



# Investigation into an electrochemical sensor for phosphate detection utilizing a cobalt-nickel alloy as a potentiometric probe

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## ABSTRACT

Phosphate compounds are abundant in nature, and their precise identification is of great significance for industries such as agriculture, manufacturing, and healthcare. Traditional spectroscopic and chromatographic techniques are difficult to achieve rapid and real-time detection due to their complex steps and the need for large equipment, while sensor technology provides an effective solution for this. This study used the steady current electrodeposition method to deposit cobalt and nickel on the surface of a copper electrode, and then carried out phosphate targeted modification on the cobalt nickel alloy electrode, successfully preparing an insoluble cobalt nickel phosphate sensor. The sensor has excellent performance, with a response slope of  $-58.8 \text{ mV dec}^{-1}$  to phosphate ions, a detection limit as low as  $10^{-6} \text{ M}$ , a linear range of  $10^{-6} \text{ M}$ - $0.1 \text{ M}$ , a response time of only 15 s, and a continuous 24-h test potential drift of less than 2 mV. The service life is as long as one month, and the selectivity coefficient for common interfering anions is less than  $-3$ . Compared with the traditional blue molybdenum colorimetric method, the detection results are highly consistent, and the recovery rate of the addition test is between 97 % and 98 %. In practical applications, this sensor can quickly and accurately determine the phosphate content in water bodies in the field of water quality monitoring, and timely insight into the eutrophication status of water bodies; In agricultural soil analysis, it can effectively detect the level of phosphate in soil and provide key basis for rational fertilization. Compared with traditional sensing technology, this new type of sensor has significant advantages in detection efficiency and accuracy, which can fully meet the needs of real-time on-site online monitoring and has great potential for application in promoting the development process of related industries.

## 1. Introduction

Phosphoric acid serves as a critical element within living beings,

essential for sustaining vital functions. It forms an integral part of essential biomolecules including DNA, RNA, and ATP, and is involved in various biochemical transformations and the production of energy.

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Consequently, measuring the levels of phosphate can provide insights into an organism's physiological condition and metabolic activities, which holds considerable importance for the fields of biomedical study and the identification of illnesses. Furthermore, phosphorus, a key nutrient essential for vegetation development, plays a crucial role in farming outputs, influencing both the quantity and quality of harvests. When cultivators measure phosphate levels in soil and aquatic systems, they can apply fertilizer accurately to boost harvests, enhancing both productivity and crop excellence. Such practices are vitally important for maintaining steady food supplies and advancing sustainable farming practices. Furthermore, vigilance in tracking phosphate levels is essential in environmental conservation and the oversight of water purity. The release of high amounts of phosphate constitutes a primary factor in contaminating water sources, precipitating eutrophication that can result in ecological harm and the degradation of water quality. By detecting the concentration of phosphate in water bodies, pollution sources can be detected and controlled in a timely manner, protecting the health and ecological balance of water resources. The detection of phosphates has wide applications in industrial production and food safety. For instance, within the realms of food manufacturing and the creation of drinks, phosphates serve roles as both preservatives and agents for stabilization and taste improvement. Through the measurement of phosphate levels in edibles, one can ascertain the conformity and safety of such consumables.

Globally and within national borders, the identification of phosphates remains a fervently studied subject. At present, the current standard methods for detecting phosphates include continuous flow ammonium molybdate spectrophotometry [1], ion chromatography [2], and phosphomolybdate blue spectrophotometry [3]. However, these methods are limited by their reliance on large instruments, the need for pre-processing, and the complexity of operations, and cannot meet the requirements of real-time online detection on site. The emergence of electrochemical sensors has to some extent solved the above problems. Because electrochemical sensors are low-cost, easy to operate, portable, and do not rely on large analytical instruments, they can achieve real-time on-site online monitoring, which is incomparable to traditional spectroscopic and chromatographic methods.

Over the past few years, substantial advancements have occurred in the study of electrochemical sensors for phosphate ions, offering an innovative technique for the quick and precise identification of phosphate levels. The working principle of the phosphate ion electrochemical sensor is based on the electrochemical interaction between phosphate ions and electrode materials. Through the refinement of electrode material functionality and the strategic choice of electrochemical techniques, one can attain highly sensitive and selective identification of phosphate ions. At present, research on phosphate ion electrochemical sensors mainly focuses on improving electrode materials, optimizing detection methods, and practical applications of sensors.

Scientists are dedicated to the advancement of electrode substances that exhibit enhanced sensitivity, specificity, and durability. For example, new electrode materials such as nanomaterials [4–7], composite materials [8–10], and biomaterials [11–13] are widely used in the preparation of phosphate ion electrochemical sensors. These substances possess outstanding electrochemical characteristics, which can significantly enhance the responsiveness of detection devices. Moreover, scientists have refined the electrode substance by employing techniques such as surface alterations [14–16] and the incorporation of dopants [17] to boost the sensor's efficacy even more. With respect to sensing techniques, scientists persistently refine electrochemical strategies to enhance the precision and responsiveness of phosphate ion identification. Standard electrochemical approaches utilized consist of cyclic voltammetry [18], linear sweep voltammetry [19], and potentiometry [20], among others. Each of these techniques carries distinct pros and cons, and scientists select suitable sensing strategies according to specific requirements. In addition, researchers have also attempted to

combine electrochemical methods with other techniques, such as optical methods [21], biosensors [22], etc. To enhance the capability to identify phosphate ions effectively.

