{2+}]$) and the potential generated between the WO_2I_2/P1HP sensor and the reference electrode is depicted using the simple potentiometric method. As the concentration of Cd^{2+} ions increase, the produced potential also increases, displaying a linear relationship. The slope of this linear relationship is calculated to be 29.7 mV/decade, within the concentration range of 10^{-4} to 10^{-1} M. This promising slope indicates the high sensitivity of the prepared WO_2I_2/P1HP sensor towards Cd^{2+} ions, as small changes in the ion concentration lead to significant changes in the generated potential. Furthermore, the detection limit of the WO_2I_2/P1HP sensor for Cd^{2+} ions is determined to be 5×10^{-5} M. This low detection limit implies that the sensor can accurately and effectively detect even trace amounts of Cd^{2+} ions in a sample. The combination of high sensitivity and a low detection limit makes the WO_2I_2/P1HP sensor a promising candidate for sensitive and precise detection of Cd^{2+} ions, with potential applications in environmental monitoring, industrial processes, and health-related fields.

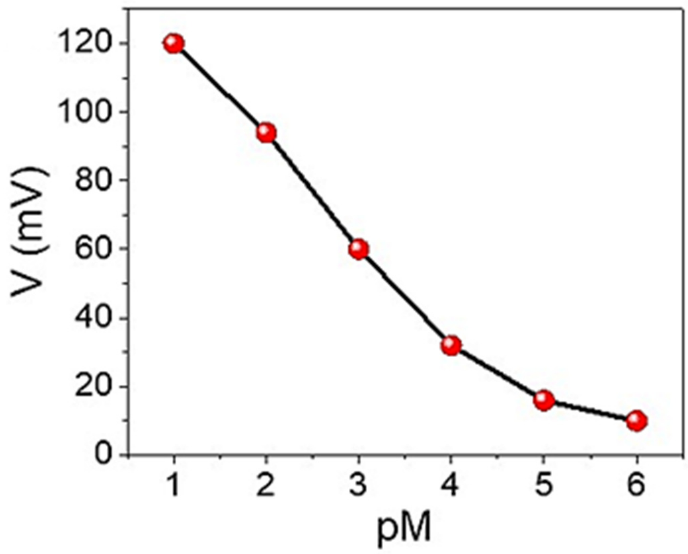

Figure 4. The calibration curve for Cd^{2+} ions by WO_2I_2/P1HP sensor through a potentiometric technique.

In Figure 5a, the electro-analytical Cd^{2+} sensing using the cyclic voltammetry technique with the WO_2I_2/P1HP sensor is shown. As the concentration of Cd^{2+} ions in the aqueous solution is increased from 10^{-4} to 10^{-1} M, the oxidation peak current also increases correspondingly. This observed increase in the oxidation peak current demonstrates the high sensitivity of the WO_2I_2/P1HP sensor in detecting Cd^{2+} ions. The detection of Cd^{2+} ions is performed at a potential of 0.4 V, which is the appropriate potential for the oxidation of Cd^{2+} ions. This specific potential ensures that the oxidation reaction of Cd^{2+} ions occurs optimally, allowing for accurate and reliable detection. The combination of the selected potential and the sensor's high sensitivity enables the successful detection and quantification of Cd^{2+} ions over a wide concentration range. Thus, the cyclic voltammetry results affirm the excellent sensing capabilities of the WO_2I_2/P1HP sensor for Cd^{2+} ions, making it a promising tool for various applications in environmental monitoring and analytical chemistry.

