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Amperometric Highly Sensitive Phosphate Ion Sensor Based on the Electrochemically Modified Ni Electrode

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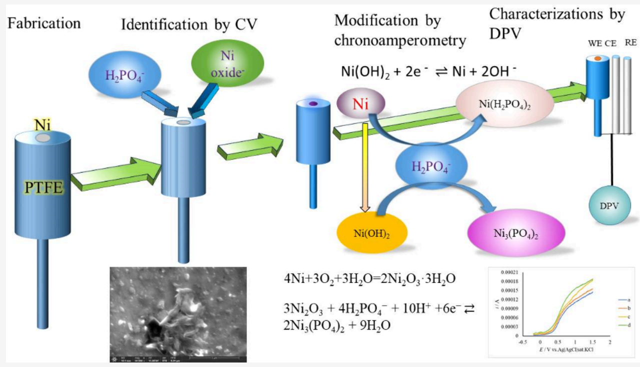
ABSTRACT: We present a study of high-performance electrochemical phosphate sensors, which are exquisitely designed and easy to operate. We innovatively utilized the insolubility of nickel phosphate and developed a new type of sensor through electrochemical methods. The experiment first used cyclic voltammetry to determine −0.4 V as the optimal electrochemical modification potential and used constant potential electrodeposition technology to form a nickel oxide layer on the surface of the nickel electrode, which serves as the active layer in response to phosphate ions. The changes in the surface structure and chemical composition of the electrode before and after modification were thoroughly characterized by scanning electron microscopy and energy scattering spectroscopy analysis. The performance evaluation of the sensor shows that the modified nickel electrode has excellent responsiveness to phosphate ions in the concentration range of 10^{-7} to 10^{-10} mol/L, with a detection lower limit of 10^{-10} mol/L. As the concentration decreases, a shoulder peak appears at ∼0.63 V and the current change shows a regular increase. Compared with traditional detection methods, this sensor exhibits higher stability and practicality and is suitable for the rapid identification of phosphates in real samples. In summary, this study successfully developed a fast, sensitive, and wide response range current type electrochemical phosphate sensor, which has broad application prospects in environmental monitoring, water quality analysis, and biomedical fields.



■ INTRODUCTION

Phosphorus is a ubiquitous substance in nature. Following calcium, phosphorus is the next most prevalent mineral found in the human body, making up roughly 1% of total body weight.[1,2] When present in the environment, phosphorus typically takes the form of either inorganic salts or organic phosphate esters. The inorganic salts consist of three different types of phosphates: PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$.[3,4] The lack of phosphate may lead to muscle weakness and bone mineralization in the human body, but excessive phosphate content can cause renal dysfunction.[5−9] Natural water and wastewater also contain phosphates. If excessive phosphate is present in wastewater discharged from human production and daily life, it can cause water pollution and frequent eutrophication in lakes and coastal waters.[10−12] The environment is safeguarded by phosphate ions, which are not only essential to the human body but also of great significance.[13] Therefore, the current research trend is how to conveniently and quickly detect phosphate ions.

There are many methods for detecting phosphate ions, and there are two types of conventional detection methods: spectrometric analysis and chromatographic analysis. Spectrometric analysis methods include ammonium molybdate spectrophotometry[14] and phosphomolybdate blue spectrophotometry,[15] while chromatographic analysis methods include ion chromatography.[16] However, these methods have complex operations and long detection times. Countless studies have been conducted on phosphate detection techniques, with fluorescence spectroscopy[17,18] being a widely employed qualitative or quantitative analysis technique that mirrors the features of substances based on fluorescence alterations. Sukhendu Mandal tested the selectivity and sensitivity of the sensor to PO_4^{3-} and Fe^{3+} through fluorescence spectroscopy. The sensor can detect phosphate ions and Fe^{3+} ions in water.[19] Compared with traditional instrument analysis methods such as chromatography and spectroscopy, electrochemical sensors have the following unique advantages in detecting phosphate ions:1. Real time monitoring and rapid response: Electrochemical sensors can achieve real-time online monitoring, with

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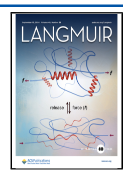

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fast response speed and the ability to obtain detection results in a short period of time, making them suitable for application scenarios that require rapid feedback. However, chromatographic and spectroscopic methods usually require longer sample processing and analysis time.2. Portability and Low Cost: Electrochemical sensors have a relatively simple structure, small size, easy portability, and low manufacturing costs, making them easy to detect on site and for large-scale applications. In contrast, chromatographs and spectrometers typically have complex equipment, high costs, and are not easy to move. 3. High sensitivity and low detection limit: As shown in this study, electrochemical sensors can detect extremely low concentrations (such as 10^{-10} mol/L) of phosphate ions with high sensitivity, which is particularly important for trace analysis. However, some spectroscopic or chromatographic techniques may have limited sensitivity in low concentration detection. 4. Easy operation and maintenance: Electrochemical sensors are relatively easy to operate and maintain, with low maintenance costs. They do not require complex sample pretreatment and professional knowledge to operate. In contrast, chromatographic and spectroscopic analysis often require professional technical personnel to operate and maintain. 5. Strong environmental adaptability: Electrochemical sensors have relatively loose requirements for detecting the environment and can operate under various conditions, such as extreme pH values, temperature changes, etc., while chromatographic and spectroscopic analysis may have stricter requirements for experimental conditions. 6. Low energy consumption: Electrochemical sensors have lower energy consumption during operation, making them more energy-efficient and environmentally friendly, while chromatographs and large-scale spectroscopic equipment often consume more energy. In summary, electrochemical sensors exhibit significant advantages over traditional chromatography and spectroscopy methods in detecting phosphate ions due to their fast, sensitive, portable, cost-effective, and easy operation. They are particularly suitable for situations that require fast and real-time monitoring.

