Int. J. Electrochem. Sci., 16 **(2021)** Article ID: 210641, doi: 10.20964/2021.06.49

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

An All-Solid-State Phosphate Ion-Selective Electrode Using $BiPO_4$ as a Sensitive Membrane

Jianbo Wu, Yifan Zhou, Pingping Zhang, Chuqing Zhang, Ying Ye*

Ocean College, Zhejiang University, Zhoushan 316021, China
*E-mail: marin011@zju.edu.cn

Received: 28 January 2021 / *Accepted:* 6 March 2021 / *Published:* 30 April 2021

In this work, a novel all-solid-state phosphate ion selective electrode (ISE) was constructed using a Pt/Bi/$BiPO_4$ electrode. The Bi particles were electrodeposited using a function generator and a Schottky diode in bismuth potassium citrate solution. A $BiPO_4$ sensitive membrane was fabricated by electroplating via performing chronoamperometry on an electrochemical workstation. Under the lens of SEM, both the Bi particles and the $BiPO_4$ particles formed a homogeneous layer and reached the nanoscale size range. The built electrode exhibited a sound slope of 30.31mV/decade and desirable reproductivity in response to HPO_4^{2-} in the solution. The detection limit of the electrode was measured as 7.718×10^{-7} M, and a linear range for the Na_2HPO_4 solution was exhibited from 10^{-6} M to 10^{-1} M. The average potential fluctuation of the electrode over 1 h was 1.26 mV, and the response time was less than 2 s. The proposed sensor has good selectivity for phosphate and shows satisfactory resistance to common ions such as nitrate, sulphate, acetate and carbonate for use in low-chlorine waters. The $BiPO_4$ electrode has a proven lifespan of over 90 days, demonstrating the potential for long-term *in situ* testing.

Keywords: ion-selective electrode; phosphate; all-solid-state; $BiPO_4$; nanoscale

1. INTRODUCTION

Phosphate as a pollutant has been subject to numerous studies all over the world, and extensive research has proven its high significance as an influencing factor of the eutrophication of water bodies [1]. Phosphate and many other nutrient salts accelerate algal blooms, which in turn cause a variety of water quality issues [2]. Excessive phosphate levels in the human body can cause a number of health problems, for example, it can directly damage the kidneys, the thyroid, and other organs [3, 4], as well as alter the energetic state of bones and cause cellular toxicity [5, 6]. Spectrophotometry is currently the principal method for the detection of phosphates, with the most widely used and most classical one being phosphomolybdenum blue spectrophotometric detection [7]. In addition, with the development of larger instruments, ion chromatography has also become an efficient and accurate method for phosphate determination. Based on the column-switching technique, Dahllöf et al. used a mixture of $Na_2CO_3/NaNO_3$ in different ratios as a drench solution for the determination of phosphate in seawater [8]. Karmarkar et al. successfully analyzed phosphate ion concentrations using flow injection ion chromatography at a disturbed sulfate concentration of 910 mg/L [9]. However, these analytical methods are complex, time-consuming, have low sensitivity and do not allow long-term in-situ monitoring. These limitations have driven the development of ion-selective electrodes. Such electrodes work according to electrochemical principles, are easy to fabricate, cost effective, portable, and feature high sensitivity [10-12].

Relevant attempts to manufacture phosphate electrodes have been made by various researchers. Grabner et al. presented a phosphate-sensitive electrode based on $BiPO_4$-modified glassy carbon [13]. Fikru Tafesse et al. proposed a phosphate sensor fabricated by constructing a crystal disk consisting of variable mixtures of Al powder, $AlPO_4$ and powdered copper [14]. A polyaniline conducting polymer doped with phosphate ions was applied for seawater by Huang et al. [15], whereas Xu et al. constructed a novel phosphate ion-selective sensor using a cobalt phosphate surface-coated cobalt electrode [16].

In the present study, an all-solid-state phosphate electrode was developed using Pt wire as the base material, nanoscale $BiPO_4$ as a sensitive membrane for detecting phosphorus, and Bi particles as an interlayer. The fabrication process is simple to execute, and the electrode features a linear range of 10^{-6}-10^{-1} M, a detection limit of 7.718×10^{-7} M, a response time of less than 2 s, and a lifetime of more than 90 days, thus making it suitable for the quick and reliable detection of phosphorus.

2. EXPERIMENTAL METHOD

2.1 Reagents and apparatus

The bismuth potassium citrate was obtained from Shanghai Macklin Biochemical Co., Ltd. The sodium phosphate dibasic anhydrous, sodium sulfate, sodium acetate, trisodium phosphate dodecahydrate, sodium carbonate, sulfuric acid, sodium hydroxide and Pt wire (99.95%, 0.5 mm in diameter) were obtained from Sinopharm Chemical Reagent Co., Ltd. The 0.1 M hydrochloric acid was acquired from Shenzhen Bolinda Technology Co., Ltd.