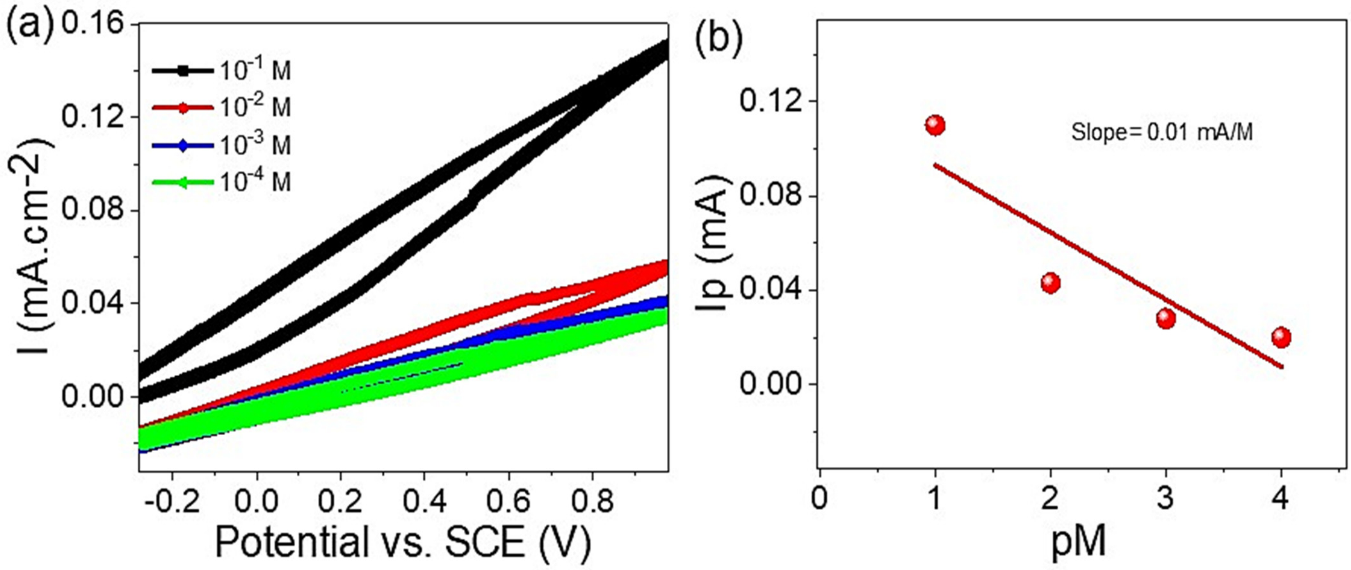

Figure 5. (**a**) Electro-analytical Cd^{2+} sensing by the WO_2I_2/P1HP sensor using the cyclic voltammetry technique and (**b**) the sensitivity curve from the relation of pM and peak current.

In Figure 5b, the sensitivity curve is presented, which shows the relation between pM (negative logarithm of [Cd^{2+}]) and the peak current obtained from the cyclic voltammetry curve in Figure 5a. The slope of this sensitivity curve represents the sensitivity of the WO_2I_2/P1HP sensor towards Cd^{2+} ions, and it is calculated to be 1×10^{-5} A/M. This small value indicates the high sensitivity of the film sensor for Cd^{2+} ions, making it a powerful tool for precise and accurate detection. The WO_2I_2/P1HP sensor's exceptional sensitivity, coupled with its simple preparation technique and low production costs, makes it a promising candidate for various applications in commercial fields and industries. Its ability to reliably detect and quantify Cd^{2+} ions in a wide concentration range makes it highly valuable in environmental monitoring, water quality assessment, and other analytical chemistry applications. Therefore, the WO_2I_2/P1HP sensor's high sensitivity and cost-effectiveness make it an attractive option for practical and impactful use in various real-world scenarios, contributing to advancements in the field of sensing technology.

The selectivity of the WO_2I_2/P1HP sensor towards Cd^{2+} ions is rigorously tested using the cyclic voltammetry technique in a three-electrode cell setup, as demonstrated in Figure 6a. Various interfering ions, each at a concentration of 0.01 M, are introduced using NaCl electrolyte to evaluate the sensor's response. However, upon analysis, no indication of peaks related to any of these interfering ions is observed, and there are no oxidation or reduction peaks detected.

