

Phosphate and Nitrate Electrochemical Sensor Based on a Bifunctional Boron-Doped Diamond Electrode

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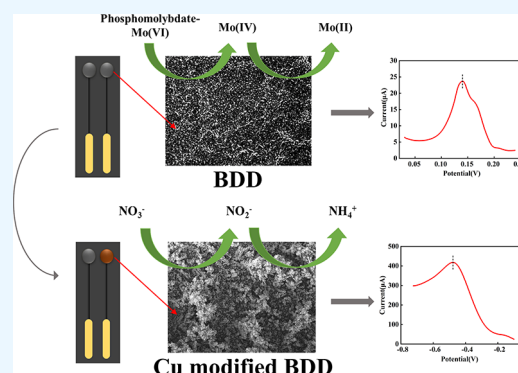
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ABSTRACT: Phosphorus and nitrogen are important elements in both environmental cycles and biological growth, and their imbalance can lead to serious environmental and biological problems. It is important to be able to monitor the concentration of nitrate and phosphate in the water online. In this paper, a bifunctional boron-doped diamond (BDD) electrode with repeatable electrochemical renewal and modification ability has been developed and used as a shared working electrode for the determination of nitrate and phosphate. First, phosphate can be detected directly with a bare BDD electrode. After a thin copper (Cu) layer was electrodeposited on the BDD electrode, nitrate could be determined. The copper layer is then removed under a positive voltage, and the BDD electrode is renewed and can be used again for phosphate detection. This method enables the detection of both phosphate and nitrate while also improving the stability and repeatability through the renewal of the electrode surface. The segmented linear ranges for phosphate were 0.02–0.4 and 0.4–3 mg/L with a detection limit of 0.004 mg/L. The sensor detected nitrate in a wide concentration range, with segmented linear relationships in the ranges of 0.07–3 and 3–100 mg/L, with a detection limit of 0.065 mg/L. The electrochemical sensor based on the BDD electrode has a good reproducibility for phosphate and nitrate detection. The relative standard deviation (RSD) values of the current responses were 2.98, 2.79, 1.66, 1.81, and 1.23%, respectively, for 35 consecutive tests in 0.05, 0.2, 0.5, 1, and 1.5 mg/L phosphate solution. The RSD values of the current responses were 2.00, 0.97, and 1.03%, respectively, for 25 consecutive tests in 5, 7, and 10 mg/L nitrate solution.



INTRODUCTION

Nitrate and phosphate ions are important components of agriculture and play a key role in maintaining the biological survival of aquatic ecosystems.¹ The excessive application of chemical fertilizers and the discharge of wastewater and sewage in modern agriculture can lead to excessive nitrates and phosphates entering surface water environments such as rivers and lakes. Excessive levels of nutrients can cause eutrophication, leading to the overgrowth of algae and plants, reducing the amount of dissolved oxygen in water, and posing significant harm to the water environment and human drinking water safety.^{2,3} Nitrates and phosphates are hazardous to human health when ingested in excess. Excess nitrate promotes the formation of nitrosamines in the body and increases the risk of cancer.⁴ Excess phosphate, on the other hand, may lead to blood pH imbalance, neuromuscular dysfunction, and kidney disease.^{5,6} Therefore, monitoring and controlling potential harmful pollutants in water environments are crucial for protecting the environment and human health.

Currently, the methods for nitrate determination mainly include atomic absorption spectroscopy, inductively coupled plasma mass spectrometry, ion chromatography, ultraviolet or visible spectroscopy, chemiluminescence, and electrophoresis.⁷

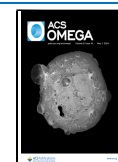
The methods for phosphate detecting include chromatography, fluorescence, and colorimetry.⁸ Though these methods can detect nitrate and phosphate accurately, they require expensive, large-scale instruments, and specialized operators. In addition, the detection process is cumbersome, time-consuming, and prone to the generation of chemical waste, leading to secondary contamination.⁹ In recent years, various methods have been explored to achieve the efficient and economical on-site detection of nitrate and phosphate. Electrochemical methods are known for their simple equipment, affordability, and user-friendliness. They have high sensitivity, good accuracy, and wide measurement range, making them suitable for real-time detection of nitrate and phosphate in the field.⁷ Portable electrochemical sensors were developed and reported. For instance, electrodeposited bismuth nanoparticle electrodes

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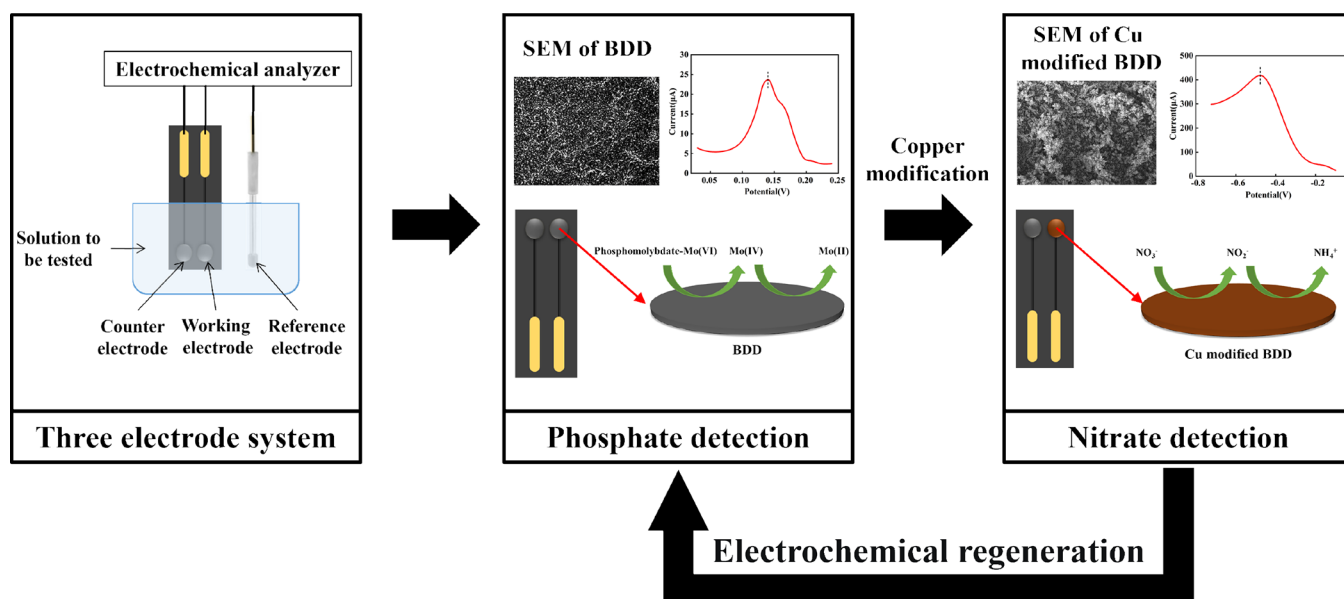