Potentiometric ion selective electrodes[4,20] and amperometric biosensors,[21] as well as electrochemical analysis, can be used to detect phosphate ions - a fact noted by Nishith R. Modi project uses phenyl urea modified calix[4] arene as a special ion carrier for rapid and accurate determination of phosphate in actual samples. Its selectivity and response are good, and it can detect various changes in phosphate concentration in wastewater.[22] Taranpreet Kaur developed a phosphate biosensor using extracellular polymers produced by Acinetobacter, which can bind to phosphates.[23]

Ion selective electrodes offer benefits such as rapid response time, exceptional sensitivity, a broad measurement range, and the potential for compact equipment design, which makes them ideal for analyzing phosphate levels in the environment. A variety of materials can be used for ion selective electrodes, with recent studies focusing on electrodes made of nickel,[24] cobalt,[25] and molybdenum.[26] This article selects Ni metal as the working electrode.

The role of phosphate ions in organisms and their surroundings is paramount, playing a critical part in the development and environment. It is crucial to detect the level of phosphate ions in the environment. Currently, traditional detection methods like spectrometry and chromatography are mostly cumbersome and require a long detection time. This necessitates the development of a rapid, uncomplicated, and highly sensitive electrochemical detector with swift response and broad measurement range.

The study implemented various methods such as cyclic voltammetry(CV), potentiostatic deposition, and differential pulse voltammetry(DPV) to conduct experiments. The Ni electrode underwent modification, and SEM and EDS techniques were utilized to analyze the surface morphology and elemental composition before and after the modification process. The modified Ni electrode exhibited a response to phosphate, leading to the development of a phosphate electrochemical sensor that is both simple and precise.

■ MATERIALS AND METHODS

Reagents. The solution was created using ultrapure water with a resistivity of 18.2 MΩ cm supplied by Shenyang Medical College, along with Na_2HPO_4, NaH_2PO_4, NaOH, NaCl, and anhydrous ethanol sourced from Sinopharm Chemical Reagent Co.,Ltd., tddmi. Nickel wire (diameter 2 mm, length 1 m), polytetrafluoroethylene column (diameter 10 mm, length 1 m), nickel plate (0.1*50*50 mm) were purchased from Tianjin Fuyu Fine Chemical Co.,Ltd., China. All chemical reagents used are analytical grade and can be directly used without further purification.

Instruments. The experiment involved performing electrochemical tests with an electrochemical workstation (CHI760E)from Shanghai Chenhua Instrument Co., Ltd. in China, SEM and EDS were conducted with a Thermo Scientific Apreo 2C from Thermo Fisher Scientific (China) Co., Ltd., and real sample test was conducted by using a UV–vis spectrophotometer (1200,, Jingke, Co., Ltd., China).

Preparation of Working Electrodes. Divide the polytetrafluoroethylene into 25 mm sections, and then employ a drilling machine of 2 mm diameter to drill through them. Subsequently, cut a nickel wire of approximately 100 mm in length. Thread the nickel wire into the polytetrafluoroethylene, align the working end plane, and grind the working end plane with 120 mesh,240 mesh,400 mesh,600 mesh, and 800 mesh sandpaper until the plane is smooth and flat. Then grind the polished deer skin to a mirror finish using 0.5 μm alumina oxide. Rinse the ready working electrodes with distilled water and anhydrous ethanol using ultrasonic cleaning for a duration of 5 min. Dry the prepared electrodes with nitrogen gas for later use

Electrochemical Measurement. Cyclic voltammetry (CV) was used to measure the three electrode system's electrochemical properties, consisting of a nickel working electrode, a platinum counter electrode and an Ag | AgCl | sat KCl reference electrode. The electrode was placed in NaH_2PO_4 solution with different concentration gradients, 0.1 mol/L NaOH solution, and all concentrations of NaH_2PO_4 solution were adjusted to pH 7 using buffer solution.

Modification of the Nickel Electrode. The study utilized a three electrode setup and employed the continuous potential deposition technique in a 0.1 mol/L sodium hydroxide solution. The cyclic voltammetry (CV) technique involves sweeping the potential applied to the working electrode between two limits at a constant rate. The resulting current is recorded as a function of the applied potential. The CV technique provides valuable information about the electrochemical reactions occurring at the electrode surface, including the identification of oxidation and reduction potentials.

Evaluation of the Response Characteristics of the Ni-Modified Electrode. DPV (Differential Pulse Voltammetry) was employed with a three electrode setup to analyze NaH_2PO_4 solutions at concentrations between 10^{-7} M and 10^{-10} M, followed by the separate analysis of NaH_2PO_4 solutions with varying concentration gradients.