The Bi particles were electrodeposited by a SG1020A function generator with a Schottky diode (S4 IN5819). The $BiPO_4$ coating process and the electrochemical performance tests on the electrode were accomplished using a CHI760D electrochemical workstation including an Ag/AgCl reference electrode (3.8 mm) obtained from Shanghai Jinghong Electronic Technology Development Co., Ltd, and a platinum electrode obtained from Gaoss Union Electronic Technology Co., Ltd. The pH of the solution was prepared and measured by an E-201F composite pH electrode (REX, Shanghai, China). A Zeiss Sigma 500 field emission scanning electron microscope (SEM, Carl Zeiss, Germany) was used for SEM analysis.

2.2 Electrode pretreatment and fabrication

A Pt wire with 4 cm length and 0.5 mm diameter was polished by alumina polishing powder with 50 nm grain size, ultrasonically cleaned with hydrochloric acid, absolute ethanol and deionized water in sequence, and finally dried for later use.

In order to form a bismuth nanoparticle coating, a SG1020A function generator was used with sinusoidal parameters of 1.2 V amplitude and 50 Hz frequency. The anode was connected to a Schottky diode and bismuth metal block in turn, and the cathode was attached to a pretreated platinum wire. Both the bismuth block and the platinum wire were placed in a 2 wt.% solution of bismuth potassium citrate and plated for 260 seconds, resulting in a uniform coating of bismuth nanoparticles on the platinum wire surface.

The electrodeposition process was carried out by chronoamperometry using a three-electrode system on the CHI760D workstation, where the platinum wire with bismuth nanoparticles acted as the working electrode, and the Pt wire and Ag/AgCl electrodes functioned as counter and reference electrodes, respectively. The above electrodes were placed in 0.1 M Na_3PO_4 and electrodeposited for 50 s at a potential of 1.2 V and a sensitivity of 10^{-2} to obtain a nanoscale $BiPO_4$ sensitive membrane.

2.3 Electrode performance

The surface morphology of the electrode was observed by scanning electron microscopy. All potential measurements were evaluated on a CHI760D electrochemical workstation using a two-electrode system open-circuit technique. When the value became stable, the potentials were recorded. A series of Na_2HPO_4 solutions prepared by serial dilutions were used as calibration solutions.

2.4 Application

In order to test the application performance of the electrodes, three samples of Nongfu spring drinking natural water (Nongfu Spring Co., Ltd) were prepared with different levels of Na_2HPO_4. The phosphate content of each sample was determined three times using the prepared electrodes. The measurement results were compared with the actual phosphate content in the phosphate-enriched samples, and the recovery values were calculated.

3. RESULTS AND DISSCUSION

3.1 Electrochemical polymerization of $BiPO_4$ sensitive membrane

The electrochemical polymerization of $BiPO_4$ sensitive membrane was carried out with an initial current of 2.587×10^{-2} A at 1.2 V potential using the chronoamperometry technique (Figure 1). During the first 1 s, the current dropped considerably due to the rapid polymerisation of $BiPO_4$ on the surface of the Pt wire. Subsequently, the current slowly decreased until stabilizing at 3.512×10^{-4} A. During this time, the $BiPO_4$ slowly polymerized and the brown bismuth nanosphere on the electrode surface gradually disappeared.

