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Research Article

A Miniaturized Electrochemical Nitrate Sensor and the Design for Its Automatic Operation Based on Distributed Model

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As one of the most common inorganic ions in daily food and ecological environment, nitrate (NO_3^-) is potentially harmful to both environment and humans. Therefore, the detection of nitrate concentration is quite important. Chemical sensors, as analytical measurement tools, usually demonstrate high selectivity, fast analysis speed, simple structure, convenient operation, and low cost and are considered to be a promising method for ion identification and detection. In this paper, a miniaturized electrochemical electrode is fabricated based on the microfabrication technology, and an electrochemical sensor for the detection of nitrate concentration in water is developed by combining the deposition technology of nanometal particles with electrochemical analysis technique. The developed electrochemical sensor utilizes electrochemical deposition to prepare a copper (Cu) granular sensitive film with a branch-cluster structure on the surface of a circular working electrode (Pt). Using copper's characteristics of electrocatalytic reduction of NO_3^- in the acid solution environment (pH = 2), the concentration of NO_3^- in the water sample was calculated by measuring the reduction current on the working electrode when the electrocatalytic reduction reaction of NO_3^- occurred on the surface of the copper-sensitive membrane. The sensitive film is characterized and detected both with the scanning electron microscope (SEM) and X-ray diffraction analysis (XRD) technique; and the microsensor is used to detect nitrate standard samples; a high detection sensitivity (24.9 μA/mmol·L^{-1}) is achieved in the concentration range of 0.0 to 3.0 mmol/L. At the same time, a MEMS three-electrode sensor without gold wire bonding and insulating glue packaging is designed, and an automatic detection system is constructed with a STM32f103 microcontroller as the controller to realize the automated detecting process for nitrate ions. At the same time, a distributed system is constructed, which can describe the nitrate concentration in every position of the water area and realize the monitoring of the whole water area. The detection system can meet the working environment under most conditions and has practical significance.

1. Introduction

Nowadays, nitrate is one of the most prevalent pollutants in surface and groundwater throughout the world. In recent decades, with the fast development of large-scale industry and agriculture as well as the rapid expansion of urban population, the level of nitrate pollution continues to increase in both developed and developing countries. Nitrate is highly soluble and migrates very fast in water or in the atmosphere. Once the nitrates generated in industrial and agricultural production enter the natural environment, they will diffuse widely with various water currents or atmospheric circulation activities. As a result, the nitrate concentration in natural water bodies is on the rise and has become a significant environmental pollution problem [1]. Many studies have proved that excessive nitrate content in water will cause serious environmental pollution and physiological diseases [2, 3]. For example, in terms of environmental pollution, nitrates will gather in local waters after flowing into lake waves with rivers. They, together with

other pollutants, cause eutrophication of water bodies and even lead to cyanobacteria outbreaks in severe cases. As for health hazards, nitrates are harmful to human health mainly through drinking water contamination. Long-term consumption of drinking water containing excessive nitrates will cause changes in blood components, which in turn induce diseases such as muscle cramps, methemoglobinemia, and even gastric cancer [2, 4]. Hence, all countries have implemented strict restrictions on the content of nitrate in drinking water [5–7]. Whether from the perspective of environmental protection or the building of healthy life, it is of great significance to establish a simple, sensitive, and accurate nitrate detection method.

At present, the commonly used nitrate ion detection methods mainly include spectrophotometry, chromatography, chemiluminescence, capillary electrophoresis, electrochemical detection, and so on [8–10]. Among them, detection methods based on optical principles usually feature the merits of low detection limit, high precision, and good sensitivity. However, there are also problems such as large instrument size, high price, complex sample preprocessing, and long time-consuming. And there are two kinds of smaller nitrate ion sensors, pen sensors and hand-held testers. In contrast, the detection method based on the electrochemical principle has the advantages of simple instrument, convenient operation, less reagents required, and easy integration with the detection circuit, which is considered to be a new type of nitrate detection method with great development prospects [11–13].

In this paper, a miniature electrochemical sensing electrode was prepared based on MEMS technology, and a copper-sensitive film was prepared on the surface of the working electrode (Pt) by potentiostatic deposition. In this way, a miniature electrochemical sensor was constructed and used for the detection of nitrate ions in water. At the same time, a novel microsensor packaging-free system is designed for the difficult packaging of MEMS technology. It does not need to use metal wires for welding and builds an automatic detection system with STM32f103 microcontroller as the controller to realize the automated detecting process for nitrate.