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Utilizing scanning electron microscopy (SEM) in conjunction with energy dispersive spectroscopy (EDS). Tests was carried out with 0.1*50*50 mm high-purity nickel sheets in a three electrode setup. The working electrode was a high-purity nickel sheet, while the counter electrode was made of platinum and the reference

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electrode was Ag | AgCl | sat KCl. The high-purity nickel electrode was altered using a potentiostatic deposition technique, with no direct contact between the electrode and the nickel sheet. The modification potential was shown to be −0.4 V according to the results in Figure 3. The modified metal sheet was cut to 0.1*10*10 mm. At this time, the high-purity nickel sheet was modified to generate Ni oxide, and the phosphate modification of Ni oxide was continued. The experimental setup consisted of a three-electrode configuration, in which the working electrode was a sheet of Ni oxide metal and the counter electrode was made of platinum. The reference electrode used was Ag | AgCl | sat. KCl electrode displayed a shifted potential of −0.4 V as indicated in the graphical data.

■ RESULTS AND DISCUSSION

Electrochemical Characteristics. CV was used to examine the electrochemical properties of Ni electrodes that had not been modified in various concentrations of NaH_2PO_4 solution. The Ni electrodes were immersed in NaH_2PO_4 solutions with concentrations ranging from 0.02 to 0.1 M, with a scanning range of −0.8 to 1 V and a scanning speed of 0.05 V s^{-1}. The cyclic voltammogram obtained is displayed in Figure 1A, revealing oxidation peaks occurring at −0.35 V across all five concentrations tested. The peak current and concentration of NaH_2PO_4 solution were found to be inversely related, as illustrated in Figure 1B. This linear relationship was further evidenced by the fact that the potential for the peak current remained constant, with no left or right deviation. Some potential deviations may be caused by experimental errors. Through multiple CV experiments on the nickel electrode, it has been observed that phosphate ions react with it, thus producing other substances on its surface instead of pure Ni. The concentration dependence experiment proves that the potential is −0.35 V, Ni reacts with phosphate ions. Under different pH conditions, the forms and distribution ratios of dihydrogen phosphate and monohydrogen phosphate ions also vary. Under pH 7, monohydrogen phosphate ion and dihydrogen phosphate ion coexist in a similar manner, with their distribution being analogous. To further verify whether the nickel electrode reacts with monohydrogen phosphate or dihydrogen phosphate, pH dependent CV experiments were conducted. The pH of 0.1 M NaH_2PO_4 solution was adjusted to 5, 5.5, 6, 6.5, and 7, respectively. CVs were performed using a three-electrode setup, which included a nickel working electrode, a platinum counter electrode, and an Ag | AgCl | sat KCl reference electrode. The data presented in Figure 2 demonstrates that as the pH level raises, the anodic peak decreases steadily, with no significant change in peak current observed between pH 5 and 6. At pH 7, a significant decrease in peak current is observed. The potential pH diagram of Ni at 25 °C and the concentration-dependent cyclic voltammogram both demonstrate that at −0.35 V, the Ni electrode dissociates Ni^{2+} and interacts with dihydrogen phosphate. Moreover, the scan rate dependency test reveals that the arithmetic square root of the scanning speed is directly proportional to the peak current, thus controlling this reaction via diffusion (Figure S2).

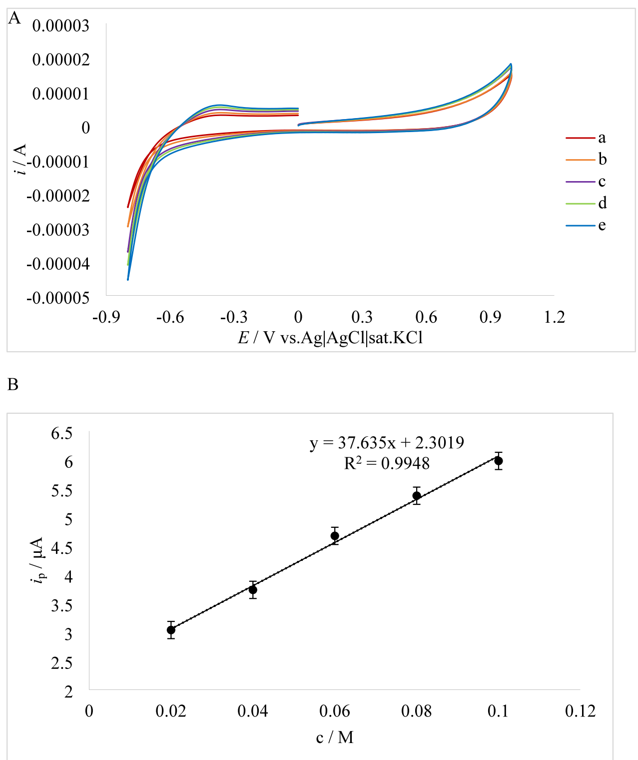

Figure 1. (A) Cyclic voltammograms of the nickel electrode in different concentrations of a NaH_2PO_4 solution: (a) 0.02, (b) 0.04, (c) 0.06, (d) 0.08, and (e) 0.1 M. (B) Relationship between concentration and peak current.