Phosphate ion electrochemical sensors are prevalent in their real-world usage, especially in sectors like environmental surveillance, farming activities, and the regulation of water purity. To illustrate, these sensors play a critical role in evaluating water quality [23] by measuring phosphate levels in aquatic ecosystems, thereby bolstering efforts in assessing water conditions and managing aquatic pollution. In agricultural production [24], sensors can be used to monitor the phosphate content in soil, providing scientific basis for crop fertilization. Furthermore, sensors that detect electrochemical activity of phosphate ions have applications in the biomedical realm [25], for instance, in monitoring the phosphate metabolic processes within living entities.

However, despite significant progress in the research of phosphate ion electrochemical sensors, there are still some challenges and issues. To begin with, there is a necessity for the enhancement of both the resilience and longevity of electrode materials to satisfy the demands of sustained, stable functionality in real-world settings. Moreover, it is imperative to advance the precision and discernment of the sensor to facilitate more precise phosphate ion monitoring. Furthermore, considerations must also be given to reducing the production expenses of these sensors and improving their convenience for use in on-the-ground applications. During the initial investigations conducted by our team of researchers, it was determined that both cobalt and nickel possess distinct pros and cons regarding their respective capacities to interact with phosphate ions [26]. On this basis, we also referred to some modification methods of other electrochemical sensors [27–44]. Therefore, in this study, cobalt and nickel was alloy modified to construct a high-performance phosphate electrochemical ion sensor.

## 2. Materials and methods

### 2.1. Reagents

The solution was prepared using ultrapure water with a resistivity of 18.2 MΩ cm provided by Shenyang Medical College, CoSO<sub>4</sub>, NiSO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, NaHCO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaCH<sub>3</sub>COOH, ammonium molybdate, boric acid, sulfuric acid, ascorbic acid, HCl, NaOH, NaCl were purchased from Tianjin Ruijinte Chemical Co. in Tianjin, China. Tianjin, China-based Tianjin Fuyu Fine Chemical Co. supplied the anhydrous ethanol that was acquired. All chemical reagents used are analytical grade (99.9 %) and can be used directly without further purification. Copper rod (diameter 2 mm, length 100 mm), the electrode reaction area is 3.14 mm<sup>2</sup>, PTFE (polytetrafluoroethylene) column (diameter 10 mm, length 30 mm), and copper plate (0.1\*50\*50 mm) were purchased from Guangtai Metal, Tianjin, China.

### 2.2. Equipment

Operate a device for electrochemical analysis from Shanghai Chenhua Instrument Co., Ltd., (China) to evaluate and analyze electroplating, electrochemical modification, and sensor performance. The electrochemical workstation was purchased from Shanghai Chenhua Instrument Co., Ltd. (Shanghai, China) Employ a sequential configuration wherein a scanning electron microscope is partnered with an energy spectrometer, specifically the Thermo Scientific Apreo 2C from Thermo Fisher Scientific (China) Co., Ltd., based in China, to analyze the surface properties of electrode materials. Scanning electron microscope purchased from Thermo Fisher Scientific (Shanghai) Instrument Co., Ltd. Utilize the UV–visible spectrophotometer from Applied Bio systems (ABI), USA, to conduct the analysis and ascertain the results using the conventional blue molybdenum colorimetric technique. Ultrasonic cleaner (purchased from JD Lianha'er Instrument Manufacturing Co., Ltd., China) is used for electrode cleaning.

### 2.3. Preparation of basic electrode

Place a solid copper shaft, which measures 2 mm across and 100 mm long, into a PTFE(polytetrafluoroethylene) tube, ensuring the dimensions are 10 mm wide and 30 mm tall. The end of the copper shaft should be flush with the PTFE tube to create a substrate working electrode with a round cross-sectional area. Grind the working end surface with sandpaper of 120 mesh, 240 mesh, 400 mesh, 600 mesh, and 800 mesh respectively until the surface is smooth and flat. Wash the ready-to-use working electrode with distilled water and dehydrated ethanol through a five-minute session of ultrasonic cleansing, followed by drying for subsequent application.

### 2.4. Preliminary optimization exploration of electroplating modification conditions

Before the formal testing, we conducted parameter testing using cyclic voltammetry. The research deployed a three-electrode setup to study the electrochemical behavior of a copper electrode immersed in cobalt sulfate and nickel sulfate solutions, employing a basic copper electrode as the active electrode, an Ag/AgCl electrode(the KCl is saturated)for reference purposes, and a platinum electrode to serve as the auxiliary electrode. Cyclic voltammetry, constant voltage electrolysis, chronopotentiometric method and time-based potential measurements were the primary techniques utilized in the analysis.

### 2.5. Fabrication of a copper electrode enhanced with a cobalt-nickel alloy

Based on the electroplating modification parameters discussed earlier, the copper electrode underwent an electroplating modification process. The solution used for electroplating contained nickel sulfate at a concentration of 0.8 M, cobalt sulfate at 0.4 M, potassium chloride at 0.2 M, and boric acid also at 0.2 M. The pH of the electrolyte is controlled at 4.5. The process was carried out at a temperature of 50 °C, employing a water bath as the heating technique. During electroplating, use a magnetic stirrer with a 250 mm magnet to stir at a speed of 1500 rpm. The electroplating method is the chronopotentiometric method, using a pure copper electrode as the working electrode. After acid washing and ultrasonic cleaning, it is dried for later use. Utilizing the Ag/AgCl electrode as the standard reference (the of KCl is saturated) and the Pt electrode as the auxiliary counterpart, the current at the cathode is established at 5 mA, with the duration of the electrodeposition process fixed at 7.5 min. After electroplating, dry it with nitrogen and place it in a self-sealing bag for later use.