Figure 1. Phosphate and nitrate detection process by using an electrochemical sensor based on a BDD electrode.

have been used to detect cadmium in hot spring water samples from tourist attractions.¹⁰ An electrochemical analyzer has been developed for the in situ detection of Pb^{2+} and Cd^{2+} .¹¹ A miniaturized BDD electrode was used to detect herbicide Picloram in the Amazon region.¹² Electrochemical methods mainly include amperometric and potentiometric methods. Potentiometric methods have poor selectivity and short service life and cannot achieve long-term accurate detection in real complex water samples.¹³ Amperometric methods mainly utilize the current generated by the oxidation or reduction of the analyte on the working electrode for detection.¹⁴ Therefore, electrode materials and electrode design play important roles in the performance of electrochemical sensors. Over the past two decades, various materials have been studied for nitrate detection through electrochemical analysis. These materials include metals and metal oxides such as Ru, Rh, Ir, Pt, Pd, Cu, Ni, and Ag,^{15–19} as well as graphene derivatives,²⁰ carbon nanotubes,¹⁶ carbon fibers,²¹ conductive polymers,⁹ and enzymes.²² Among all these catalysts, Cu has been found to be the most promising electrocatalyst for nitrate reduction reactions.⁹ Therefore, copper-based electrodes, such as copper microelectrode arrays,²³ copper comodified carbon fiber electrodes,²⁴ and nanowire-based copper electrodes,¹⁸ have been used for nitrate analysis. Electrochemical detection methods for phosphates also involve a variety of electrode materials. However, most of them suffer from several problems, including a weak response signal, low sensitivity, and large amount of molybdate reagent requirement for glassy carbon and noble metal electrodes.^{25,26} Additionally, the preparation and modification procedures for polymer-modified electrodes, bioenzyme-modified electrodes, and nanomaterial-modified electrodes are cumbersome and complicated.^{27,28} To achieve high sensitivity and accuracy in nitrate and phosphate detection, it is crucial to select sensing electrodes with excellent electrochemical properties. Boron-doped diamond (BDD) electrodes have been widely used in electrochemical applications due to their low background current, wide potential window, resistance to fouling, and ability for electrochemical regeneration.^{29–31} The renewal of BDD electrodes does not require complicated surface pretreatments

such as mechanical polishing or inert gas purging.¹² This is because BDD electrodes can be electrochemically renewed by applying a voltage, which generates hydroxyl radicals to degrade organic micropollutants on the surface of the electrodes.³²

In this study, the electrochemical regeneration ability of BDD is combined with the catalytic effect of Cu on nitrate to construct a sensor for nitrate and phosphate detection. The bare BDD electrode can directly detect phosphate, and the electrode surface modified with Cu can achieve the determination of nitrate. The Cu modified on the electrode surface can be removed at positive voltages, and the regenerated BDD electrode can be used again for phosphate detection. Based on this dual-function BDD electrode, the electrochemical sensor can detect nitrate and phosphate, as shown in Figure 1.

EXPERIMENTAL SECTION

Chemicals and Reagents. Acetone, ethanol, H_2SO_4 , and HNO_3 were from Beijing Chemical Factory. Na_2MoO_4 , KH_2PO_4 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Na_2SO_4 , and NaNO_3 were from China National Pharmaceutical Group Chemical Reagent Co., Ltd.; All reagents used were of analytical grade.

Instruments. A reference 600 electrochemical workstation (Gamry Instruments, USA), S-480 field emission scanning electron microscope (SEM, Hitachi, Japan), PHS-3C pH meter (Shanghai Leici Instruments Co., Ltd.), and Millipore Direct-Q deionized water system (Merck Millipore, USA) were used.

Fabrication and Pretreatment of Electrodes. Boron-doped diamond (BDD) film electrodes were prepared on silicon wafer by chemical vapor deposition³³ and diced with a diameter of 3 mm. Then, the electrodes were cleaned by sequential ultrasonic treatment in acetone, ethanol, and deionized water for 5 min each before use. After that, the electrodes were subjected to a +3 V voltage for 120 s in 0.5 mol/L H_2SO_4 to remove organic contaminants on the electrode surface. Then, cyclic voltammetric scanning in the range from –3 V to +3 V at a scan rate of 50 mV/s was performed to activate the electrodes. Copper as the sensing

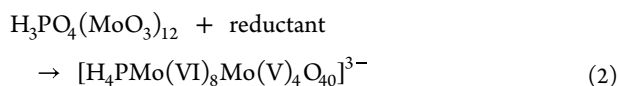
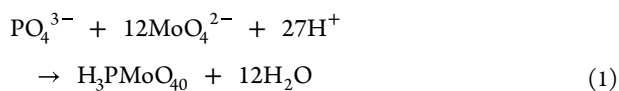
material for nitrate was modified on the electrode by using the cyclic voltammetric method. The cyclic voltammetric method was conducted with 10 cycles of scanning from 0 to -0.8 V with a scan rate of 50 mV/s. The deposition solution was 0.15 mol/L CuSO_4 solution at pH 1.

Determination of Phosphate. The analysis and detection of phosphate were carried out using an electrochemical three-electrode system with a BDD working electrode, a BDD counter electrode, and an Ag/AgCl reference electrode. The electrolyte solution for phosphate detection was a mixture of 0.7 mol/L KCl and 3.3 mmol/L Na_2MoO_4 at pH 1.5. For actual water samples, H_2SO_4 , KCl, and Na_2MoO_4 were added before detection to create a favorable electrolyte environment. The oxidation–reduction behavior of the molybdophosphate complex on the electrode surface was analyzed by cyclic voltammetry, with a scan voltage range of -0.1 to 0.6 V and a scan rate of 50 mV/s. Square wave voltammetry was used for phosphate detection, with a scan voltage range of 0.6 to 0.1 V, a pulse amplitude of 50 mV, and a pulse frequency of 50 Hz. For comparison, cyclic voltammetry was also used for detection. The reduction peak current of the molybdophosphate complex on the electrode surface was recorded to determine the concentration of the phosphate.