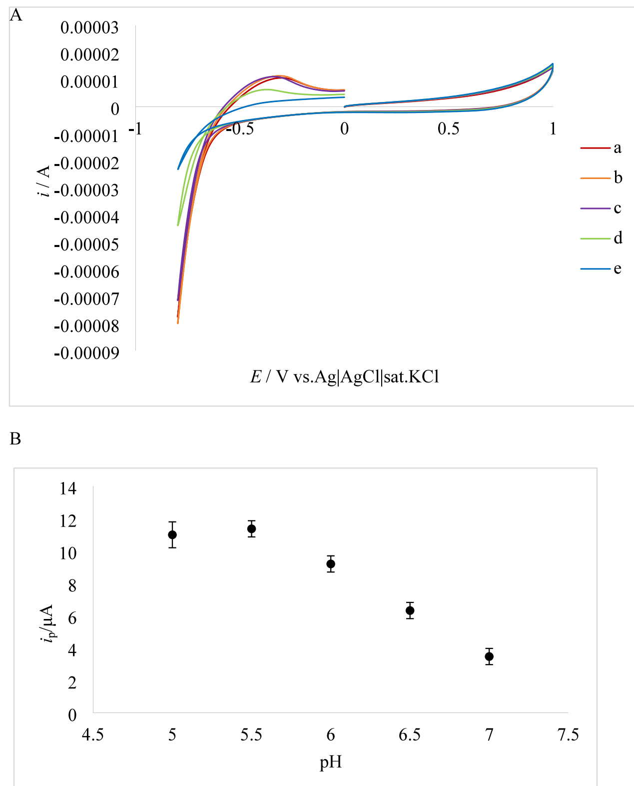

Figure 2. (A) Cyclic voltammograms and (B) pH vs peak current of the nickel electrode in a 0.1 M NaH_2PO_4 solution at (a) pH 5, (b) 5.5, (c) 6, (d) 6.5, and (e) 7.

Modification of Ni Electrodes. Figure 3 displays the outcomes of a cyclic voltammetry experiment to modify the Ni electrode, which revealed an optimal modified potential of 0.4 V. This trial was conducted with three-electrode-system. In a solution of 0.1 mol/L NaOH, the working electrode was a nickel one, the counter electrode was made of platinum, and

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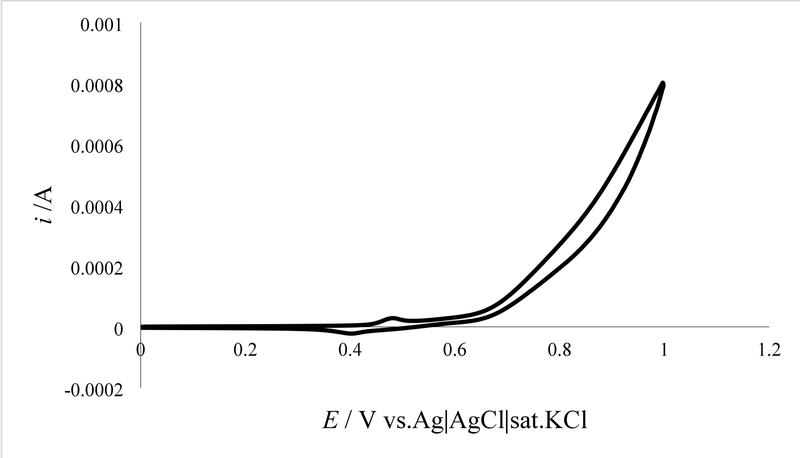

Figure 3. Cyclic voltammogram of the nickel electrode in 0.1 M NaOH.

the reference electrode was an Ag | AgCl | sat KCl electrode deposited through constant potential electrodeposition (i-t) method at a fixed potential of 0.4 V for about 2000 s. The outcome is illustrated in Figure 4, with the current decreasing

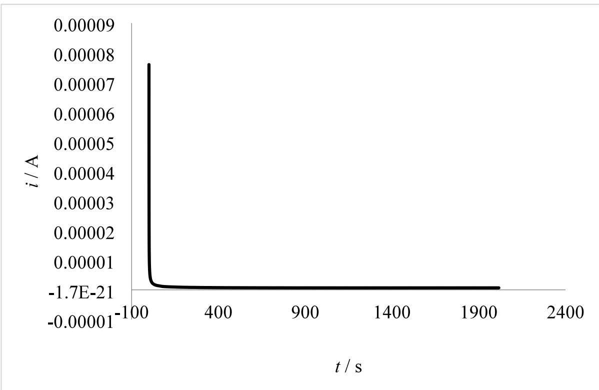

Figure 4. Current time curve of the Ni electrode at a constant potential of 0.48 V in a 0.1 M NaOH solution.

quickly to nearly 0 A once the reaction initiated. Based on the potential pH diagram of nickel at 25 °C, it can be observed from Figure S1 that under the condition of pH 13, Ni undergoes an oxidation reaction at 0.4 V, generating Ni oxide.

SEM and EDS Analysis. Using a scanning electron microscope to photograph a high-purity nickel sheet, as shown in Figure 5A, no distinguishing marks were visible on the nickel sheet's surface when magnified to 5000 times, with only a few blemishes and impurities present. The high-purity nickel sheet was modified in a sodium hydroxide solution and photographed, as shown in Figure 5B, at a magnification of 50000 times, gaps of varying sizes were observed on the nickel metal sheet. This could be attributed to hydroxide forming on its surface. To deposit the modified nickel metal onto the sheet, a constant potential electrodeposition method in NaH_2PO_4 solution was used. The film was then captured using a scanning electron microscope, as depicted in Figure 5C, with a magnification of 10000 times. Crystals of varying sizes were observed around the voids.