### 2.6. Fabrication of a phosphate-modified electrode comprised of cobalt nickel alloy

In a three electrode system, the electrochemical properties of cobalt nickel alloy modified electrodes in sodium dihydrogen phosphate solution were tested. An electrode composed of a cobalt-nickel alloy served as the active electrode, with the Ag/AgCl electrode playing the role of the reference electrode, and the platinum electrode functioning as the auxiliary electrode. The technique of cyclic voltammetry was carried out within a solution of sodium dihydrogen phosphate at 0.1 M concentration and pH 7 to determine the peak anodic current, indicative of the electrodeposition potential for both cobalt and nickel phosphate. The scanning potential range was  $-0.6\text{ V} \sim 0.2\text{ V} \sim -1.3\text{ V}$ . Subsequently, an electrode crafted from a cobalt-nickel mixture underwent a process of electrodeposition via steady voltage electrolysis, facilitating the adherence of cobalt and nickel phosphates to its exterior, consequently endowing it with a distinct reactivity towards phosphate ions.

### 2.7. Sensor performance testing

Within a dual-electrode configuration, a copper substrate modified with cobalt nickel alloy phosphate serves as the active electrode, while a silver/silver chloride electrode functions as the standard electrode. This setup is employed to evaluate the sensor's responsiveness in a phosphate ion-enriched solution, taking into account key performance metrics like the detection threshold, responsiveness, reaction speed, selectivity, consistency, and operational durability. Furthermore, the sensor's capacity to detect substances within real-world specimens was assessed through a comparison to conventional ultraviolet-visible spectrophotometric methods. Finally, an evaluation was conducted on the addition of recycling experiments.

### 2.8. Material characterization of electrode surface

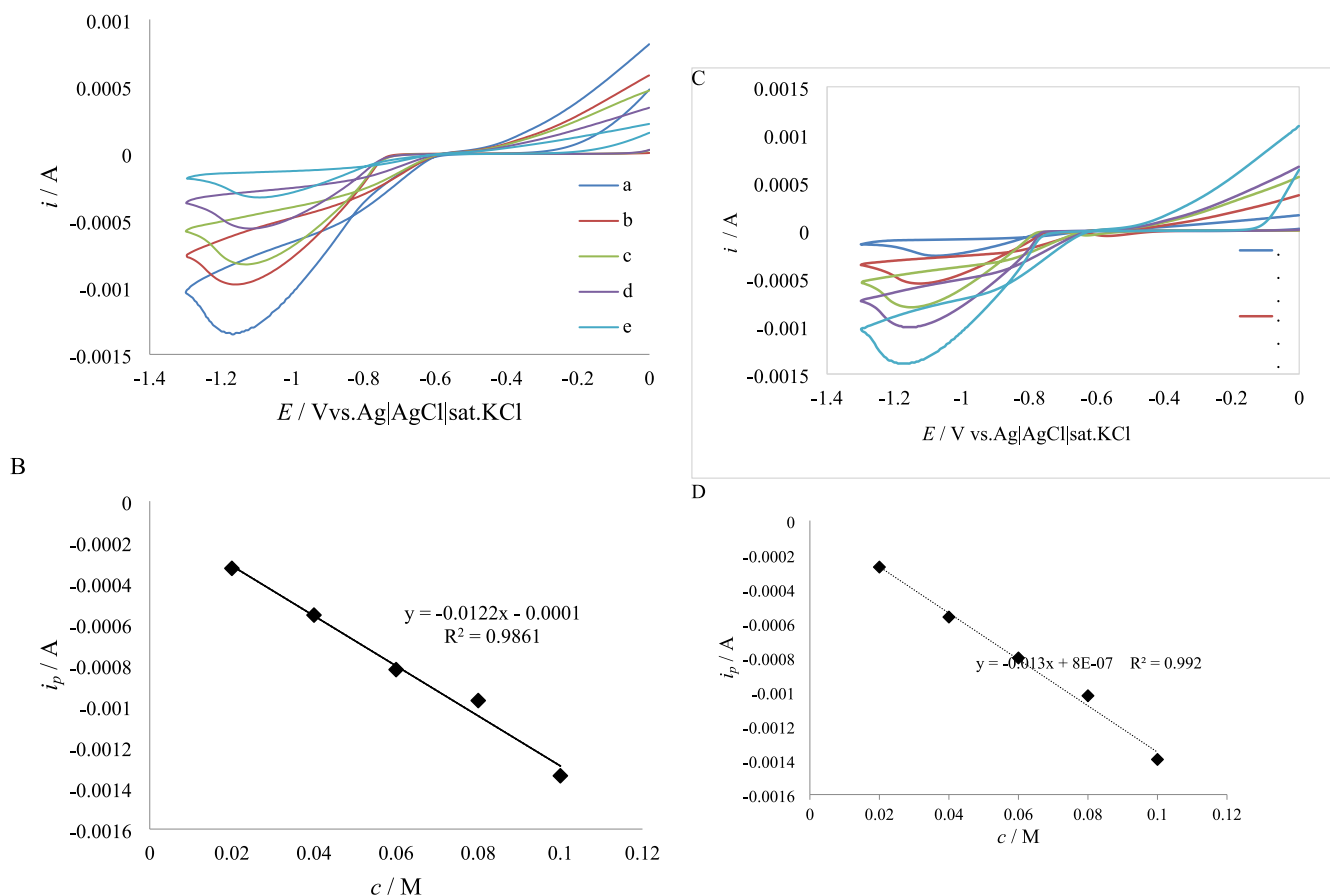
Electrochemical alteration is performed within a three-electrode setup, where a square copper sheet measuring  $50 \times 50 \times 0.1\text{ mm}$  serves as the base electrode, a silver/silver chloride electrode is utilized for reference, and a platinum electrode functions as the auxiliary electrode. The specific operation steps are the same as the above modification steps. Slice the altered copper sheet into specimens measuring  $10 \times 10 \times 0.1\text{ mm}$  using shears in preparation for scrutiny via scanning electron microscopy and spectroscopic examination, aimed at investigating both the surface structure and chemical constituents of the electrode.