2. Preparation of Microsensors

2.1. Instruments and Reagents. The instruments used are Camry Reference-600 electrochemical analyzer (USA, Gamry); AUW electronic balance (Japan, Shimadzu); Direct-Q3UV high-purity water machine (USA, Millipore); digital pH meter (Shanghai Zhiguang Instrument Co., Ltd., pHS-25 type); and S-4800 scanning electron microscope (FE-SEM, Japan, Hitachi).

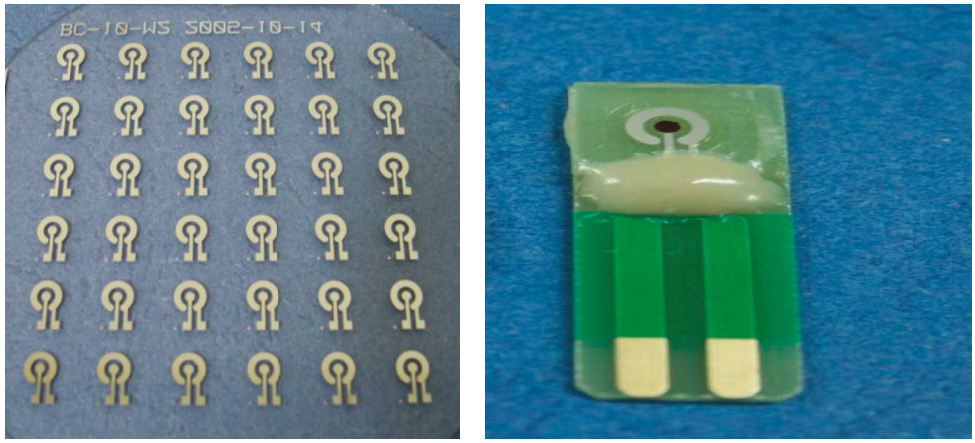
Reagents used are $CuSO_4\,5H_2O$, Na_2SO_4, $NaNO_3$, and 98% H_2SO_4 (Beijing Chemical Reagent Company); nitrate standard sample 50 mg/L (Beijing, Institute of Standardization, Ministry of Environmental Protection). Chemicals and solvents are of analytical grade, and experimental water is 30 MΩ cm deionized water. Unless otherwise specified, all solutions are obtained by dissolving quantitative solid reagents in deionized water at room temperature of 25°C. All experiments were completed in a three-electrode system, the reference electrode was Ag/AgCl reference electrode (CHI111, China, Shanghai Chenhua), and the working electrode and counter electrode were laboratory-made miniature sensing electrodes.

2.2. Preparation of Sensing Electrodes. The fabrication process of miniature electrochemical sensing electrodes has been reported in detail in other papers [14, 15]. It mainly uses photolithography, sputtering, lift-off, scribing, packaging, and other process steps, which can realize the batch preparation of sensing electrodes to ensure the consistency of different electrodes. The specific structure of the sensor is mainly a micrometal electrode system prepared by MEMS technology, and a polymer layer sensitive to specific materials is prepared on the working electrode by the electrochemical method. The prepared microsensing electrode is shown in Figure 1(a): the working electrode and the counter electrode which is usually made of Pt [16–18] are in symmetrical circular-ring structures, and the area of the working electrode is 1.0 mm^2; the whole size is 10 mm × 10 mm; the electrode is attached to the printed circuit board, soldered to the gold finger on the PCB using gold wire, sealed to the PCB with insulating glue, as shown in Figure 1(b), and then dried at 60°C for 12 hours.

2.3. Preparation of Copper-Sensitive Film. The encapsulated microsensing electrodes were immersed in copper sulfate solution (pH = 2.0, 100 mmol/L $CuSO_4$). Electrochemical deposition was performed on the working surface of the microelectrode using Chronoamperometry Scan through an electrochemical workstation (deposition time was 160 s, and deposition potential was −0.3 V). In order to prevent the deposited copper from being oxidized in the air after the deposition is completed, the surface of the electrode is rinsed with deionized water, and the electrode is placed in deionized water for preservation. When using the potentiostatic method to modify the electrode, the electrochemical deposition curve is shown in Figure 2.