An energy dispersive spectrometer (EDS) was utilized to analyze the elemental makeup of the three sample surfaces. Figure 6A depicted the EDS spectrum of Nickel, and the EDS results of pure Ni showed obvious peaks at 0.02, 0.86, and 7.46 keV, all of which were Ni elements. Figure 6B displayed the Ni oxide spectrum. Figure 6C displays the EDS spectrum of Ni's phosphate compound, which reveals that the modified Ni metal is an O element, as evidenced by its three peaks and the obvious ones at 0.26 and 0.52 keV. After phosphate deposition, the Ni metal still shows a peak at 2.14 keV, where phosphate element is present. Therefore, the conclusion is better verified. We conducted surface scanning of the energy spectrum to explore the composition of the modified electrode, and the results are displayed in Figure S4. This was done by generating nickel hydroxide on the modified Ni metal surface, followed by phosphate deposition which created a nickel phosphate compound, nickel oxide is generated on the surface. Based on the above material characterization and analysis, the response mechanism of this sensor can be preliminarily explained by the equations from (1) to (5)

$$Ni^{2+} + 2e^- \rightleftharpoons Ni \tag{1}$$

$$Ni(OH)_2 + 2e^- \rightleftharpoons Ni + 2OH^- \tag{2}$$

$$Ni(H_2PO_4)_2 + 2e^- \rightleftharpoons Ni + 2H_2PO_4^- \tag{3}$$

$$2Ni_3O_4 + 3Ni(H_2PO_4)_2 \leftrightarrow 3Ni_3(PO_4)_2 + 6H_2O + O_2 \tag{4}$$

$$2NiO + Ni(H_2PO_4)_2 \leftrightarrow Ni_3(PO_4)_2 + 2H_2O \tag{5}$$

Evaluation of the Response Characteristics of Ni Oxide. Following the potentiostatic deposition (amperometric i-t curve) process to modify the Ni electrode, a layer of Ni oxide formed on its surface. The reactivity of the Ni oxide toward dihydrogen phosphate ions was analyzed using differential pulse voltammetry (DPV). The experimental setup consisted of a three electrode system, comprising the working electrode, counter electrode, and reference electrode. The modified Ni electrode served as the working electrode, while the platinum electrode was used as the counter electrode. Additionally, a Ag | AgCl | sat KCl electrode was utilized as the reference electrode and a $10^{-7} \sim 10^{-10}$ mol/L sodium dihydrogen phosphate solution was prepared. The findings are depicted in Figure 7, and it can be found that Ni oxide has a good response effect on phosphate ions with a concentration of $10^{-7} \sim 10^{-10}$ mol/L. As the concentration decreases, shoulder peaks appear at around 0.63 V, and the current

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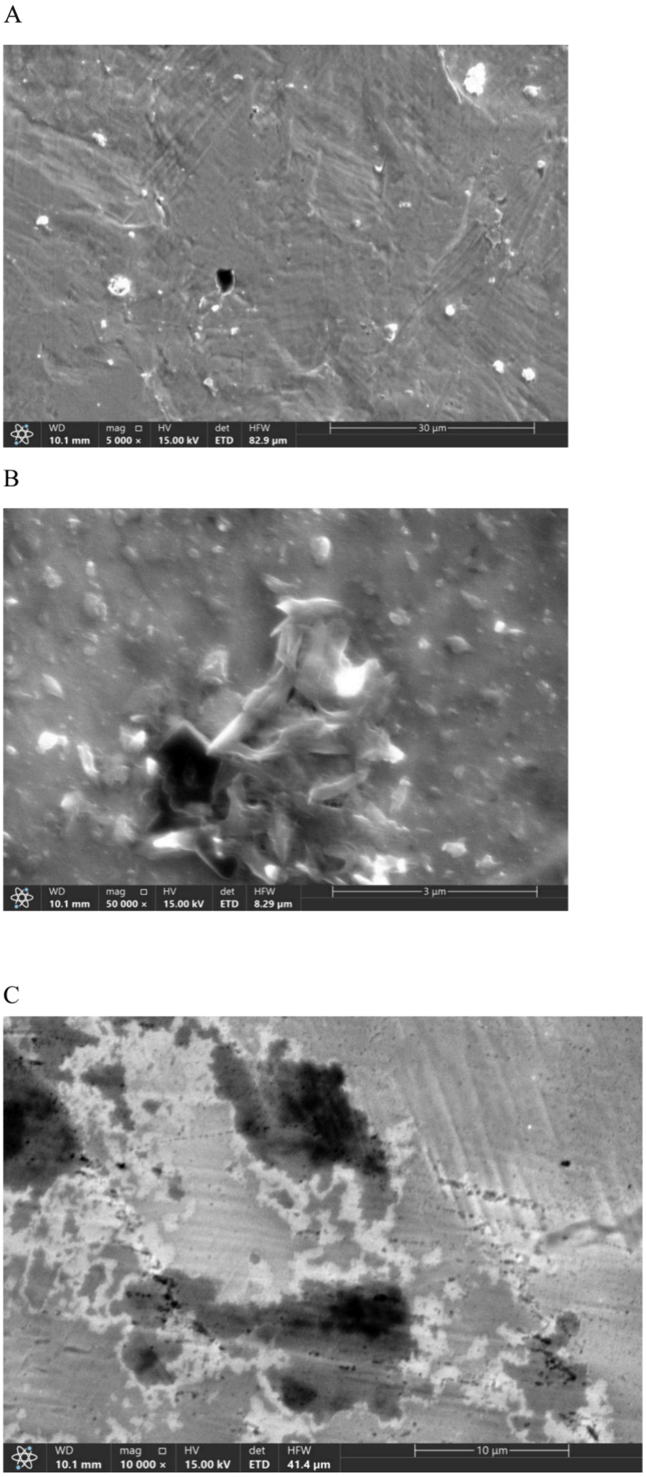

Figure 5. Scanning electron microscope images of Ni, nickel oxides, and nickel phosphate compounds: (A) high-purity nickel sheet, (B) Ni oxide, and (C) phosphate compounds.