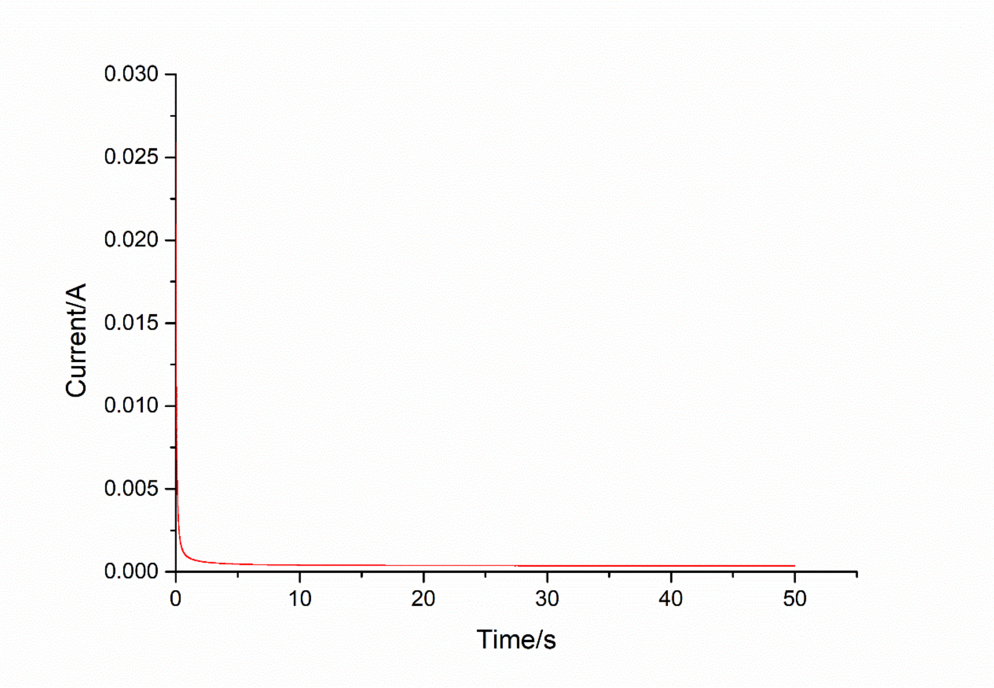
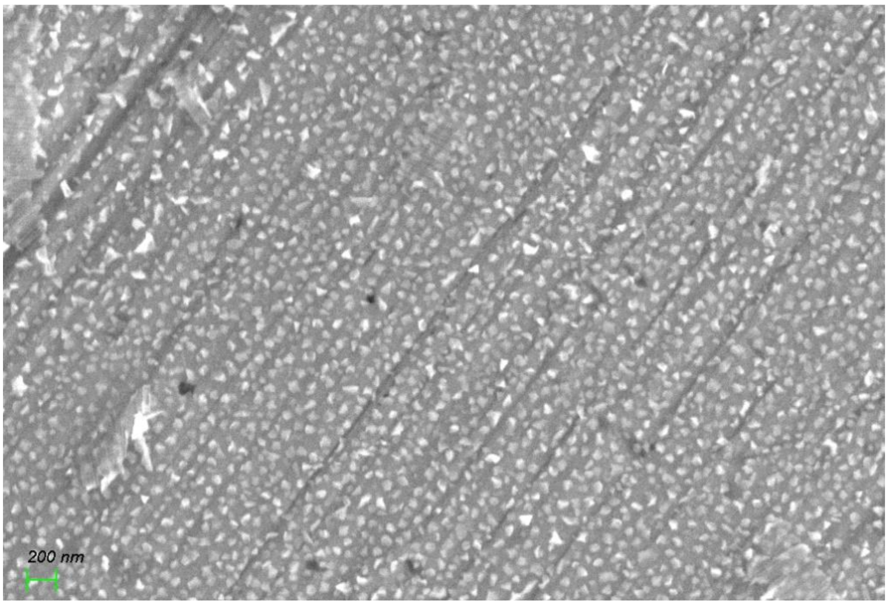


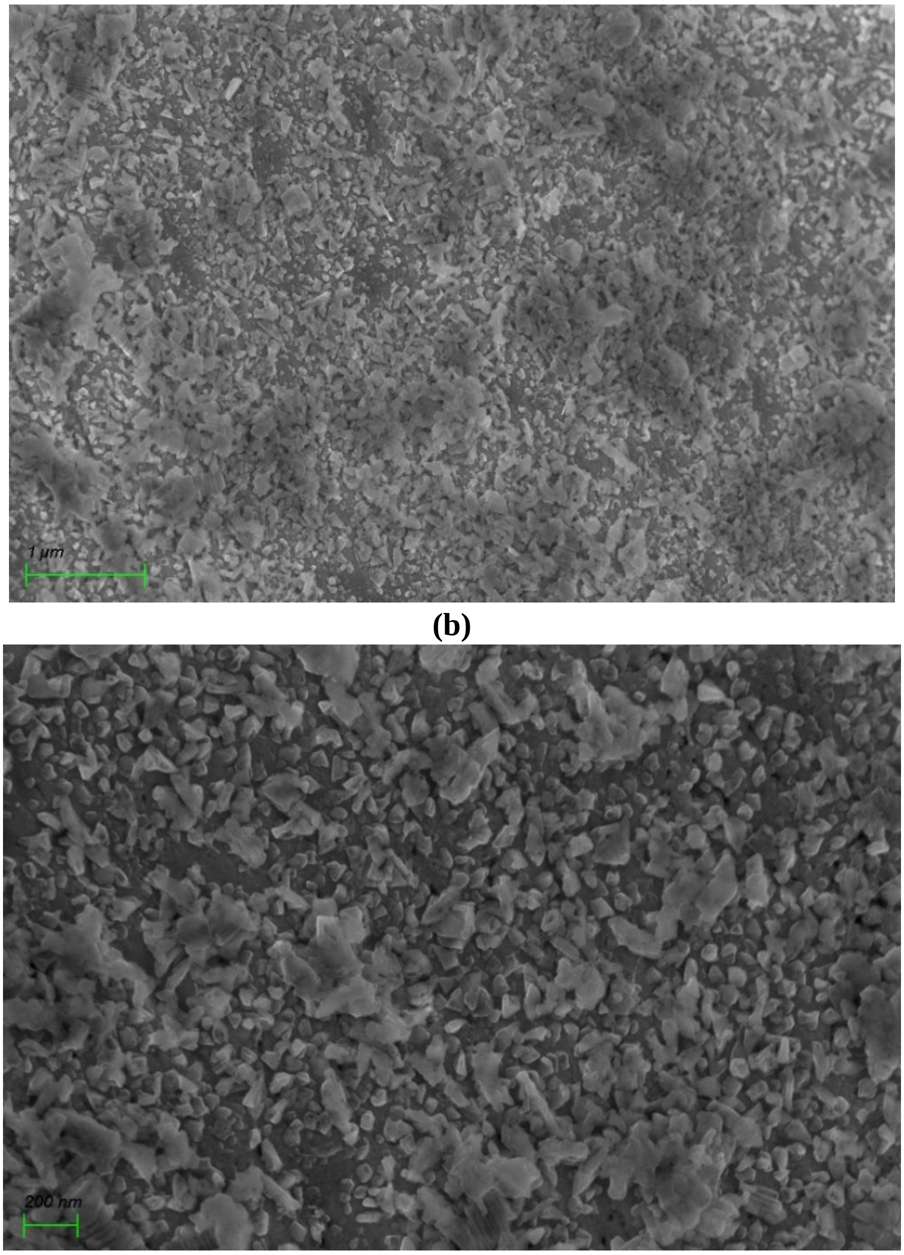
Figure 1. Current–time curve of $BiPO_4$ membrane polymerization based on chronoamperometry at 1.2 V potential.