## 3. Results and discussion

### 3.1. Electrochemical characteristics of copper electrodes in solutions containing cobalt nickel ions

We conducted a preliminary exploration of the electrochemical behavior of copper electrodes in cobalt sulfate and nickel sulfate solutions using cyclic voltammetry, constant potential electrolysis, and chronopotentiometry. Firstly, we tested the electrochemical concentration dependence of copper electrodes in nickel sulfate solution. The cyclical voltammetry graph (refer to Fig. 1A) indicates that the cathodic peak current, observed in the voltage range of  $-1.1\text{ V}$  to  $-1.2\text{ V}$ , escalates concurrently with the rising concentration of nickel sulfate in the electrolyte. Such an increase corroborates that the identified cathodic peak corresponds to the reduction of nickel ions into metallic nickel atop the copper electrode surface. Moreover, Fig. 1B illustrates the proportional relation between the peak current and the concentration of nickel sulfate. The square of R is 0.9861, which basically proves that this peak is the reduction peak of nickel. Similarly, in Fig. 1C, the cathodic peak appearing between  $-1.1\text{ V}$  and  $-1.2\text{ V}$  also corresponds to the concentration of cobalt sulfate. With a rising amount of cobalt sulfate, there is a corresponding incremental rise in the cathodic peak current, as illustrated in Fig. 1D. Furthermore, the regression equation that relates the concentration of cobalt ions to the peak current yields an R-squared value of 0.992, confirming the occurrence of a reduction reaction involving cobalt ions at the surface of the copper electrode, as evidenced by this particular peak.

Following that, to investigate the workings of electrochemical processes at the electrode interface, we performed an experiment varying the scan rates. At different potential scan rates, copper electrodes exhibit distinct redox peaks in both cobalt sulfate and nickel sulfate solutions. The data presented in Fig. S1 indicates that as the scanning speed rises, there is a corresponding increase in peak current, along with a shift of the peak potential towards more negative values. In Fig. S2, it can be seen that there is a linear relationship between the peak current and the arithmetic square root of the scanning speed, and the square of R is 0.9893. This can prove that this electrochemical reaction is diffusion controlled.

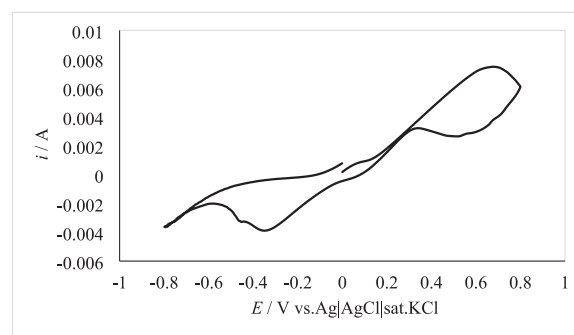


**Fig. 1.** Cyclic voltammetry curves of Cu electrode in different concentrations of  $\text{NiSO}_4$  (A, a: 0.02 M; b: 0.04 M; c: 0.06 M; d: 0.08 M; e: 0.1 M.) and the relationship of concentration and peak current at  $-1.1 \text{ V}$  (B);  $\text{CoSO}_4$  (C, a: 0.02 M; b: 0.04 M; c: 0.06 M; d: 0.08 M; e: 0.1 M.) and the relationship of concentration and peak current at  $-1.1 \text{ V}$  (D).

### 3.2. Electrochemical properties of copper electrodes modified with cobalt-nickel alloy

We used chronopotentiometry to electroplate cobalt nickel alloy onto the surface of copper electrodes under specific conditions. The plating current at the cathode has been configured to 5 mA, while the duration of the electroplating process spans 450 s. Referencing Fig. S3, it is evident that the initial electroplating potential registered at  $-1.2 \text{ V}$ , aligning with the cyclic voltammetry trajectory observed in the preliminary trial. As electroplating progresses, the potential gradually shifts towards a positive direction. Throughout the duration of the electroplating process, ranging from 100 to 200 s, a notable shift in voltage occurs, potentially linked to the creation and subsequent bursting of bubbles atop the electrode's surface. After 400 s of electroplating, the potential tends to stabilize and eventually reaches  $-0.8 \text{ V}$ . This gradual process is the electroplating of cobalt and nickel on the copper electrode.