increases regularly, proving that the detection line is 10^{-10} mol/L. In Figure 7, the peak of DPV for phosphate ions belongs to the shoulder peak and overlaps with the subsequent peaks. So it does not seem very obvious, so we performed another differentiation on DPV, as shown in the following figure. After differentiation, a peak roughly appeared, and we then smoothed it out to obtain a clearer peak (Figure S5). In order to confirm the conclusion, solutions with varying

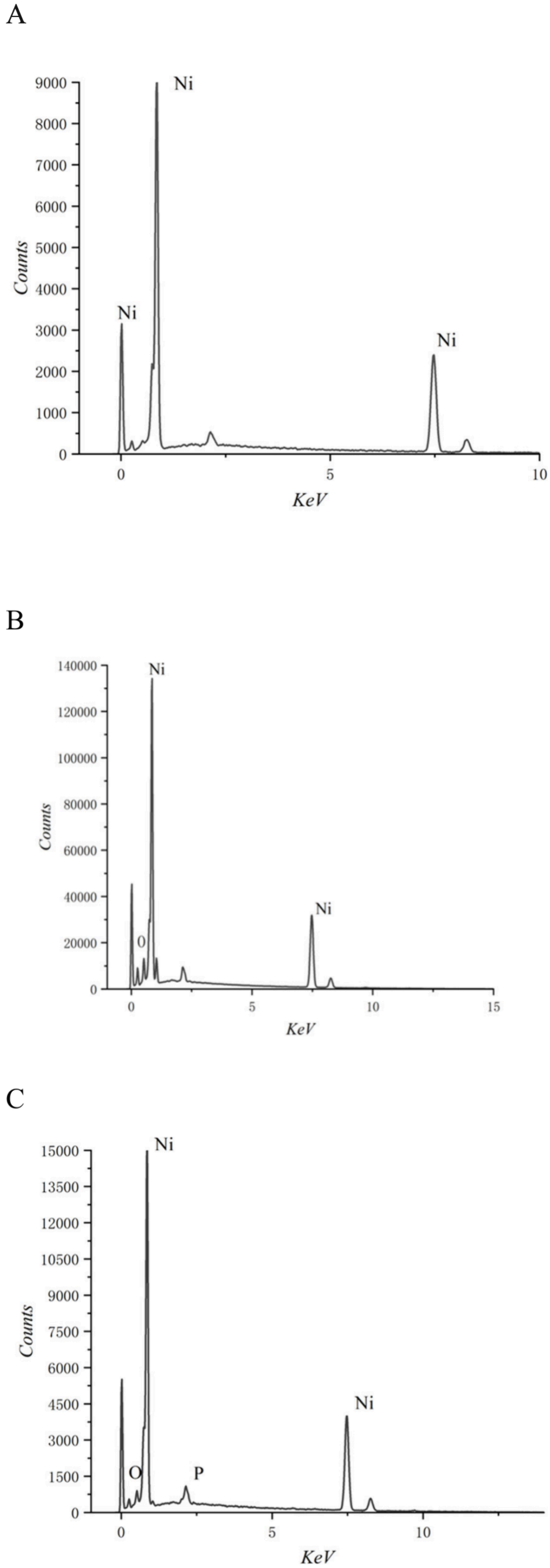

Figure 6. EDS spectrum of (A) pure Ni, (B) Ni oxide, and (C) nickel phosphate compounds.

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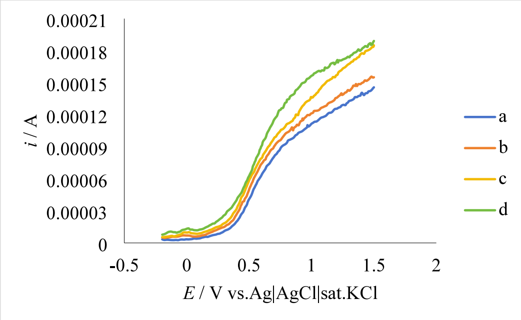

Figure 7. Differential pulse voltammetry curves of Ni oxide in different concentrations of a NaH_2PO_4 solution at (a) 10^{-7}, (b) 10^{-8}, (c) 10^{-9}, and (d) 10^{-10} M.

gradients of $10^{-10} \sim 10^{-8}$ mol/L were prepared and adjusted to a pH of 7. It is apparent that the peak current at 0.63 V consistently rises as the concentration increases, displaying a linear correlation with concentration, as depicted in Figure 8. The sensitivity of the current sensor is 5013 A/mol.

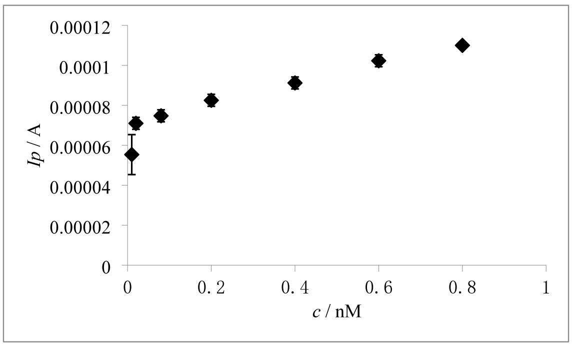

Figure 8. Relationship between differential pulse voltammetry peak current and concentration of nickel oxide in NaH_2PO_4 solutions of different concentrations.