Determination of Nitrate. The analysis and detection of nitrate were carried out using an electrochemical three-electrode system, with a BDD electrode modified with Cu as the working electrode, a BDD electrode as the counter electrode, and a Ag/AgCl electrode as the reference electrode. The electrolyte solution for nitrate detection was a 0.1 mol/L Na_2SO_4 solution at pH 1.5. For actual water samples, H_2SO_4 and Na_2SO_4 were added before detection to create a favorable electrolyte environment. Linear sweep voltammetry was used for nitrate detection, with a scan voltage range of -0.8 to -0.1 V, a pulse amplitude of 25 mV, and a pulse frequency of 50 Hz. For comparison, pulse voltammetry was also used for detection. The reduction peak current of nitrate on the electrode surface catalyzed by Cu was recorded to determine the concentration of nitrate.

RESULTS AND DISCUSSION

Principle of Phosphate Detection. The traditional spectrophotometric method involves the chelation reaction between phosphate and molybdate in an acidic environment, resulting in the formation of a phosphomolybdate complex. This complex is then reduced to phosphomolybdenum blue (PMB) by the addition of ascorbic acid as the reducing agent. The concentration of phosphate in the tested sample is determined by measuring the absorbance of PMB. The main reaction equations are as follows:



The electrochemical detection method applies a reduction potential to induce a reduction reaction of the phosphomolybdate complex on the electrode surface. This method avoids the problems associated with a long color reaction time, difficulty in ensuring stability, and secondary pollution. The magnitude of the reduction current of the phosphomolybdate

complex is correlated with the concentration of phosphate in the solution, thus enabling the detection of phosphate in water by measuring the reduction current. The reaction process of phosphate electrochemical detection is shown in Figure 1.

Figure 2 shows the cyclic voltammetry curves of the BDD electrode in phosphate solutions with different concentrations.

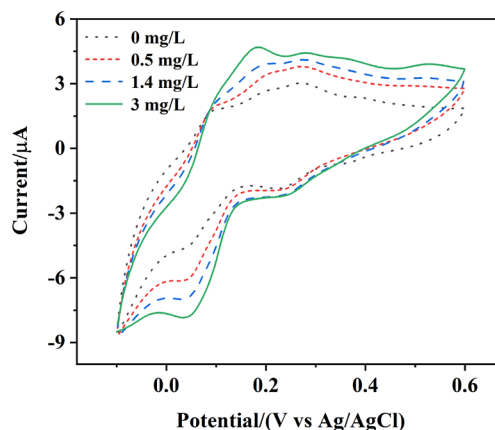


Figure 2. Cyclic voltammetry curves of the BDD electrode in phosphate solutions.

The cyclic voltammetry scanning voltage range was from -0.1 to $+0.6$ V, and the scanning rate was 50 mV/s. The background electrolyte solution used for testing contains 0.7 mol/L KCl and 3.3 mmol/L Na_2MoO_4 at a pH of 1.5. As shown in Figure 2, two reduction current peaks appeared at about $+0.25$ V and $+0.05$ V potentials, corresponding to the processes of Mo^{6+} reduction to Mo^{4+} and Mo^{4+} reduction to Mo^{2+} .³⁴ At the same time, there were two oxidation current peaks in the response curve corresponding to the oxidation process of the phosphomolybdate complex. The presence of oxidation and reduction peaks indicated that the phosphomolybdate complex exhibits good electrochemical activity on the BDD electrode surface, making it suitable for the electrochemical detection of phosphate. The peak current of oxidation and reduction increased as the phosphate concentration increased, demonstrating the good response of the BDD electrode to phosphate concentrations.

Principle of Nitrate Detection. In an acidic environment, copper can catalyze the complex reduction reaction of nitrate ions. The reaction produces nitrite, ammonium ions, and ammonia, among other products. However, most of these products are only intermediate products of the reaction. Ammonia ions are widely recognized as the final product of the reaction,³⁵ as shown in Figure 1 and eq 3

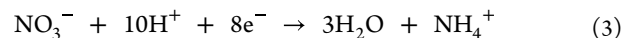


Figure 3 displays the linear scanning curves of the copper-modified BDD electrode in nitrate solutions. A distinct reduction peak was observed in the response curve at approximately -0.6 V. The analysis suggests that nitrate can be reduced under the catalytic effect of copper. By using the property, the detection of nitrate concentration can be achieved.

Electrochemical Regeneration of BDD Electrodes.

This study presents a nitrate and phosphate detection sensor based on a dual-function BDD electrode. The BDD electrode has the ability to detect phosphate directly. When the electrode

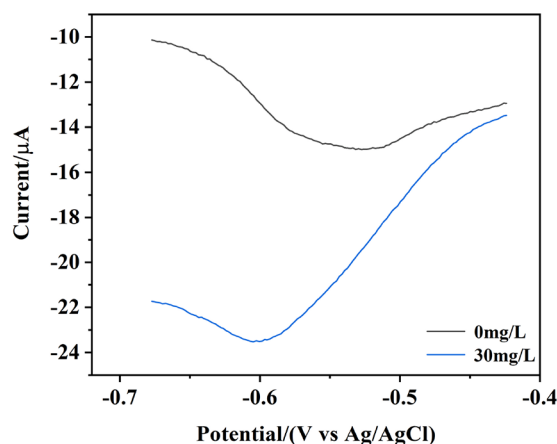


Figure 3. Linear scanning curves of the BDD electrode in nitrate solutions.

surface is modified with Cu as a catalyst, it can be used for determining the nitrate. The modified Cu can be removed at a positive voltage, and the regenerated BDD electrode can be used again for phosphate detection. Table 1 shows variation of

Table 1. Elemental Composition of the Surface of the BDD-Modified Cu Electrode before and after Electrochemical Regeneration

element	wt % (before electrochemical regeneration)	wt % (after electrochemical regeneration)
B	0.00	5.92
C	38.01	94.08
Cu	61.99	0.00

the elemental composition of the electrode surface. It can be seen that after electrochemical regeneration at positive voltage, copper on the electrode surface was completely removed and the electrode was regenerated to be a bare BDD electrode for phosphate detection. Meanwhile, the sensitivity and stability of the nitrate-sensitive electrode can be ensured by renewing and remodeling the nitrate sensing film on the electrode surface, and the influence of the passivation process occurring on the surface of the electrode in the electrochemical detection can be solved.