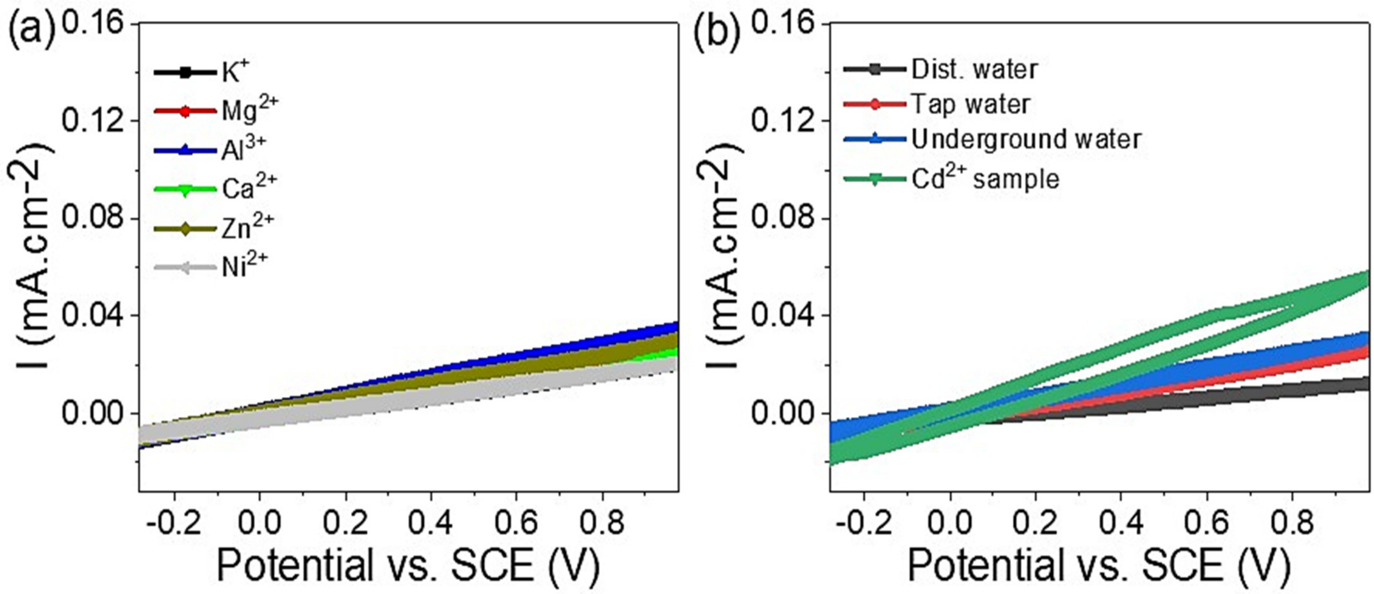

Figure 6. Electro-analytical Cd^{2+} sensing by the WO_2I_2/P1HP sensor using cyclic voltammetry: (**a**) selectivity and (**b**) natural and lab sample testing.

This exceptional behavior confirms the high selectivity of the fabricated WO_2I_2/P1HP sensor specifically towards Cd^{2+} ions. Its ability to precisely detect Cd^{2+} ions without any response to interfering ions demonstrates the reliability and accuracy of the sensor in complex environments. The results emphasize the potential applicability of this sensor in various real-world scenarios, where selective detection of specific ions is critical for accurate analysis and monitoring purposes.

To further assess the selectivity and practical applicability of the WO_2I_2/P1HP sensor, it is crucial to study its response to various real-world water samples containing different levels of Cd^{2+} ions (Figure 6b). Distilled water, tap water, and underground water are tested as Cd^{2+}-free samples, and additional Cd^{2+} ions (lab samples) are introduced to evaluate the sensor's performance. As indicated in the resulting curves, no indication peaks are observed in the absence of Cd^{2+} ions, confirming the sensor's specificity towards Cd^{2+} ion sensing. However, when Cd^{2+} ions are present in the water samples, the sensor exhibits characteristic peaks corresponding to the detection of Cd^{2+} ions. This response validates the sensor's capability to accurately and selectively detect Cd^{2+} ions even in the presence of various other elements and contaminants commonly found in natural water sources. The remarkable technical advantages and straightforward preparation process of this sensor make it an ideal candidate for electroanalytical detection of Cd^{2+} ions in aqueous solutions. Its ability to reliably distinguish and quantify Cd^{2+} ions in diverse water samples, including those from natural sources, highlights its potential for practical applications in environmental monitoring and water quality assessment.

The high sensitivity and selectivity of the WO_2I_2/P1HP sensor towards Cd^{2+} ions are attributed to the strong affinity of the sensor materials to interact with Cd^{2+} ions. Cd^{2+} ions tend to form relatively weak coordination bonds with the inorganic components, particularly the iodine and oxide materials within WO_2I_2. Additionally, P1HP exhibits a significant affinity for Cd^{2+} ions, driven by the electrostatic attraction between the Cd^{2+} ions and the nitrogen atom within this polymer.