Post-electroplating, the electrode was subjected to various electrochemical evaluations, such as cyclic voltammetry, the outcomes of which are depicted in Fig. 2. These results reveal that within a sodium dihydrogen phosphate medium, the cobalt nickel alloy electrode presents two separate anodic peaks, specifically at  $0.3 \text{ V}$  and  $0.6 \text{ V}$ , corresponding to the electrodeposition potentials for cobalt phosphate and nickel phosphate, respectively. Therefore, we used  $0.6 \text{ V}$  and  $0.3 \text{ V}$  as the starting potentials for constant potential electrolysis to electrodeposit cobalt nickel alloy electrodes, resulting in the formation of cobalt phosphate and nickel phosphate on the electrode surface (Fig. S4). In Fig. S4, it can be seen that there is a slight increase in current at approximately 20 s during electrodeposition under two different potential conditions. The observed corrosion on the electrode's surface leads to a



**Fig. 2.** CV curve of Co—Ni alloy electrode in  $0.1 \text{ M NaH}_2\text{PO}_4$  solution.

larger surface area, which in turn boosts the current. Evaluations utilizing the constant potential electrolysis approach indicate that both cobalt phosphate and nickel phosphate reliably accumulate on the modified cobalt-nickel alloy electrode. This accumulation results in the formation of an even coating that enhances the sensor's sensitivity and selectivity.

### 3.3. Performance of cobalt nickel alloy phosphate modified electrode

Upon evaluating the reactivity of electrodes modified with cobalt nickel alloy phosphate in a dual-electrode setup, the subsequent findings were ascertained:

As shown in Fig. 3, this sensor can detect  $10^{-6} \text{ M}$  phosphate ions with a linear range of  $0.1 \text{ M}$  to  $10^{-6} \text{ M}$ . It can be used for trace detection of

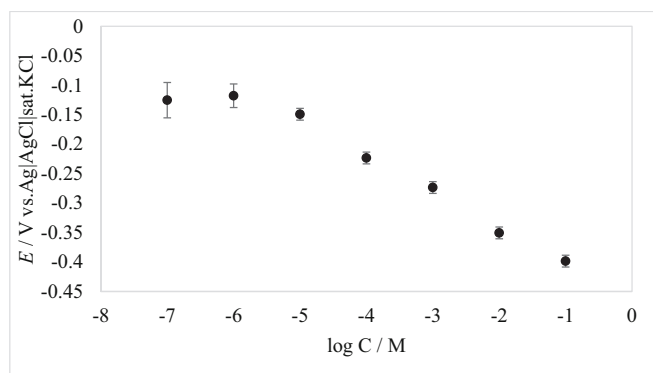


Fig. 3. Response characteristics of Co—Ni alloy modified electrode in  $\text{NaH}_2\text{PO}_4$  standard solution at pH 4.

phosphate ion concentration in water samples. In terms of sensitivity (i.e. response slope, which characterizes the rate at which the sensor output signal changes with the concentration of the measured substance), we can also see from Fig. 3. The sensor demonstrates a high degree of sensitivity, as evidenced by its response potential, which reveals a robust linear correlation to phosphate ion concentration. According to the Nernst equation, the logarithm of the ratio of the reduced state to the oxidized state is proportional to the electrode potential. By substituting all constants into the Nernst equation, it can be theoretically obtained that for every ten fold change in concentration, the electrode potential changes by 59.1 mV. Notably, the sensor's reaction gradient within the linear span of  $10^{-6}$  M up to 0.1 M registers at  $58.8 \text{ mV dec}^{-1}$ , remarkably proximate to the anticipated Nernstian response of  $59.1 \text{ mV dec}^{-1}$ . Furthermore, the coefficient of determination, R-squared, is reported to be 0.991. Therefore, the sensitivity (response slope) of this sensor can be said to be Nernst response.

Besides the gradient of the response, the span of linearity (sensitivity), and the threshold of detection, the quickness of response holds significant importance as well. For this particular detector, the time required for the output to achieve 90 % of its potential shift is quantified using the  $t_{90}$  metric. Through Fig. S5 It can be seen that the  $t_{90}$  of this sensor is within 15 s, indicating that this sensor has the ability to respond quickly to phosphate ions and can be used for on-site rapid detection and real-time monitoring. We performed a potential stability analysis lasting 24 h to verify the sensor's key feature of dependable, long-term monitoring (i.e. potential drift, manifested as a slow and sustained shift in the output signal of the sensor over time in the absence of significant external interference and with a constant concentration of the measured substance). As shown in Fig. S6, after 24 h of continuous potential testing, the fluctuation of the potential was less than 2 mV, which was caused by changes in room temperature. Therefore, we can say that this sensor has good stability and can be used for long-term continuous monitoring of actual water samples. Moreover, the durability of the sensing device is a critical variable, as illustrated in the Fig. S7, the response curve of this sensor did not show significant changes within one month of use. However, after two months of use, the response curve shifted. Currently, should additional utilization be necessary, recalibration of the sensor must occur. The above tests can fully prove that this sensor can be used for on-site rapid detection, and can also be used for real-time online long-term monitoring of actual water samples.