Real Sample Test and Recovery Test. We use the blue molybdenum colorimetric method as the traditional phosphate ion detection method to compare the detection performance with this sensor. The blue molybdenum colorimetric method, also known as the phosphorus molybdenum blue colorimetric method, is a commonly used analytical method for determining the phosphate content in water or solution. This method is based on the reaction between phosphate ions and molybdates under certain conditions to generate blue phosphorus molybdenum blue complexes, whose color depth is directly proportional to the concentration of phosphate ions. The content of phosphate can be quantitatively determined through colorimetric analysis

Table 1 reveals that the test results of the current sensor are comparable to those of conventional methods, suggesting its practicality. To further assess its recovery, the addition recovery test was utilized. It was found that the recovery of current sensor was more than 96% in various common liquid samples (Table 2).

Table 1. Real Sample Test Compared to the Results of a Conventional Phosphomolybdate Blue Spectrometer

sample	current sensor (mM)	colorimetry (mM)
vinegar	1.7 ± 0.1	1.8 ± 0.1
apple juice	3.6 ± 0.2	3.8 ± 0.1
waste water	1.3 ± 0.2	1.1 ± 0.2

Table 2. Recovery Test in Different Solutions

sample	added (mM)	found (mM)	recovery rate (%)
distilled water	10.0	9.9 ± 0.1	98
tap water	10.0	9.8 ± 0.1	98
milk	10.0	9.6 ± 0.3	96

In actual sample anti-interference testing, the Soft Hard Acid Base Theory (HSAB Theory) can be used to explain, which is a theory used to describe the strength of Lewis acid−base interactions, distinguishing between "hard" (small, high charge density, weak polarization ability) and "soft" (large, low charge density, strong polarization ability) acid bases. The core nickel oxide film of this ion sensor directly affects the selectivity of the target ion against other competing ions due to its material hardness. According to the HSAB theory, by selecting membrane materials with "soft" or "hard" properties that match the target ion, the affinity of the membrane to the target ion can be optimized, thereby improving the selectivity of the sensor and reducing the interference of nontarget ions (i.e., interfering ions). When designing the sensing mechanism of this sensor, we consider the type of interaction between phosphate ions and the sensing interface (hard soft pairing), which can effectively reduce nonspecific adsorption caused by mismatched hard soft acid−base interactions, enhance the specificity of the sensor, and improve anti-interference performance. Choosing sensing materials that match the chemical properties of the target ion can not only improve the selectivity of the sensor, but also enhance its stability in long-term use or harsh environments, reducing signal drift and interference caused by environmental factors.

■ CONCLUSION

This study develops a phosphate ion sensor based on Ni electrode. CV was utilized to identify the steady potential of the altered Ni electrode, while constant potential deposition technique was employed to modify the Ni electrode. The Ni electrode was examined using a scanning electron microscope both pre and post modification, allowing for analysis of any shifts in morphology and characteristics present on the electrode surface. Phosphate ion response of the modified Ni electrode was determined through the use of differential pulse voltammetry. The study revealed that, when the pH of the solution was 7, Ni oxide was formed on the surface of a modified Ni electrode. This electrode displayed an excellent reaction to phosphate ions at concentrations ranging from 10^{-7}−10^{-10} M, with a detection limit of 10^{-10} M and remarkable potential stability. Compared with existing reported phosphate ion sensors, this sensor has the advantages of higher sensitivity and simple modification method, and is suitable for long-term real-time online monitoring of phosphate ions in various liquid samples.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.4c02342.

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Potential pH diagram of Ni at 25 °C, cyclic voltammetry curves of the nickel electrode in a 0.1 M NaH_2PO_4 solution at pH 7 and different scanning rates, experimental image of the three-electrode system, and map scanning EDS spectrum of the modified Ni electrode (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Calvo, M. S.; Lamberg-Allardt, C. J. Phosphorus. *Adv. Nutr.* **2015**, *6* (6), 860−862.

(2) Lürling, M.; Mackay, E.; Reitzel, K.; Spears, B. M. Editorial - A critical perspective on geo-engineering for eutrophication management in lakes. *Water Res.* **2016**, *97*, 1−10.

(3) Meng, Q. T.; Wang, Y.; Yang, M.; Zhang, R.; Wang, R. J.; Zhang, Z. Q. A new fluorescent chemosensor for highly selective and sensitive detection of inorganic phosphate (Pi) in aqueous solution and living cells. *RSC Adv.* **2015**, *5* (66), 53189−53197.

(4) Zhao, B.; Liu, T.; Fang, Y.; Wang, L. Y.; Kan, W.; Deng, Q. G.; Song, B. Actuators. A new selective chemosensor based on phenanthro[9,10-d] imidazole-coumarin with sequential "on-off-on" fluorescence response to Fe~(3+) and phosphate anions and its application in live cell. *Sens. Actuators, B* **2017**, *246*, 370−379.

(5) Auesukaree, C.; Homma, T.; Tochio, H.; Shirakawa, M.; Kaneko, Y.; Harashima, S. Intracellular phosphate serves as a signal for the regulation of the PHO pathway in Saccharomyces cerevisiae. *J. Biol. Chem.* **2004**, *279* (17), 17289−17294.

(6) Alipanahpour Dil, E.; Ghaedi, M.; Asfaram, A.; Tayebi, L.; Mehrabi, F. A ferrofluidic hydrophobic deep eutectic solvent for the extraction of doxycycline from urine, blood plasma and milk samples prior to its determination by high-performance liquid chromatography-ultraviolet. *J. Chromatogr. A* **2020**, *1613*, 460695.