2.4. Package-Free System for Miniature Sensors. MEMS is a key technology for the preparation of modern microsensors, and three-electrode microsystems are commonly used electrochemical sensors based on MEMS technology, featuring simple preparation, easy batch production, and stable performance. However, in the actual preparation process, it is necessary to use gold wire pressure welding. At the same time, the gold wire is easy to break when packaged with insulating glue, and the efficiency is low. Therefore, this paper designs a MEMS three-electrode sensor without gold wire bonding and insulating glue packaging, as shown in Figure 3.

In this paper, the screws inserted through the fixing hole make the electrode on the pressing device closely fit with the microelectrode system, so as to ensure that the electrode is closely combined with the external circuit. The pressing device and the unique groove design of the microelectrode in



(a) (b)

Figure 1: Photo of sensing electrodes: bulk-fabricated sensing electrodes. (a) Unpackaged electrodes. (b) Packaged electrode on PCB.

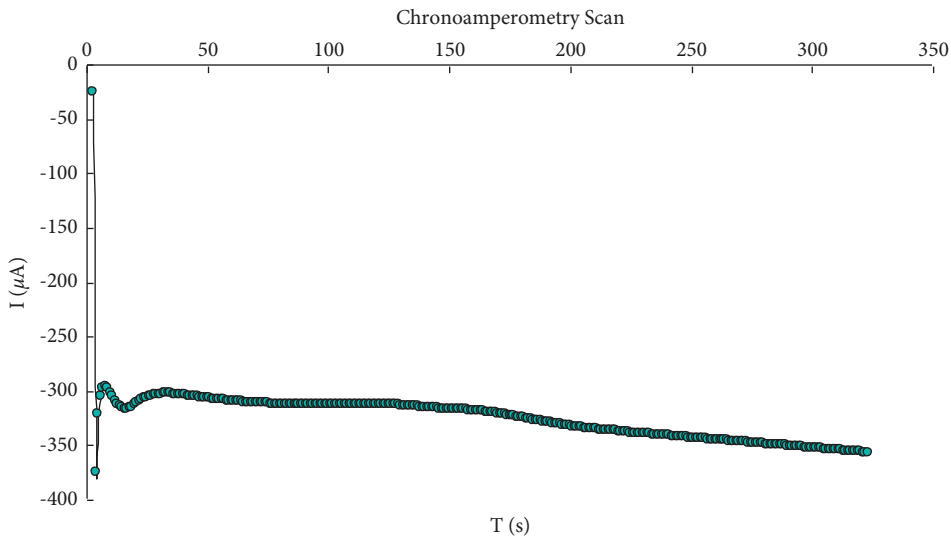


Figure 2: Potentiostatic deposition scanning curve: potential −0.3 V; time 160 s.

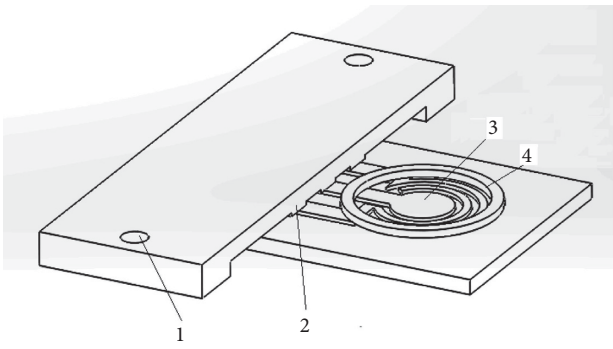


Figure 3: (1) Fixing hole, (2) screen-printed electrode, (3) microelectrode system, and (4) microreaction tank.

the PCB and the conductive glue instead of the gold wire are used. In this way, it effectively avoids the disadvantages of the existing three-electrode microsensor system that need to use a gold wire ball bonding machine for pressure bonding, the use of insulating glue to make the gold wire easy to break and fall off, and the low efficiency of the use of insulating glue, which improves the reliability, avoids the sensors to be a disposable chip, and is convenient for the regeneration and the reuse of the sensors.