Optimization of the Experimental Conditions for Phosphate Detection. The electrochemical detection performance of the sensing electrode is directly affected by the chosen electrochemical detection method. This study experimentally compared the effects of cyclic voltammetry (CV) and square wave pulse voltammetry (SWV) on the detection sensitivity of the sensor. Compared with CV, SWV can reduce the bilayer current and has a higher sensitivity and resolution as well as lower detection limit. Figure 4 displays the relationship between the current response and the phosphate concentration by using CV and SWV. The results indicated that the SWV method yielded higher current responses and a higher sensitivity for phosphate detection. Therefore, SWV was used for phosphate detection in subsequent studies.

The concentration of molybdate is a crucial factor in the complexation reaction as it affects the generation of phosphomolybdate complexes and the magnitude of the reduction current of phosphomolybdate complexes. Various concentrations of molybdate were added to the solution under test to investigate the impact of the molybdate concentration

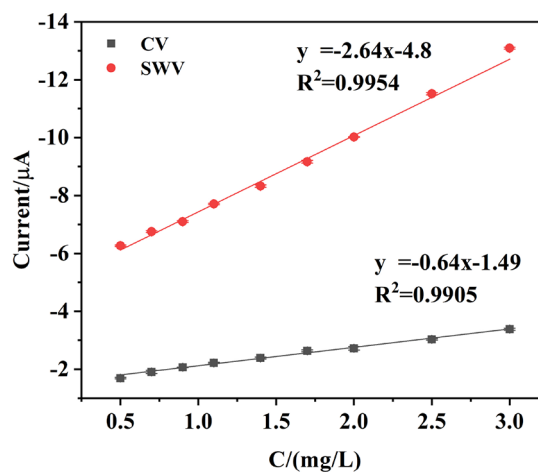


Figure 4. Response curves of cyclic voltammetry and square wave pulse voltammetry for phosphate detection.

on phosphate detection. As shown in Figure 5A, in the absence of molybdate, no electrochemical reduction reaction occurred, resulting in very low response current values. As the concentration of molybdate increased, the reduction current value increased. This suggests that a complex between the phosphate and molybdate needs to be formed before electrochemical reduction can take place. At low molybdate concentrations, fewer phosphomolybdate complexes were formed, resulting in a small reduction current value. The maximum reduction current was achieved at a molybdate concentration of 3.3 mmol/L. When the molybdate concentration exceeded 3.3 mmol/L, the reduction current tended to decrease once again. This may be due to the partial conversion of molybdate to molybdic acid in an acidic environment. Molybdic acid is slightly soluble and can produce a white precipitate, which hinders the complexation of molybdate and phosphate. Therefore, 3.3 mmol/L molybdate was chosen as the complexing agent for subsequent phosphate detection.

The ionic strength of the supporting electrolyte solution also has a great effect on the detection current. The effect of the solution ionic strength on phosphate detection was investigated by adding different concentrations of KCl. Figure 5B shows that as the KCl concentration increased from 0 to 0.7 mol/L, the reduction current also increased. The maximum reduction current strength was observed at a KCl concentration of 0.7 mol/L. However, at higher KCl concentrations, the background current increased, resulting in a low signal-to-noise ratio and an insignificant reduction peak current signal. Therefore, the concentration of KCl in the supporting electrolyte was selected to be 0.7 mol/L.

An acidic environment is necessary for the complexation reaction of phosphate with molybdate. To promote the formation of phosphomolybdate complexes and improve the current signal for phosphate detection, the pH value of the supporting electrolyte was optimized. The pH value of the electrolyte solution was changed by adjusting the concentration of H₂SO₄. The effect of the pH value on the current response is shown in Figure 5C. At high pH values, the reduction current was weak due to the low concentrations of H⁺ ions in the solution. This makes complexation between phosphate and molybdate. As the pH value decreased, the reduction current increased. The maximum reduction current was achieved when the pH is 1.5. When the pH value was

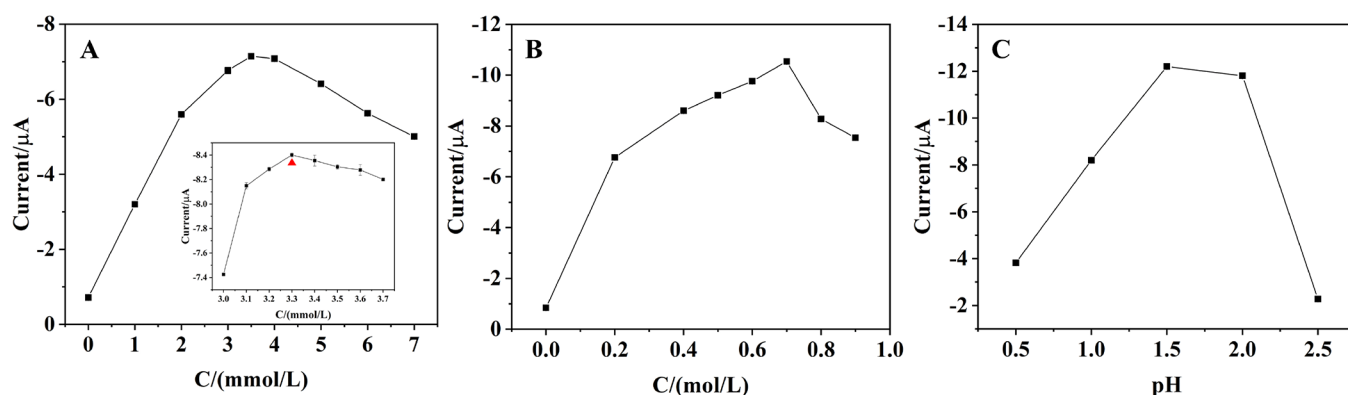


Figure 5. Influence of (A) molybdate concentration, (B) KCl concentration, and (C) pH value in the supporting electrolyte on a reduction current of 0.2 mg/L phosphate.