3.2 SEM analyses

Figure 3 (a), (b) and (c) present the SEM image of a Bi particle layer formed on the surface of a Pt wire at a 19,000× magnification, a SEM image of a $BiPO_4$ film formed on the surface of a Bi particle layer at 15,000× magnification and a SEM image of a $BiPO_4$ membrane at 34,000× magnification, respectively.



(a)



(b)

(c)

Figure 2. SEM images of the $BiPO_4$ electrode. (a) The Bi particle layer viewed at 19,000× magnification, (b) the $BiPO_4$ membrane viewed at 15,000× magnification and (c) the $BiPO_4$ membrane viewed at 34,000× magnification.

As seen in Figure 2, the bismuth particles form a uniform coating on the surface of the platinum wire after electrification, and the reliable combination of nanoscale Bi and platinum wire substrate results in a more robust film sensitivity at a later stage. Figure 2(b) demonstrates that the bismuth phosphate layer is evenly covered with a $BiPO_4$ sensitive film after the electrochemical polymerization of the bismuth particles. At 34,000× magnification, the $BiPO_4$ is attached to the electrode surface in the form of dense lumpy particles (Figure 2(c)).

3.3 Detection limit, linear range, and calibration curve of $BiPO_4$ electrode

In order to measure the detection limit and linear range of the $BiPO_4$ electrode, a series of solutions of Na_2HPO_4 at concentrations of 10^{-1} M, 10^{-2} M, 10^{-3} M, 10^{-4} M, 10^{-5} M, 10^{-6} M, 10^{-7} M, and 5×10^{-8} M were prepared and used to for calibration. The calibrated potential of each solution was recorded and results were plotted in Figure 3. The detection limit was defined as the intersection of straight and tangent parts of the calibration curve [17]. As shown in Figure 3, the linear range of the $BiPO_4$ electrode was determined as 1×10^{-6}–1×10^{-1} M with a line of fit of $y = -30.317x + 228.07$ and an R^2 value of 0.9964. The detection limit was determined as 7.718×10^{-7} M, indicating that the $BiPO_4$ electrode has a wide response range and a low detection limit. Our electrode has a wider detection range compared with the recently reported phosphate electrodes, and its lower detection limit is better than the 10^{-5}M detection limit of most existing electrodes [13, 16].