By combining these favorable chemical and physical properties, this sensor holds great promise for the cost-effective and straightforward detection of Cd^{2+} ions, eliminating the need for complex techniques. This potential opens up opportunities for industrial applications in the realm of Cd^{2+} ion detection.

4. Conclusions

A highly promising nanocomposite thin film with a distinctive flower-like structure, consisting of WO_2I_2 and P1HP, is synthesized through a two-step process. This involves the oxidation of 1-H pyrrole using iodine and subsequent reaction with Na_2WO_4. The resulting flower-shaped structures have an average size of approximately 20 nm.

The potential of this WO_2I_2/P1HP nanocomposite for simple potentiometric sensing of Cd^{2+} ions is evaluated within a concentration range spanning from 10^{-6} to 10^{-1} M. Remarkably, this nanocomposite demonstrates excellent sensing capabilities within a concentration range of 10^{-4} to 10^{-1} M, exhibiting a Nernstian slope of 29.7 mV/decade and an impressive detection limit of 5×10^{-5} M. Furthermore, employing cyclic voltammetry as an electroanalytical technique, the sensor exhibits high sensitivity, with a value of 1.0×10^{-5} A/M. This underscores its notable selectivity for detecting Cd^{2+} ions even in the presence of other ions such as Zn^{2+}, Ni^{2+}, Ca^{2+}, and Mg^{2+}. Moreover, this sensor shows great promise for detecting Cd^{2+} ions in real samples, suggesting its potential applicability in commercial settings.