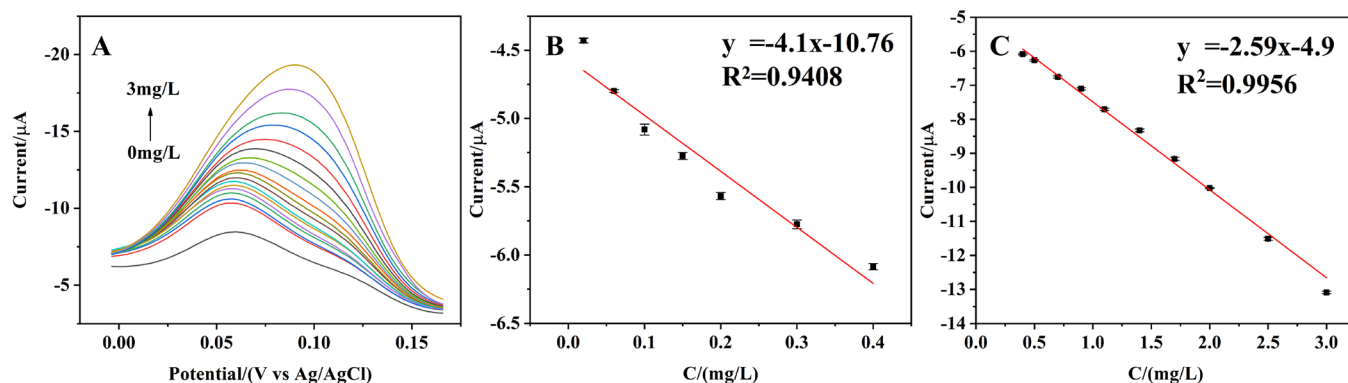


Figure 6. (A) Square wave pulse voltammograms of BDD measured in phosphate solutions with different concentrations (0–3.0 mg/L). Calibration curves for phosphate within concentrations of (B) 0.02–0.4 mg/L and (C) 0.4–3.0 mg/L.

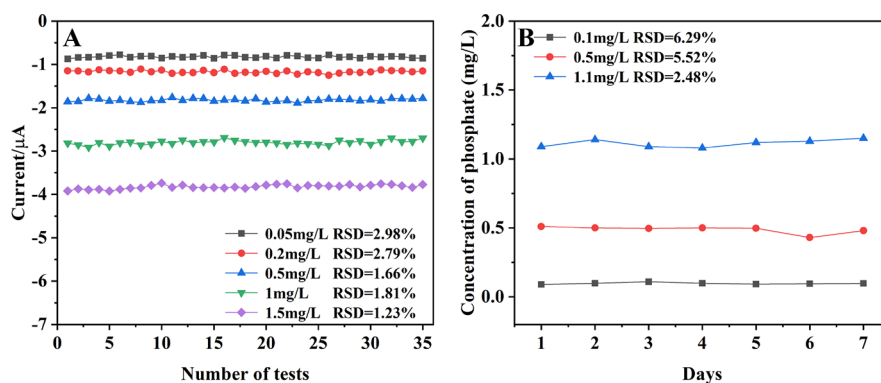


Figure 7. (A) Response current in 0.05, 0.2, 0.5, 1, and 1.5 mg/L phosphate solution for 35 consecutive tests. (B) Detection results in 0.1, 0.5, and 1.1 mg/L phosphate solution for the long-term (7 days) stability tests.

decreased further, the reduction reaction of excess H^+ in the solution will compete with that of the phosphomolybdate complex. This competition inhibits the reduction reaction of the phosphomolybdate complex and reduces the reduction current. Therefore, an electrolyte solution with pH of 1.5 was selected as the electrolyte solution for the complexation reaction.

Performance for Phosphate Determination. The electrochemical response of the phosphate sensor, based on the BDD electrode, was tested using phosphate standard solutions with concentrations ranging from 0 to 3 mg/L. The optimized detection parameters were used with the electrolyte solution containing 0.7 mol/L KCl and 3.3 mmol/L molybdate

at pH 1.5. The square-wave pulse voltammetric curves of the BDD measured in phosphate solutions are shown in Figure 6A, and the reduction peak current increased with the increase in phosphate concentration. The sensor was able to detect phosphate in a wide concentration range with segmented linear relationships in the ranges of 0.02–0.4 mg/L (Figure 6B) and 0.4–3 mg/L (Figure 6C), respectively. Also, the sensitivities were 4.1 and 2.59 $\mu\text{A}\cdot\text{L}/\text{mg}$, respectively. A higher sensitivity in the low concentration range was displayed. The detection limit for phosphate was calculated to be 0.004 mg/L by dividing the three times standard deviation of the blank signal by the slope of the calibration curve. This value meets the detection requirements for Class I to Class V water (0.02–0.4

Table 2. Performance Comparison of Different Phosphate Electrochemical Sensors

electrode	method	LOD	linear range	sensitivity	ref
Mo _x O _y /PDAAQ/GC	SWV	0.009 μM	0.03 to 4 μM	0.711 μA μM ⁻¹	37
coated pencil graphite electrode	DPV	1.25 μM	10 to 100 μM	38.1 nA μM ⁻¹	38
CBNPs/SPEs	CV	4.2 μM	5 to 100 μM	0.219 μA μM ⁻¹	39
microplotter-printed graphene	CV	2.2 μM	1 to 600 μM	0.32 μA μM ⁻¹	40
BDD	SWV	1.3 μM	0.6 to 12.9 μM	127 nA μM ⁻¹	this work
			12.9 to 96.9 μM	80 nA μM ⁻¹	

mg/L) as specified in the Chinese national surface water quality standards.³⁶

The electrochemical sensor based on the BDD electrode has good reproducibility for phosphate detection. The relative standard deviation (RSD) values of the current responses were 2.98, 2.79, 1.66, 1.81, and 1.23%, respectively, for 35 consecutive tests in 0.05, 0.2, 0.5, 1, and 1.5 mg/L phosphate solution (Figure 7A). Phosphate standard solutions with concentrations of 0.1, 0.5, and 1.1 mg/L were tested for 7 days, as shown in Figure 7B. The relative standard deviations (RSDs) were 6.29, 5.52, and 2.48%, respectively.

Table 2 presents a comparison of the performance of the developed phosphate sensor based on a boron-doped diamond electrode with other reported phosphate electrochemical sensors. The sensor demonstrates superior detection performance without electrode modification compared to other phosphate sensors.