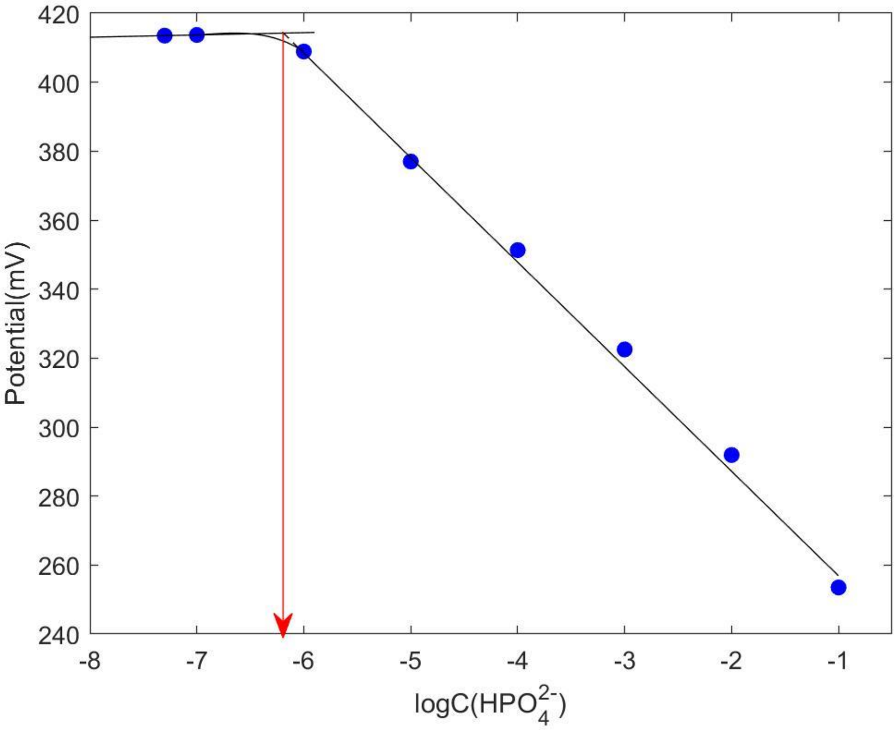


Figure 3. Electrode performance in 5×10^{-8}–10^{-1} M Na_2HPO_4 solution.

3.4 Electrode response curve and repeatability

Figure 4 shows the calibration curve of the bismuth phosphate electrode in Na_2HPO_4 solution with a concentration range of 10^{-6} to 10^{-1} M and a calibration time of 200 s for each concentration setting. The recorded potentials from 10^{-6} M to 10^{-1}M were 408.9 mV, 377.0 mV, 351.3 mV, 322.5 mV, 291.9 mV and 253.5 mV, and from 10^{-1} M to 10^{-6} M, they increased again to 292.1 mV, 322.1 mV, 349.9 mV, 377.2 mV and 409.8 mV. The proposed phosphate electrode showed a stable response to all Na_2HPO_4 solutions.

Response time is defined as the time required for the electrode potential value to reach stability and is an important characteristic affecting the accuracy of real-time monitoring and throughput of the sensor [18]. Figure 4 shows that the $BiPO_4$ electrode responded rapidly within about 1-2 s. This is due to the tightness of the sensitive membrane and the substrate material, as well as the high conductivity of the membrane that makes the $BiPO_4$ electrode sensitive. The potential was relatively stable in each solution, with less than 2 mV of potential drift observed over 200 s. Many of the phosphate electrodes reported in recent years have response times in the range of 10-60 s [19-21], compared to which our electrode features a significant improvement. Meanwhile, the good reproducibility of the sensor is demonstrated by commensurate potentials at given concentration values.

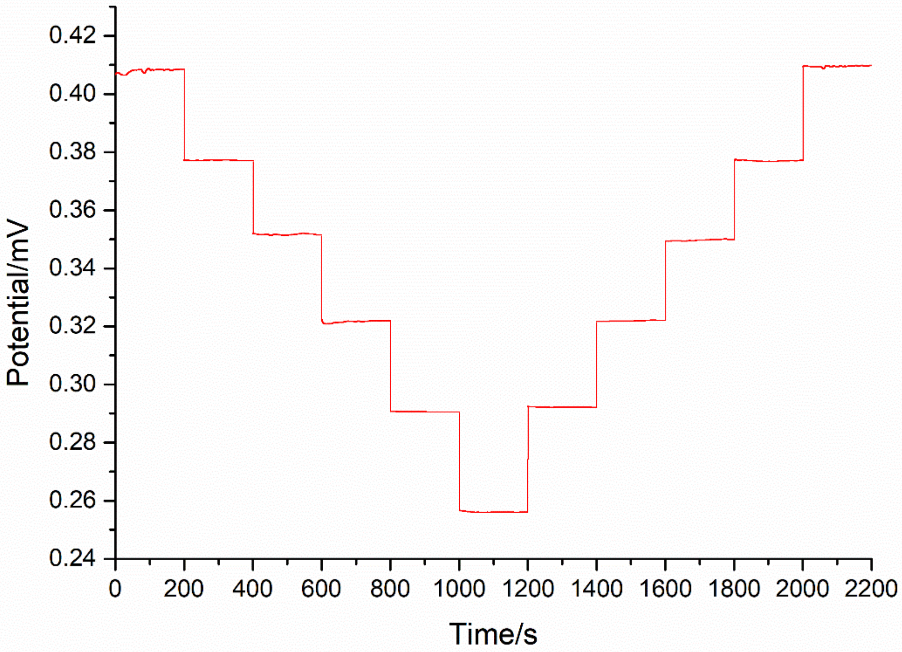


Figure 4. The calibration curve of the $BiPO_4$ electrode for Na_2HPO_4 solutions with concentrations ranging from 10^{-6} M to 10^{-1} M.