The flower-shaped WO_2I_2/P1HP thin film sensor exhibits considerable promise as a sensor with high sensitivity and selectivity for detecting Cd^{2+} ions. Its ability to follow Nernstian behavior, achieve a low detection limit, and effectively detect Cd^{2+} ions in real-world samples position it as a robust candidate for commercial applications in the field of Cd^{2+} ion detection.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Çelebi, H.; Gök, G.; Gök, O. Adsorption Capability of Brewed Tea Waste in Waters Containing Toxic Lead(II), Cadmium (II), Nickel (II), and Zinc(II) Heavy Metal Ions. *Sci. Rep.* **2020**, *10*, 17570. [CrossRef] [PubMed]
2. Peng, W.; He, Y.; He, S.; Luo, J.; Zeng, Y.; Zhang, X.; Huo, Y.; Jie, Y.; Xing, H. Exogenous Plant Growth Regulator and Foliar Fertilizers for Phytoextraction of Cadmium with *Boehmeria Nivea* [L.] Gaudich from Contaminated Field Soil. *Sci. Rep.* **2023**, *13*, 11019. [CrossRef]
3. Li, B.; Zhang, X.; Tefsen, B.; Wells, M. From Speciation to Toxicity: Using a "Two-in-One" Whole-Cell Bioreporter Approach to Assess Harmful Effects of Cd and Pb. *Water Res.* **2022**, *217*, 118384. [CrossRef]
4. Forghani Tehrani, G.; Rubinos, D.A.; Kelm, U.; Ghadimi, S. Environmental and Human Health Risks of Potentially Harmful Elements in Mining-Impacted Soils: A Case Study of the Angouran Zn–Pb Mine, Iran. *J. Environ. Manag.* **2023**, *334*, 117470. [CrossRef] [PubMed]
5. Wu, X.; Wu, P.; Gu, M.; Xue, J. Trace Heavy Metals and Harmful Elements in Roots and Rhizomes of Herbs: Screening Level Analysis and Health Risk Assessment. *Chin. Herb. Med.* **2022**, *14*, 622–629. [CrossRef]
6. Ahmed, A.M.; Shaban, M. Nanoporous Chromium Thin Film for Active Detection of Toxic Heavy Metals Traces Using Surface-Enhanced Raman Spectroscopy. *Mater. Res. Express* **2020**, *7*, 015084. [CrossRef]
7. Rabia, M.; Elsayed, A.M.; Alnuwaiser, M.A. Decoration of Poly-3-methyl Aniline with As(III) Oxide and Hydroxide as an Effective Photoelectrode for Electroanalytical Photon Sensing with Photodiode-like Behavior. *Micromachines* **2023**, *14*, 1573. [CrossRef]
8. Karbalaee Hosseini, A.; Tadjarodi, A. Luminescent Cd Coordination Polymer Based on Thiazole as a Dual-Responsive Chemosensor for 4-Nitroaniline and $CrO4^{2-}$ in Water. *Sci. Rep.* **2023**, *13*, 269. [CrossRef]
9. Zhan, W.; Chen, Z.; Hu, J.; Chen, X. Vertical CuO Nanowires Array Electrodes: Visible Light Sensitive Photoelectrochemical Biosensor of Ethanol Detection. *Mater. Sci. Semicond. Process.* **2018**, *85*, 90–97. [CrossRef]
10. Shoaie, N.; Daneshpour, M.; Azimzadeh, M.; Mahshid, S.; Khoshfetrat, S.M.; Jahanpeyma, F.; Gholaminejad, A.; Omidfar, K.; Foruzandeh, M. Electrochemical Sensors and Biosensors Based on the Use of Polyaniline and Its Nanocomposites: A Review on Recent Advances. *Mikrochim. Acta* **2019**, *186*, 465. [CrossRef]
11. Lan, T.; Fallatah, A.; Suiter, E.; Padalkar, S. Size Controlled Copper (I) Oxide Nanoparticles Influence Sensitivity of Glucose Biosensor. *Sensors* **2017**, *17*, 1944. [CrossRef]
12. Khalil, M.M.; Issa, Y.M.; Zayed, S.I.M.; Ali, F.Q. New Potentiometric Membrane Sensors for Determination of Alverine Citrate in Pharmaceutical Compounds and Biological Fluids. *Int. J. Adv. Res.* **2014**, *2*, 1096–1109.
13. El Nady, J.; Shokry, A.; Khalil, M.; Ebrahim, S.; Elshaer, A.M.; Anas, M. One-Step Electrodeposition of a Polypyrrole/NiO Nanocomposite as a Supercapacitor Electrode. *Sci. Rep.* **2022**, *12*, 3611. [CrossRef]
14. Ebrahim, S.; Shokry, A.; Khalil, M.M.A.; Ibrahim, H.; Soliman, M. Polyaniline/Ag Nanoparticles/Graphene Oxide Nanocomposite Fluorescent Sensor for Recognition of Chromium (VI) Ions. *Sci. Rep.* **2020**, *10*, 13617. [CrossRef]
15. Xing, Y.; Liu, Z.; Li, B.; Li, L.; Yang, X.; Zhang, G. The Contrastive Study of Two Thiophene-Derived Symmetrical Schiff Bases as Fluorescence Sensors for Ga^{3+} Detection. *Sens. Actuators B Chem.* **2021**, *347*, 130497. [CrossRef]
16. Aydın, E.B.; Aydın, M.; Sezgintürk, M.K. A Label-Free Electrochemical Biosensor for Highly Sensitive Detection of GM2A Based on Gold Nanoparticles/Conducting Amino-Functionalized Thiophene Polymer Layer. *Sens. Actuators B Chem.* **2023**, *392*, 134025. [CrossRef]
17. Sadia, M.; Khan, J.; Khan, R.; Kamran, A.W.; Zahoor, M.; Ullah, R.; Bari, A.; Ali, E.A. Rapid Detection of Cd^{2+} Ions in the Aqueous Medium Using a Highly Sensitive and Selective Turn-On Fluorescent Chemosensor. *Molecules* **2023**, *28*, 3635. [CrossRef] [PubMed]
18. Gudadur, K.S.; Veluswamy, P. Flexible Reversible Polymer Nano-Composite Thin Film Patch for Wearable Temperature Sensor. *Surf. Interfaces* **2023**, *39*, 102975. [CrossRef]
19. Ganesha, H.; Veeresh, S.; Nagaraju, Y.; Devendrappa, H. MoS_2/Polymer Nanotube Composite Material Used for the Electrochemical Sensor Detection of Biologically Active Compounds. *Inorg. Chem. Commun.* **2023**, *156*, 111228. [CrossRef]
20. Rabia, M.; Trabelsi, A.B.G.; Elsayed, A.M.; Alkallas, F.H. Porous-Spherical Cr_2O_3-$Cr(OH)_3$-Polypyrrole/Polypyrrole Nanocomposite Thin-Film Photodetector and Solar Cell Applications. *Coatings* **2023**, *13*, 1240. [CrossRef]
21. Sayyah, S.M.; Shaban, M.; Rabia, M. Electropolymerization of *m* -Toluidin on Platinum Electrode from Aqueous Acidic Solution and Character of the Obtained Polymer. *Adv. Polym. Technol.* **2018**, *37*, 126–136. [CrossRef]
22. Sayyah, E.-S.M.; Shaban, M.; Rabia, M. A Sensor of *m* -Cresol Nanopolymer/Pt-Electrode Film for Detection of Lead Ions by Potentiometric Methods. *Adv. Polym. Technol.* **2018**, *37*, 1296–1304. [CrossRef]
23. Coşkun, S.; Koziol, K.K.K. Synthesis of High Aspect Ratio WO_2 Nanostructures. *J. Nanoparticle Res.* **2016**, *18*, 51. [CrossRef]
24. Dinh, T.D.; Zhang, D.; Tuan, V.N. High Iodine Adsorption Performances under Off-Gas Conditions by Bismuth-Modified ZnAl-LDH Layered Double Hydroxide. *RSC Adv.* **2020**, *10*, 14360–14367. [CrossRef]
25. Srinivasan, P.; Madhu, D.K.; Pedugu Sivaraman, S.; Nagarajan, S.; Rao, C.V.S.B.; Chinaraga, P.K.; Mohan, A.M.; Deivasigamani, P. Chromoionophoric Probe Imbued Porous Polymer Monolith as a Three-in-One Solid-State Naked-Eye Sensor for the Selective Sensing and Recovery of Ultra-Trace Lead, Mercury, and Cadmium Ions from Industrial/Environmental Samples. *Chem. Eng. J.* **2023**, *471*, 144627. [CrossRef]