Regarding the sensor's specificity (i.e. selectivity coefficient, reflecting the degree of selectivity of the sensor towards the target substance relative to other possible interfering substances), its performance was assessed by introducing various prevalent competing ions, like nitrate ( $\text{NO}_3^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ), among others.) to the phosphate ion solution using the mixed solution method. The formula for computation is depicted in eq. (1), while Table 1 displays that the sensor exhibits significant discernment towards phosphate ions. With selectivity

Table 1

Selectivity coefficient of common anions measured by mixed solution method.

| Anion              | $\log K_{\text{pot}}$ |
|--------------------|-----------------------|
| $\text{NO}_3^-$    | $-3.2 \pm 0.2$        |
| $\text{Cl}^-$      | $-3.8 \pm 0.2$        |
| $\text{SO}_4^{2-}$ | $-4.1 \pm 0.3$        |
| $\text{HCO}_3^-$   | $-3.9 \pm 0.2$        |
| $\text{Ac}^-$      | $-3.2 \pm 0.2$        |

coefficients uniformly beneath  $-3$ , it is evident that the sensor's sensitivity is only compromised if the interfering ion's concentration exceeds the desired phosphate ion by a thousand fold. Consequently, it can be concluded that the sensor retains its robust selectivity amid an abundance of competing ions.

$$E_{\text{ISE}} = E' + \frac{RT}{n_B F} \ln \left( a_B + K_{B,A}^{\text{pot}} a_A^{\frac{z_B}{z_A}} \right) \quad (1)$$

To assess the real-world efficacy of the sensor, its analytical outcomes were juxtaposed against those obtained using the conventional blue molybdenum colorimetric approach. Table 2 indicates that the sensor's performance closely aligns with established techniques. When measured against these conventional techniques, the sensor's usage is more straightforward and expedient, eliminating the necessity for intricate sample preparation procedures. Meanwhile, this sensor also has the advantages of easy portability and low detection cost, making it more suitable for various application scenarios like industry waste water and hydroponics in argiculture. We also conducted a recycling test to evaluate the detection capability of the sensor in actual samples. Upon introducing varying quantities of benchmark phosphate ions into a solution with a set phosphate ion concentration, the aggregate concentration is gauged and from this, the recuperation rate is determined. The results showed a recovery rate between 97 % and 98 %, indicating that the sensor can accurately detect the concentration of phosphate ions in actual samples. In addition, we compared our study with other similar studies, and Table 4 shows that our phosphate sensor has superior electrochemical performance. For example, using only metal cobalt oxide and cobalt phosphate, the response time is very slow, up to 5–10 min, and the detection limit is not high, about  $10^{-5}$  M. (See Table 3.)

### 3.4. Material characterization of electrode surface

Upon conducting an exhaustive analysis of the sensor's reactive capabilities, we sought to clarify the underlying reaction processes by employing techniques from the field of materials science to examine the electrode's surface. Initial observations were made using a scanning electron microscope, with the findings presented in Fig. 4A, which reveals that the surface of the unaltered pure copper electrode displays barely any discernible features. And in Fig. 4B and C, we can clearly observe the formation of some sheet-like and block shaped crystalline protrusions on the surface of cobalt nickel alloy modified electrodes. And in Fig. 4D-F, it can be clearly seen that there is significant crystallization on the surface of the cobalt nickel alloy electrode modified with phosphate. As for what these morphologies are specifically, we conducted EDS analysis and obtained them through Fig. 5. We can see that there are no other elements on the surface of the pure copper electrode except for copper. Upon alteration of the cobalt-nickel alloy,

Table 2

Real sample test comparing to conventional phosphomolybdate blue spectrometer.

| Sample          | Current sensor(mM) | Colorimetry(mM) |
|-----------------|--------------------|-----------------|
| Coke            | $5.8 \pm 0.2$      | $5.6 \pm 0.1$   |
| Apple juice     | $3.6 \pm 0.2$      | $3.2 \pm 0.1$   |
| Lab waste water | $15.2 \pm 0.2$     | $14.9 \pm 0.2$  |