3.5 Electrode stability

The long-term stability of the electrode was tested for one hour with different concentrations of Na_2HPO_4 solution. As shown in Figure 5, the electrode potential was relatively stable with little fluctuation during the test. The highest potentials measured were 410.7, 377.8, 350.1, 322.9, 292.4 and 256.7mV at 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} M concentrations, respectively, while the lowest potentials were 409.1, 376.7, 348.9, 321.5, 291.7 and 255.3mV, respectively. The average value of potential fluctuations was 1.26 mV. Potential fluctuations were relatively large at low concentrations of the solution, either due to the instability of the solution or because the low concentration was close to the lower detection limit of the electrode.

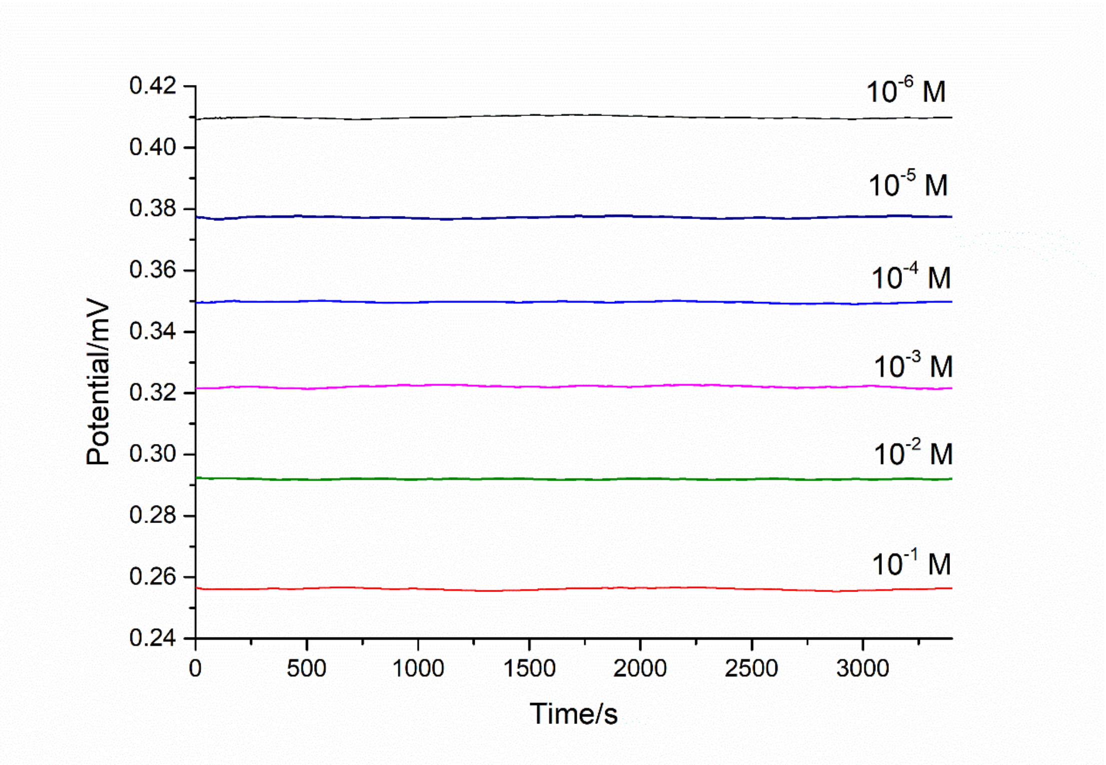


Figure 5. 1-h potential measurements of the $BiPO_4$ electrode in Na_2HPO_4 solutions with concentrations ranging from 10^{-6} M to 10^{-1} M.

3.6 Interference study

Natural waters have a more complex ionic environment than laboratory calibration solutions, therefore the selectivity of an electrode for the prevalent ions is extremely important for the application of that electrode in natural waters. In this work, the selectivity of phosphate electrodes for phosphate ions was assessed using the fixed interference method (IFM), where the selectivity factor (Ki,j) is an important indicator of the electrode's resistance to interference. This factor is calculated as follows:

$$\mathrm{Ki,j} = \frac{a_i}{a_j^{\frac{z_i}{z_j}}} \qquad (1)$$

where

a_i = lower limit of detection of primary ions in the presence of interfering ions
a_j = activity of interfering ions
z_i = charge of primary ions
z_j = charge of interfering ions

The smaller the selectivity factor, the more resistant the electrode is to interference. In general, log Ki,j < 0 means that the electrode has good resistance to specific interfering ion *j*. The smaller the selectivity factor, the more resistant the electrode is to interference [22]. With a fixed interfering ion concentration of 10^{-2} M, the log Ki,j values for the $BiPO_4$ electrode were calculated as -1.16, -3.63, -1.12, -2.41 and 1.81 for nitrate, sulphate, acetate, carbonate and chloride interferences, respectively. Chloride ions show strong interference with the electrode, probably because the solubility product of

BiOCl is too small (K_{SP}(BiOCl) = 1.8×10^{-31}) and the bismuth ion is susceptible to chloride ions, indicating that this electrode is not suitable for use in high chloride-containing environments.