Optimization of the Experimental Conditions for Nitrate Detection. Nitrate is usually detected using pulse voltammetry (DPV) and linear scanning voltammetry (LSV) methods.^{41,42} In electroanalytical chemistry, square wave voltammetry (SWV) and differential pulse voltammetry (DPV) are often observed to be more sensitive techniques than linear scanning voltammetry (LSV) due to their sampling methods that minimize the charging current (non-Faraday process). However, some research studies have shown that LSV is more sensitive than DPV in electrochemical testing.⁴³ To improve the current response and sensitivity of the detection, the effect of detection methods on the performance of nitrate detection was investigated. Figure 8 shows the

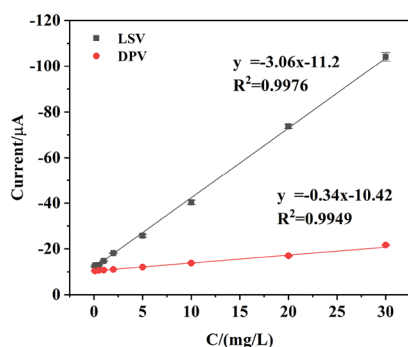


Figure 8. Response curves of DPV and LSV for nitrate detection.

response curves of different concentrations of nitrates by using DPV and LSV. It can be seen that for solutions with the same concentration of nitrates, LSV provided a more pronounced reduction current response and a higher sensitivity compared with DPV. Therefore, LSV was used for nitrate detection in subsequent studies.

To improve the detection performance of the sensor, the main parameters for copper deposition including CuSO₄

concentration, pH value, and number of scanning circles were optimized. As shown in Figure 9A, when the concentration of CuSO₄ in the deposition solution was low, the response current was weak due to the low deposition efficiency and insufficient density of the copper thin film. The maximum current response was achieved at a CuSO₄ concentration of 150 mM. When the concentration of CuSO₄ was too high, the response was also weak. This may be due to the copper film being too thick and prone to detachment.

During the cyclic voltammetric scanning process, H⁺ ions can be reduced into gas, which can increase the porous structure, specific surface area, and catalytic reaction contact surface of the nitrate-sensitive layer. This promoted the reduction of the nitrate ions. However, excessive H⁺ concentration can lead to a decline in the stability of the copper film, making it prone to detachment. A low concentration of H⁺ may not allow for the formation of a loose structure, which can also reduce the current response, as shown in Figure 9B.

When there were few scanning circles, the copper layer did not have enough time to form a cluster structure. An increase in the number of scanning circles may cause the deposited nitrate-sensitive layer to detach due to excessive thickness. Therefore, with the deposition solution CuSO₄ concentration of 150 mM, pH = 1, and the number of scanning circles for 10 circles, the response signal was the largest. Therefore, the subsequent experiments were set using these parameters.

The BDD electrode surface was modified with copper as the sensing film by using the cyclic voltammetry method. SEM was used to characterize the electrode surface. Figure 10A displays the surface of the bare BDD electrode. Figure 10B illustrates the loose, porous dendritic structure of the BDD electrode modified with copper. During the cyclic voltammetry deposition of copper, the growth rate of the copper film increased as the deposition potential increased. At this point, the selective orientation of copper crystals began, resulting in rapid growth of a particular type of copper crystal. This caused protrusions on the surface area and the formation of dendritic structures in the 3D direction of growth. Dendrites in turn cause an uneven electric field distribution on the deposited surface, which in turn accelerates the growth and aggregation of the dendrites. The dendritic structure grew layer by layer, with an increase in the number of scanning circles during cyclic voltammetry. Eventually, a dense branch cluster structure was formed. This allowed the specific surface area of the nitrate-sensitive coating to be increased, thus improving its catalytic efficiency. Figure 10C displays the EDX spectrum of the electrode surface, revealing only the presence of Cu and C elements. The relative proportion of Cu elements is 91.48%. As shown in Figure 10D,E, the elemental carbon and elemental copper distributions on the modified electrode were characterized using EDS (energy-dispersive spectrometry).

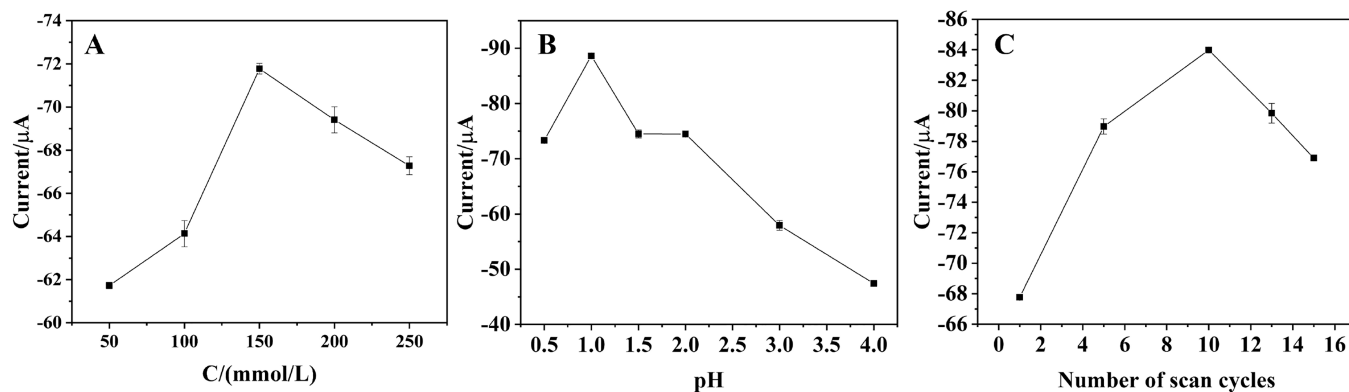


Figure 9. Influence of (A) CuSO_4 concentration, (B) pH value, and (C) number of scan cycles on the reduction current of nitrate.