(7) Zhao, H. X.; Liu, L. Q.; Liu, Z. D.; Wang, Y.; Zhao, X. J.; Huang, C. Z. Highly selective detection of phosphate in very complicated matrixes with an off-on fluorescent probe of europium-adjusted carbon dots. *Chem. Commun. (Cambridge, U. K.).* **2011**, *47* (9), 2604−2606.

(8) Sun, S.; Jiang, K.; Qian, S.; Wang, Y.; Lin, H. Applying Carbon Dots-Metal Ions Ensembles as a Multichannel Fluorescent Sensor Array: Detection and Discrimination of Phosphate Anions. *Anal. Chem.* **2017**, *89* (10), 5542−5548.

(9) Vervloet, M. G.; Sezer, S.; Massy, Z. A.; Johansson, L.; Cozzolino, M.; Fouque, D. The role of phosphate in kidney disease. *Nature reviews. Nephrology.* **2017**, *13* (1), 27−38.

(10) Udnan, Y.; McKelvie, I. D.; Grace, M. R.; Jakmunee, J.; Grudpan, K. Evaluation of on-line preconcentration and flow-injection amperometry for phosphate determination in fresh and marine waters. *Talanta.* **2005**, *66* (2), 461−466.

(11) Katano, H.; Ueda, T. Spectrophotometric determination of phosphate anion based on the formation of molybdophosphate in ethylene glycol-water mixed solution. *Anal. Sci.* **2011**, *27* (10), 1043−1047.

(12) Jia, X.; Chen, D.; Bin, L.; Lu, H.; Zhang, R.; Zheng, Y. Highly selective and sensitive phosphate anion sensors based on AlGaN/GaN high electron mobility transistors functionalized by ion imprinted polymer. *Sci. Rep.* **2016**, *6*, 27728.

(13) Karthikeyan, R.; Berchmans, S. Inorganic-Organic Composite Matrix for the Enzymatic Detection of Phosphate in Food Samples. *J. Electrochem. Soc.* **2013**, *160* (6), B73−B77.

(14) Ganesh, S.; Khan, F.; Ahmed, M. K.; Velavendan, P.; Pandey, N. K.; Kamachi Mudali, U. Spectrophotometric determination of trace amounts of phosphate in water and soil. *Water Sci. Technol.* **2012**, *66* (12), 2653−2658.

(15) Zhu, X. T.; Zhu, Z. X.; Ye, M. Y. Photocatalytic Degradation of Organic Phosphorus in Microreactor and On-line Detection of Total Phosphorus. *Fenxi Huaxue* **2019**, *47* (1), 106−111.

(16) Biesaga, M.; Schmidt, N.; Seubert, A. Coupled ion chromatography for the determination of chloride, phosphate and

sulphate in concentrated nitric acid. *J. Chromatogr. A* **2004**, *1026* (1–2), 195–200.
(17) Liu, J. Y.; Liu, Y. B.; Wang, W.; Zhang, S. Q.; Tang, L.; Ma, P. Y.; Song, D. Q.; Fei, Q. A ratiometric fluorescent sensor for the detection of phosphate. *Luminescence.* **2023**, *38* (2), 152–158.
(18) Callan, J. F.; de Silva, A. P.; Ferguson, J.; Huxley, A. J. M.; O'Brien, A. M. Fluorescent photoionic devices with two receptors and two switching mechanisms: applications to pH sensors and implications for metal ion detection. *Tetrahedron.* **2004**, *60* (49), 11125–11131.
(19) Chandra Rao, P.; Mandal, S. Europium-Based Metal-Organic Framework as a Dual Luminescence Sensor for the Selective Detection of the Phosphate Anion and Fe(3+) Ion in Aqueous Media. *Inorg. Chem.* **2018**, *57* (19), 11855–11858.
(20) Gasperini, L.; Maniglio, D.; Motta, A.; Migliaresi, C. An Electrohydrodynamic Bioprinter for Alginate Hydrogels Containing Living Cells. *Tissue Eng., Part C* **2015**, *21* (2), 123–132.
(21) Engblom, S. O. The phosphate sensor. *Biosens. Bioelectron.* **1998**, *13* (9), 981–994.
(22) Modi, N. R.; Patel, B.; Patel, M. B.; Menon, S. K. Novel monohydrogenphosphate ion-selective polymeric membrane sensor based on phenyl urea substituted calix[4]arene. *Talanta.* **2011**, *86*, 121–127.
(23) Kaur, T.; Ganguli, A.; Ghosh, M. Development of exobiopolymer-based biosensor for detection of phosphate in water. *Water Sci. Technol.* **2013**, *68* (12), 2619–2625.
(24) Cheng, W. L.; Sue, J. W.; Chen, W. C.; Chang, J. L.; Zen, J. M. Activated nickel platform for electrochemical sensing of phosphate. *Anal. Chem.* **2010**, *82* (3), 1157–1161.
(25) Xiao, D.; Yuan, H.-Y.; Li, J.; Yu, R.-Q. Surface-Modified Cobalt-Based Sensor as a Phosphate-Sensitive Electrode. *Anal. Chem.* **1995**, *67* (2), 288–291.
(26) Xu, K.; Kitazumi, Y.; Kano, K.; Sasaki, T.; Shirai, O. Fabrication of a Phosphate Ion Selective Electrode Based on Modified Molybdenum Metal. *Anal. Sci.* **2020**, *36* (2), 201–205.

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