26. Anju, P.V.; Deivasigamani, P. Structurally Engineered Ion-Receptor Probe Immobilized Porous Polymer Platform as Reusable Solid-State Chromogenic Sensor for the Ultra-Trace Sensing and Recovery of Mercury Ions. *J. Hazard. Mater.* **2023**, *454*, 131431. [CrossRef]
27. Bukhari, A.; Ijaz, I.; Gilani, E.; Nazir, A.; Zain, H.; Shaheen, A.; Hussain, S.; Imtiaz, A. Highly Rapid and Efficient Removal of Heavy Metals, Heavy Rare Earth Elements, and Phenolic Compounds Using EDTA-Cross-Linked MXene Polymer Composite: Adsorption Characteristics and Mechanisms. *Chem. Eng. Res. Des.* **2023**, *194*, 497–513. [CrossRef]
28. Deligonul, N.; Yildiz, I.; Bilgin, S.; Gokce, I.; Isildak, O. Green Fluorescent Protein-Multi Walled Carbon Nanotube Based Polymeric Membrane Electrode for Bismuth Ion Detection. *Microchem. J.* **2023**, *190*, 108710. [CrossRef]
29. Shirzadmehr, A.; Afkhami, A.; Madrakian, T. A New Nano-Composite Potentiometric Sensor Containing an Hg^{2+}-Ion Imprinted Polymer for the Trace Determination of Mercury Ions in Different Matrices. *J. Mol. Liq.* **2015**, *204*, 227–235. [CrossRef]
30. Ghosh, S.K.; Das, N.C. Characterization of Various Polymer Composite Sensors. In *Polymeric Nanocomposite Materials for Sensor Applications*; Woodhead Publishing Series in Composites Science and Engineering; Woodhead Publishing: Sawston, UK, 2023; pp. 121–140. [CrossRef]
31. Verma, A.; Gupta, R.; Verma, A.S.; Kumar, T. A Review of Composite Conducting Polymer-Based Sensors for Detection of Industrial Waste Gases. *Sens. Actuators Rep.* **2023**, *5*, 100143. [CrossRef]
32. Ngoensawat, U.; Pisuchpen, T.; Sritana-anant, Y.; Rodthongkum, N.; Hoven, V.P. Conductive Electrospun Composite Fibers Based on Solid-State Polymerized Poly(3,4-Ethylenedioxythiophene) for Simultaneous Electrochemical Detection of Metal Ions. *Talanta* **2022**, *241*, 123253. [CrossRef] [PubMed]