**Table 4**  
Comparison of related reports.

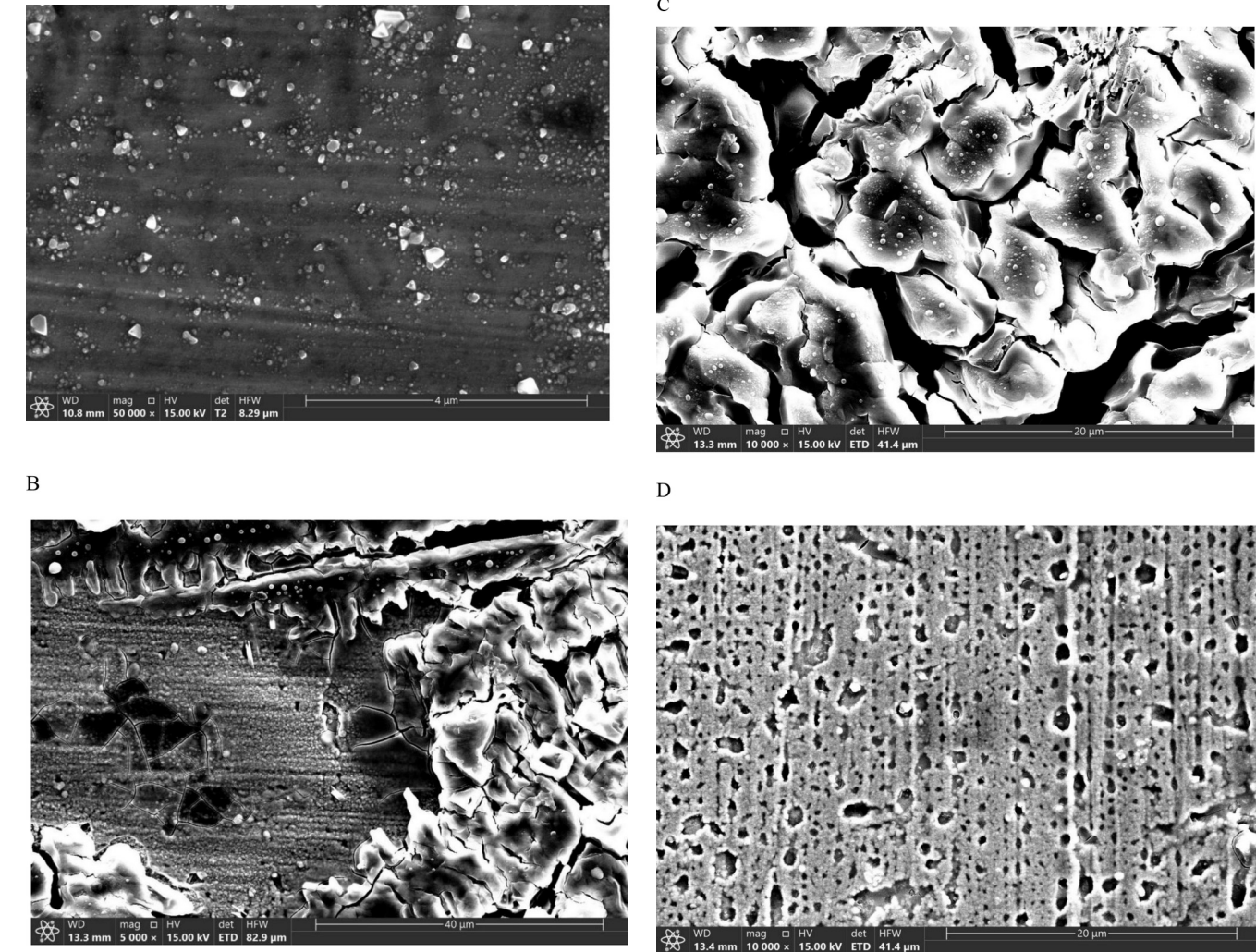
| Material type                                   | Linear range                         | Detection limit          | Response time | Reference    |
|-------------------------------------------------|--------------------------------------|--------------------------|---------------|--------------|
| Tungsten base                                   | 10 <sup>-6</sup> -10 <sup>-1</sup> M | 10 <sup>-6</sup> M       | 1 min         | [27]         |
| Nanometre IIP                                   | 10 <sup>-5</sup> M-0.1 M             | 4.0 × 10 <sup>-6</sup> M | 25 s          | [28]         |
| Co <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> | 10 <sup>-4</sup> M-0.1 M             | 10 <sup>-5</sup> M       | 5 min         | [29]         |
| Cobalt-nickel alloy electrode                   | 10 <sup>-6</sup> M-0.1 M             | 10 <sup>-6</sup> M       | 15 s          | Current work |

**Table 3**  
Recovery test in different solution.

| Sample          | Added (mM) | Found (mM) | Recovery rate(%) |
|-----------------|------------|------------|------------------|
| Distilled water | 10.0       | 9.8 ± 0.1  | 98               |
| Tap water       | 10.0       | 9.8 ± 0.1  | 98               |
| Milk            | 10.0       | 9.7 ± 0.3  | 97               |

pronounced peaks corresponding to cobalt and nickel were evident on the surface of the electrode, with the peak size indicating a greater relative amount of cobalt compared to a diminished relative amount of nickel. Subsequent to the phosphate modification of the cobalt-nickel alloy electrode, substantial presence of phosphorus, oxygen, and sodium

was detected. This series of spectral results confirms that cobalt nickel alloy has indeed been successfully electrodeposited onto the surface of copper electrodes. According to Fig. S8 and Fig. S9, we can see that under the responsive potential and pH conditions, both cobalt and nickel undergo responsive oxidation reactions, which indirectly supports our hypothesis. At 25 °C, the standard electrode potential of the silver chloride electrode is +0.224 V (relative to the standard hydrogen electrode SHE). Therefore, based on the potential-pH diagram, we can prove that the electrochemical reactions occurring on the electrode surface are the generation of oxides and hydroxides of cobalt and nickel. Therefore, the response mechanism of cobalt nickel alloy modified electrodes can be explained by formula (2–7), that is, the corresponding insoluble phosphate is generated on the cobalt nickel surface, and there is a dynamic precipitation dissolution equilibrium, which makes it responsive to phosphate ions. In summary, the surface of the cobalt nickel alloy modified electrode forms a uniform coating, which contains elements such as cobalt, nickel, and phosphorus. The micrograph from the scanning electron microscope reveals the detailed structure of the altered surface, and energy-dispersive spectroscopy validates the elemental composition. These findings underscore the effective fabrication of the cobalt-nickel alloy phosphate-treated electrode surfaces and account for their superior electrochemical behavior.



**Fig. 4.** SEM images of the surface of Cu electrode(A), Co—Ni alloy electrode(B and C) and Co—Ni alloy modified electrode(D, E and F).