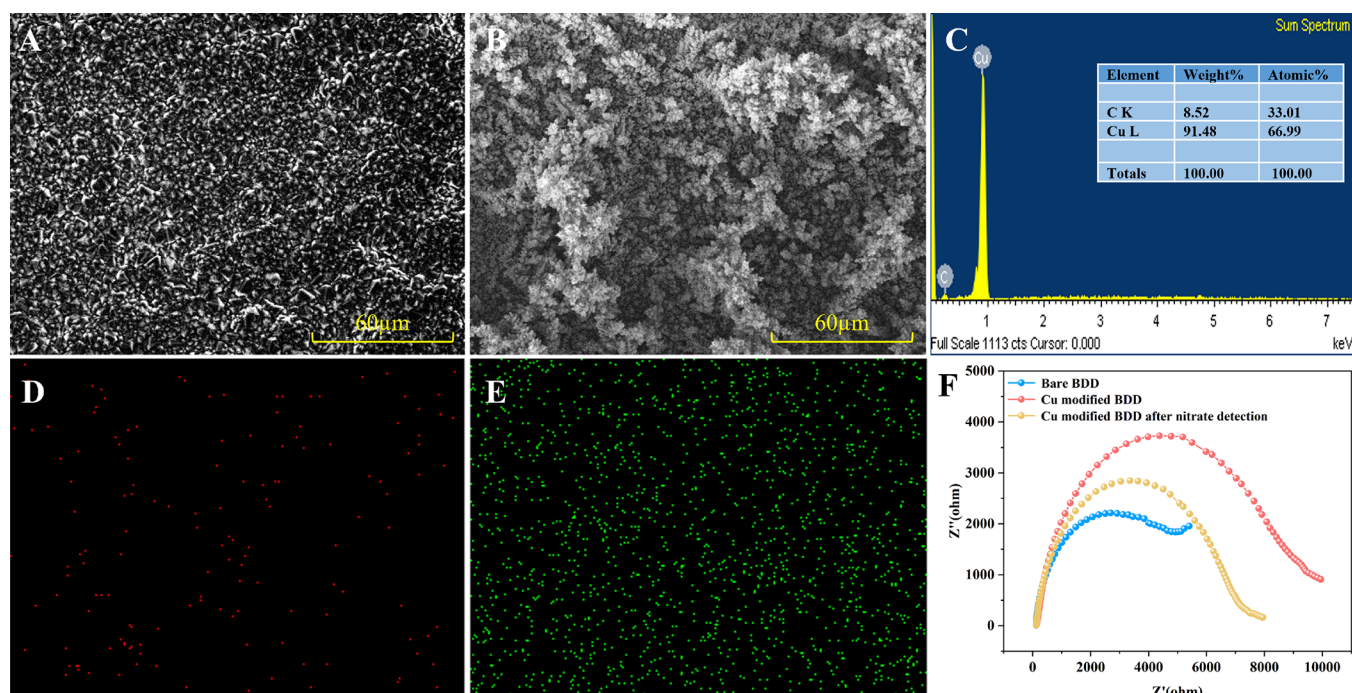


Figure 10. SEM images of the (A) bare BDD electrode and (B) copper-modified BDD electrode. (C) EDX of the copper-modified BDD electrode. EDS elemental mapping images of (D) carbon and (E) copper on the copper-modified BDD electrode. (F) EIS for the bare BDD electrode, Cu-modified BDD electrode, and electrode after detection of nitrate.

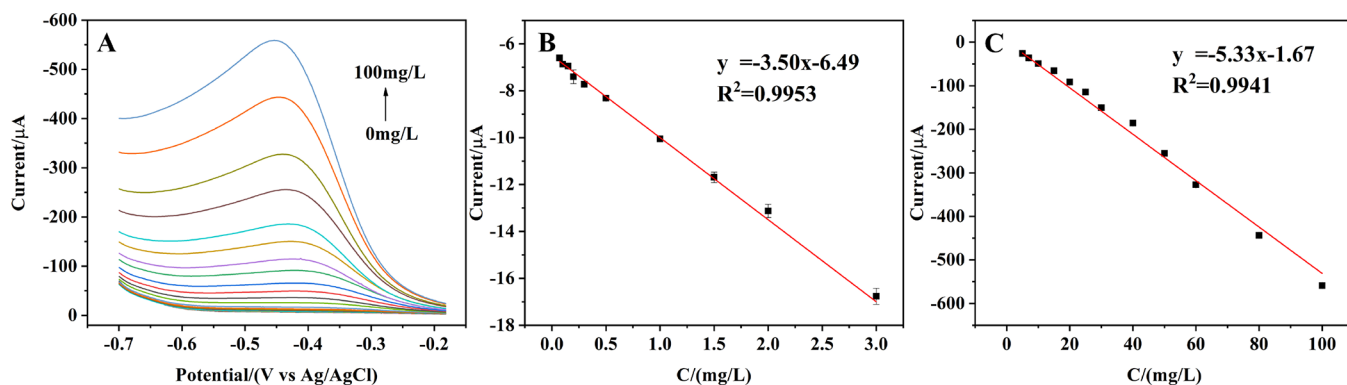


Figure 11. (A) Linear scanning voltammograms of BDD measured in nitrate solutions with different concentrations (0.07–100 mg/L). Calibration curves for nitrate within concentrations of (B) 0.07–3 mg/L and (C) 3–100 mg/L.

The modified electrode surface exhibited a uniform distribution of elemental copper. This indicates that a uniform copper

film was successfully deposited on the electrode surface. Figure 10F shows the EIS (electrochemical impedance spectroscopy)

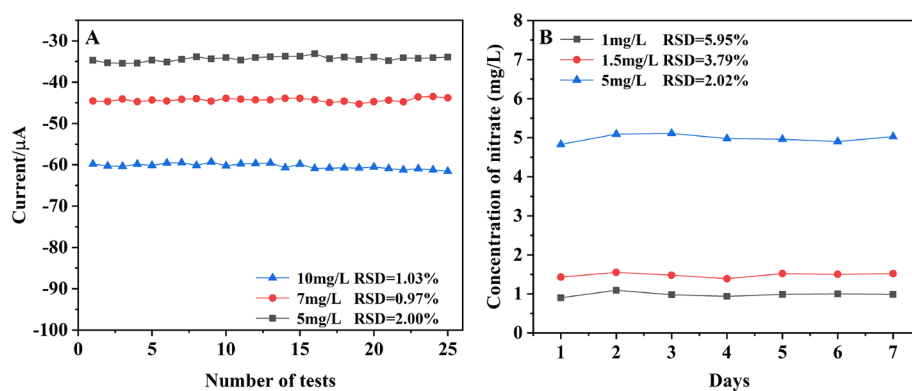


Figure 12. (A) Response current in 5, 7, and 10 mg/L nitrate solution for 25 consecutive tests. (B) Detection results in 1, 1.5, and 5 mg/L nitrate solution for the long-term (7 days) stability tests.