3.7 Lifespan of electrode

The lifetime of an electrode determines whether it is suitable for long-term monitoring [23]. To determine the lifetime, the $BiPO_4$ electrode was stored in deionised water for 90 days and tested periodically in a standard Na_2HPO_4 solution, when the slope and R^2 values of the fitted line were calculated. As seen in Table 1, the slope was stable between the values of -29.59 to -30.54 over 90 days and the R^2 value was greater than 0.99, indicating that our $BiPO_4$ electrode is guaranteed to be accurate over 90 days of continuous use in an aqueous environment. Most existing phosphate electrodes have a lifespan of 1 to 2 months [15, 16, 20], while the proposed electrode has a longer lifespan and thus better application value.

Table 1. Performance of $BiPO_4$ electrode (mV) in the range of 10^{-6}–10^{-1} M Na_2HPO_4 over 90 days

Days	10^{-6} M	10^{-5} M	10^{-4} M	10^{-3} M	10^{-2} M	10^{-1} M	slope	R^2
1	408.9	377.0	351.3	322.5	291.9	253.5	-30.31	>0.99
3	409.5	372.5	342.6	323.0	289.9	249.2	-30.54	>0.99
7	406.6	374.1	343.1	320.3	292.4	253.1	-29.59	>0.99
14	410.2	373.3	347.0	321.4	290.7	257.6	-29.61	>0.99
30	407.6	375.1	348.0	319.2	288.1	256.0	-29.93	>0.99
60	406.3	372.6	341.9	322.0	286.4	254.1	-29.70	>0.99
90	405.2	371.8	342.1	318.2	288.5	249.0	-30.05	>0.99

3.8 Comparison of $BiPO_4$ electrode and preciously reported electrodes

Table 2. The potential drifts of the $BiPO_4$ electrode calibrated in 10^{-3} M Na_2HPO_4 under different pH conditions.

pH	Potential drifts/mV			Average/mV
	NO.1	NO.2	NO.3	
4	2.4	4.1	3.8	3.4
5	1.9	1.4	1.2	1.5
6	0.3	0.2	0.5	0.3
7	0.2	0.5	0.5	0.4
8	0.3	0.2	0.3	0.3
9	0.9	1.2	1.1	1.1
10	2.7	3.4	3.5	3.2

The methods of Huang et al. were used to investigate the effect of pH on the $BiPO_4$ electrode [15]. The Na_2HPO_4 concentration was fixed at 10^{-3} M, and a series of solutions with different pH values were prepared using NaOH and H_2SO_4. Three identical $BiPO_4$ electrodes were used for this experiment. Table 2 shows the maximum value of the potential drifts of the electrode when calibrated for 200 s in the prepared Na_2HPO_4 solution under pH values of 4 to 10. It can be observed that the electrode is suitable in the pH 5-9 range, as the potential drift at this level is less than 2 mV over 200 seconds.

3.9 Comparison of the $BiPO_4$ electrode and previously reported electrodes

A comparative summary of the performance of the proposed electrode and some previously reported electrodes is presented in Table 3. Our electrode shows superior performance and a larger detection limit compared to other electrodes. The fast response time of this electrode also improves the accuracy of the sensor for real-time monitoring. The further properties of the electrode are also excellent, indicating its potential value for long-term *in situ* monitoring.

Table 3. Performance comparison of the proposed $BiPO_4$ electrode and other electrodes previously reported in the literature

Membrane materials	Linear concentration range/M	Detection limit/M	Response time/s	Lifespan	Slope
Nanoscale $BiPO_4$ (this work)	$10^{-6} \sim 10^{-1}$	7.718×10^{-7}	<2	More than 90 days	-30.0±0.7
$BiPO_4$ (composited on glassy carbon) [13]	$10^{-4} \sim 10^{-1}$	--	<30	--	-40.0
Polyaniline/H_3PO_4 doped polyaniline [15]	$10^{-6} \sim 10^{-1}$	10^{-6}	<1	40 days	-28.28~ -33.52
Cobalt phosphate [16]	$10^{-5} \sim 10^{-1}$	10^{-5}	<30	More than 28 days	-39.0±1
Mixtures of Al, $AlPO_4$ and Cu powder [14]	$10^{-6} \sim 10^{-1}$	10^{-6}	<60	--	40.0

3.10 Application example of proposed electrode

The source of samples used for the experiment, Nongfu Spring drinking natural water (Nongfu Spring Co., Ltd) is high-quality natural water that contains silicate, calcium, sodium, magnesium and potassium ions, and has a pH around 7.5. The initial phosphate content of water samples was less than 0.1 mg/L (1.04×10^{-6} M). Amounts from 4.32×10^{-5} M to 2.24×10^{-2} M of Na_2HPO_4 were added to the four samples used for the electrode application performance tests. Each sample was tested three times with the prepared electrode to obtain a phosphate detection level. The mean value of the detected P content was compared with the actual enrichment value to gain the recovery rate. As shown in Table 4, the recovery rates ranged from 92.82% to 99.11%, reflecting the high accuracy and application performance of the electrode in drinking water testing.