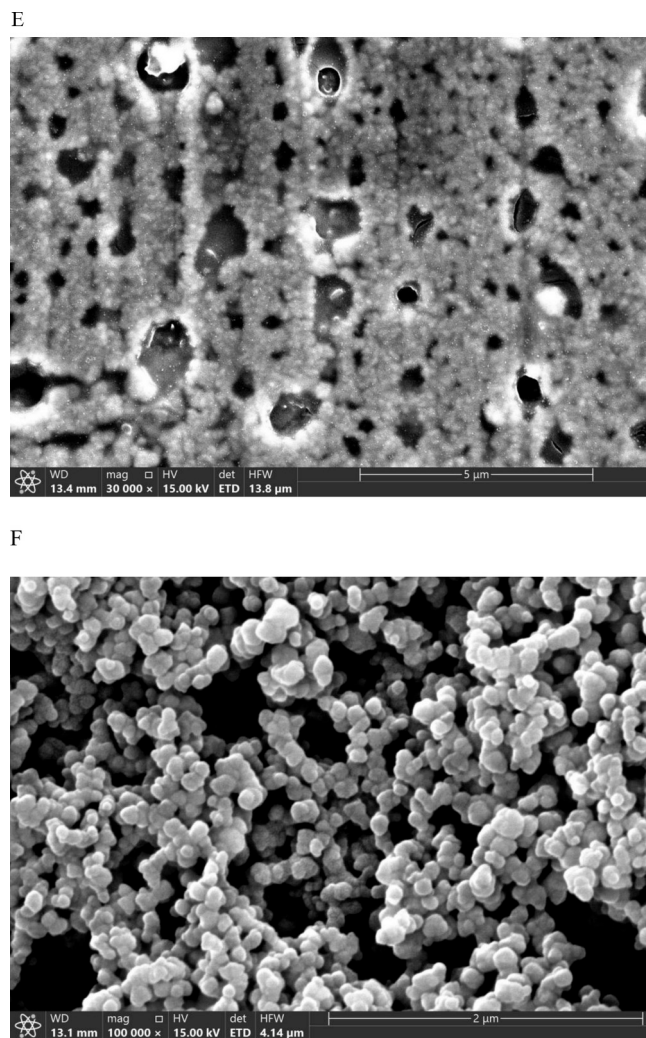


Fig. 4. (continued).

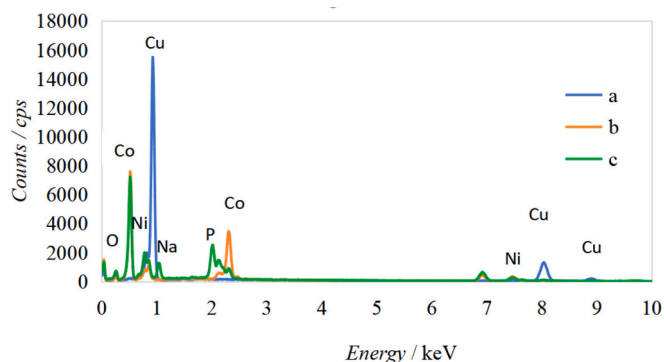


Fig. 5. Energy dispersive spectrometry of Cu electrode(a), Co—Ni alloy electrode(b) and Co—Ni alloy modified electrode(c).



#### 4. Conclusions

Utilizing a fixed current electroplating technique, deposited layers of cobalt and nickel onto the cobalt-nickel alloy electrode and performed targeted phosphatization on its surface to synthesize an insoluble cobalt-nickel phosphate coating. The response slope of this sensor to phosphate ions is  $-58.8 \text{ mV dec}^{-1}$ , the detection limit is  $10^{-6} \text{ M}$ , the linear range is  $10^{-6} \text{ M}$  to  $0.1 \text{ M}$ , the response time is  $15 \text{ s}$ , and the potential drift of continuous testing for  $24 \text{ h}$  is less than  $2 \text{ mV}$ . The service life of the sensor is  $1 \text{ month}$ , and the selectivity coefficient for common interfering anions is below  $-3$ . When contrasted against the classic blue molybdenum colorimetric approach, the experimental outcomes demonstrate a high degree of correlation, with the precision of the supplementary recovery assay ranging from  $97\%$  to  $98\%$ . The cobalt nickel alloy phosphate modified electrode developed in this study not only overcomes the shortcomings of existing detection methods, but also provides a new solution for rapid, accurate, and stable detection of phosphate ions. This type of sensor is suitable for various application scenarios, especially in situations that require high-precision and real-time monitoring, such as water quality monitoring, soil analysis, food processing, etc., and has broad application prospects. Future work will continue to focus on material optimization, improvement of detection methods, and multifunctional integration to further enhance sensor performance and expand its application areas, promoting the widespread application of this technology in environmental protection, food



safety, and medical diagnosis, and providing strong support for solving current environmental and health problems. Through these efforts, we believe that the sensor will continue to improve and develop, becoming one of the key technologies in the field of phosphate ion detection, significantly improving the detection efficiency and accuracy of related industries, and promoting sustainable socio-economic development.

### CRedit authorship contribution statement

**Kebin Xu:** Writing – original draft, Methodology, Investigation. **Jingjing Xing:** Writing – original draft, Investigation. **Minjie Mei:** Writing – review & editing, Investigation, Funding acquisition, Data curation. **Jie Wu:** Formal analysis. **Xin Huang:** Methodology. **Xiu Zhang:** Methodology. **Yilin Liu:** Methodology. **Yudong Wu:** Methodology. **Yang Zhang:** Methodology. **Fu Ren:** Supervision. **Xin Li:** Writing – review & editing, Supervision, Conceptualization.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.microc.2025.114928>.

### Data availability

Data will be made available on request.

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