Table 3. Performance Comparison of Different Nitrate Electrochemical Sensors

electrode	method	LOD	linear range	sensitivity	ref
Ag nanoparticles electrodeposited on a Au electrode	SWV	0.9 nM	0.9 nM to 1000 μM	12 $\mu\text{A mM}^{-1}$	45
Cu electrodeposited on a Pt microelectrode	CA		0 to 3500 $\mu\text{mol/L}$	31 $\mu\text{A mM}^{-1}$	46
Cu microspheres decorated on polyaniline on a microneedle	DPV	8 μM	20 to 6000 μM	141.69 $\mu\text{A/cm}^2 \text{ mM}$	47
Cu-SPCEs	LSV	91 nM	50 to 750 μM	0.1042 $\mu\text{A m M}^{-1}$	48
copper nanowire array	CV	9 μM	10 to 1500 μM	0.73 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	49
Cu/BDD	LSV	4.6 μM	5 to 214 μM 214 to 7143 μM	0.25 $\mu\text{A mM}^{-1}$ 0.38 $\mu\text{A mM}^{-1}$	this work

for the bare BDD electrode, Cu-modified BDD electrode, and electrode after detection of nitrate. After cathodic pretreatment, the bare BDD electrode was in a state of hydrogen adsorption. The process of modifying copper gradually changed the diamond electrode to oxygen adsorption, which was weakened by the reduction process of nitrate detection. It was observed that the impedance of the BDD electrode with surface oxygen adsorption was larger than that of the BDD electrode with hydrogen adsorption.⁴⁴ Therefore, modifying the copper film increases the electrode impedance, which subsequently decreases after nitrate detection. However, the electrode impedance tends to stabilize during the detection process. The experimental results show that the change in the electrode impedance does not affect the detection effect. This is because the electrode state can be controlled through a pretreatment.

Performance for Nitrate Determination. Subsequently, the response current values of the sensors were examined in relation to the concentration of nitrate ions by using linear scanning. The LSV curves of the BDD measured in nitrate solutions are shown in Figure 11A, and the reduction peak current increased with the increase in nitrate concentration. The sensor was able to detect nitrate in a wide concentration range with segmented linear relationships in the ranges of 0.07–3 mg/L (Figure 11B) and 3–100 mg/L (Figure 11C). The sensitivities were 3.50 and 5.33 $\mu\text{A}\cdot\text{L}\cdot\text{mg}^{-1}$, respectively. The detection limit for nitrate was calculated to be 0.065 mg/L by dividing the three times standard deviation of the blank signal by the slope of the calibration curve.

The electrochemical sensor based on the BDD electrode has good reproducibility for nitrate detection. The same copper-modified BDD electrode was tested at least 300 times. The relative standard deviation (RSD) values of the current responses were 2.00, 0.97, and 1.03%, respectively, for 25 consecutive tests in 5, 7, and 10 mg/L nitrate solution (Figure

12A). Nitrate standard solutions with concentrations of 1, 1.5, and 5 mg/L were tested for 7 days, as shown in Figure 12B. The relative standard deviations (RSDs) were 5.95, 3.79, and 2.02%, respectively.

Table 3 presents a comparison of the performance of the developed nitrate sensor based on a boron-doped diamond electrode to other reported phosphate electrochemical sensors. This nitrate sensor is capable of detecting nitrate at various concentrations due to its wider linear range compared to other nitrate sensors.

Determination in Actual Water Samples. The sensor was used to test for nitrates and phosphates in real water samples. The actual water samples were selected from local tap water, river water, and lake water. H_2SO_4 and electrolytes were added to the actual water samples to adjust them to a suitable electrolyte environment before electrochemical testing. The standard addition method was used to compare the detection results of the added values to the measured values. The results for phosphate and nitrate determination are shown in Tables 4 and 5, respectively. The recoveries of the developed sensors for

Table 4. Analysis Results of Phosphate in Actual Water Samples

sample	added (mg/L)	measured (mg/L)	recovery (% , $n = 3$)
river water 1	1.5	1.48	98.7
river water 2		1.49	99.3
lake water 1		1.51	100.7
lake water 2		1.53	102.0
lake water 3		1.45	96.7
lake water 4		1.45	96.7
lake water 5		1.46	97.3
lake water 6		1.49	99.3
lake water 7		1.46	97.3
lake water 8		1.49	99.3

Table 5. Analysis Results of Nitrate in Actual Water Samples

sample	added (mg/L)	measured (mg/L)	recovery (% , n = 3)
tap water 1	7	6.45	92.1
lake water 1		7.48	106.9
lake water 2		6.91	98.7
lake water 3		6.79	97.0

the detection of phosphate in tap water samples, river water samples, and lake water samples were between 96.7 and 102.0%, and the recoveries for the detection of nitrate were between 92.1 and 106.9%. The test results indicate that the electrochemical sensor based on the BDD electrode prepared in this study has the potential to be applied to the detection of nitrate and phosphate in real water samples.

CONCLUSIONS

In this article, a bifunctional BDD electrode with reproducible electrochemical updating and modification capabilities was investigated. We used this electrode as a common working electrode to determine the concentrations of nitrate and phosphate. The BDD electrode was used for the direct detection of phosphate. A thin layer of copper was electro-deposited on the BDD electrode to enable nitrate detection. The copper layer was then removed at a positive voltage to renew the BDD electrode for further phosphate detection. In this way, the electrochemical sensor enables detection of both phosphate and nitrate. The renewal of the electrode surface can ensure the reproducibility and stability of the detection. The linear range of phosphate detection was from 0.02 to 0.4 mg/L and from 0.4 to 3 mg/L, with a detection limit of 0.004 mg/L. The sensor detected nitrate in a wide concentration range, with segmented linear relationships in the ranges of 0.07–3 and 3–100 mg/L, with a detection limit of 0.065 mg/L. The utilization of the dual-function BDD electrode can simplify the sensor's structure, circuit system, and flow system. Additionally, the use of a newer electrode surface can enhance the stability and reproducibility of the detection process and resolve the passivation issue with conventional electrochemical electrodes. Consequently, the dual-function BDD electrode and its detection method will be integrated with the flow system to enable automatic monitoring of phosphate and nitrate levels in water.

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Notes

The authors declare no competing financial interest.

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