Table 4. Water sample testing of Na_2HPO_4 by the proposed $BiPO_4$ electrode

Sample	Na_2HPO_4 (M)		Recovery (%)
	Added	Detected	
NO.1	4.32×10^{-5}	4.01×10^{-5}	92.82
NO.2	2.32×10^{-4}	2.18×10^{-4}	94.96
NO.3	7.11×10^{-3}	6.84×10^{-3}	96.23
NO.4	2.24×10^{-2}	2.22×10^{-2}	99.11

4. CONCLUSIONS

In summary, this study presented an electrochemically fabricated novel all-solid phosphate ion-selective electrode with platinum wire as the base material, Bi nanoparticles as the interlayer and $BiPO_4$ as the sensitive film. The linear response of the prepared ISE to Na_2HPO_4 ranges from 10^{-6} to 10^{-1} M, and its calculated calibration slope is -30.31 mV/decade, which is consistent with the theoretical Nernstian slope for divalent ions. The combination of precious metals and nanotechnology allows the electrode to be optimized for longevity, short response time, low detection limits and other beneficial aspects compared with previous approaches, thus providing excellent overall performance. The $BiPO_4$ electrode is stable over a pH range of 5-9, and has excellent selectivity for HPO_4^{2-} compared to common ions, such as sulphate, nitrate, carbonate and acetate, in the aqueous environment. Although the proposed electrode cannot be currently used in highly chlorinated water environments due to the strong interference caused by Cl^-, it is still of high value for freshwater environments, such as glacial water. The reduction of interference of chloride ions is a planned aspect of relevant future studies.

ACKNOWLEDGMENTS
We are very grateful for the assistance we received from Dr Huang. We are also very grateful for the facilities provided by the Physical and Chemical Laboratory of Marine Resources, Department of Oceanography, Zhejiang University.

References

1. H. S. Ayele and M. Atlabachew, *Environmental Science and Pollution Research*,28(2021)14233.
2. M. Karydis, *Glob. Nest. J.*, 11(2009)373.
3. R. Kumar, *Current Opinion in Nephrology and Hypertension*, 18(2009)281.
4. E. Slatopolsky and S. Moe, *Kidney International*, 79(2011)S1.
5. S. Khoshniat, A. Bourgine, M. Julien, P. Weiss, J. Guicheux and L. Beck, *Cellular and Molecular Life Sciences*, 68(2011)205.
6. B. E. C. Nordin, *Nutrition*, 13(1997)664.
7. J. Murphy and J. P. Riley, *Anal. Chim. Acta*, 26(1962)31.
8. I. Dahllöf, O. Svensson and C. Torstensson, *Journal of Chromatography A*, 771(1997)163.
9. S. V. Karmarkar, *Journal of Chromatography A*, 850(1999)303.

10. M.-R. Huang, G.-L. Gu, Y.-B. Ding, X.-T. Fu and R.-G. Li, *Chinese Journal of Analytical Chemistry*, 40(2012)1454.
11. A. Michalska, *Electroanalysis*, 24(2012)1253.
12. J. Bobacka, *Electroanalysis*, 18(2006)7.
13. E. W. Grabner, I. Vermes and K. H. Konig, *J. Electroanal. Chem.*, 214(1986)135.
14. F. Tafesse and M. Enemchukwu, *Talanta*, 83(2011)1491.
15. Y. F. Huang, J. Li, T. Y. Yin, J. J. Jia, Q. Ding, H. Zheng, C. T. A. Chen and Y. Ye, *J. Electroanal. Chem.*, 741(2015)87.
16. K. Xu, Y. Kitazumi, K. Kano and O. Shirai, *Electrochimica Acta*, 282(2018)242.
17. R. P. Buck and E. Lindner, *Pure and Applied Chemistry*, 66(1994)2527.
18. L. Xing, *Int. J. Electrochem. Sci.*,(2017)1506.
19. M. Asadnia, A. G. P. Kottapalli, J. M. Miao, A. B. Randles, A. Sabbagh, P. Kropelnicki and J. M. Tsai, *J. Micromech. Microeng.*, 24(2014)12.
20. Y. Li, T. Jiang, X. Yu and H. Yang, *Journal of The Electrochemical Society*, 163(2016)B479.
21. M. Asadnia, A. G. P. Kottapalli, J. M. Miao, A. B. Randles, A. Sabbagh, P. Kropelnicki and J. M. Tsai, *J. Micromech. Microeng.*, 24(2013)015017.
22. D. Ammann. *Ion-Selective Microelectrodes: Principles, Design and Application*. 1986. Springer-Verlag Berlin Heidelberg.
23. Y. F. Zhou, J. B. Wu, P. P. Zhang, Q. J. Wang and Y. Ye, *Int. J. Electrochem. Sci.*, 14(2019)9647.