2.5. Automatic Detection System and Model Analysis. Usually the detection takes place in a large place such as a lake, so the automatic detection system consists of several automatic detection subunits (SUa) and a main processing unit (MU); each automatic detection unit consists of a single-chip microcontroller and has an identity code, while using the wireless transmission module for signal transmission to the main processing unit [19, 20]. The main processing unit collects and processes the information. This information includes the temperature, the automatic detection unit ID number, and the structure of the system as shown in Figure 4. The contact method between subunits

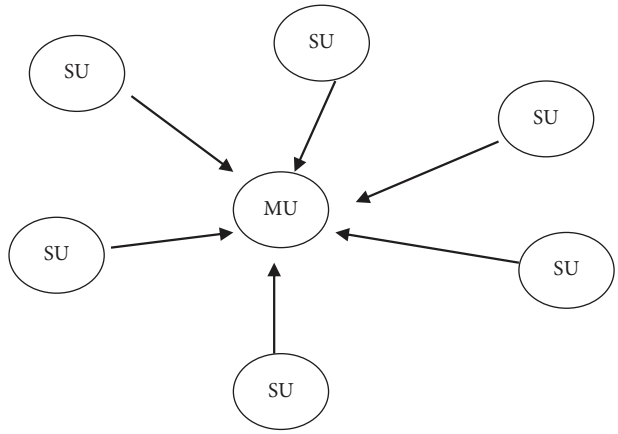


Figure 4: Schematic model of node structure of automatic detection system.

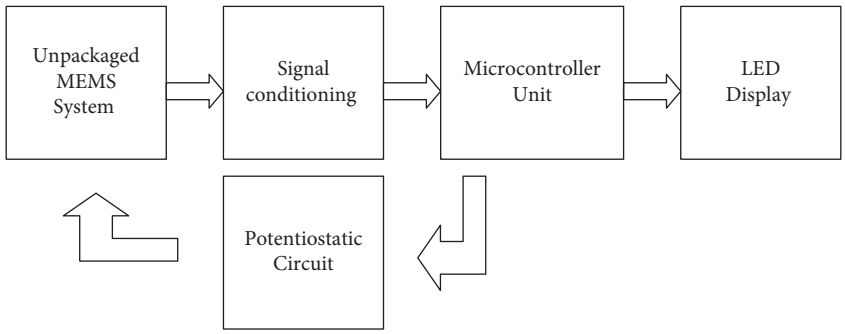


Figure 5: Structure and composition diagram of the automatic detection system.

and main processing unit was bluetooth communication mode.

In order to satisfy the online automatic detection of nitrate microsensor based on MEMS technology, the system consists STM32f103 microcontroller as controller, HX711 as signal converter, signal conditioning circuit and constant potential circuit, unpackaged MEMS system, and display circuit, as shown in Figure 5. The controller applies a constant voltage to the electrochemical sensor in the MEMS system through the potentiostatic circuit, so that the sensor generates a current signal, which is carefully processed by the signal conditioning circuit and converted into a voltage signal.

The TU is a signal transmission unit; usually a fixed monitored water area has multiple transmission units, each of which is responsible for receiving the signal from the attached MU, as shown in Figure 6; the signal is processed and sent to the central processing unit for storage and display. Tu is composed of signal receiving circuit, memory circuit, and signal transmitting circuit.

In the wireless data acquisition model as shown in Figure 7, each SU unit has an identification tag, which only communicates with the adjacent MU one-to-one. The MU receives the detection data, and the TU unit will also receive the data of the nearby MU unit one-to-one, and the data are transmitted wirelessly to the central control room for display.

3. Results and Discussion

3.1. Micromorphological Characterization and Material Analysis of Sensitive Materials. Scanning electron microscope (SEM) was used to observe the microscopic topography of the electrodeposited working electrode surface. As shown in Figure 8, a layer of loose branch-like structure was formed on the surface of the platinum working electrode after the potentiostatic deposition treatment. In the local magnified image, it can be found that the surface of the working electrode has been completely covered by the granular material. There are also branch-like protruding structures locally, which are formed by interconnected particles with a particle size of about 200 nm and protruding upwards from the electrode surface and depositing continuously along a certain spatial direction.

In order to investigate the composition of the materials generated on the electrode surface after electrodeposition treatment, X-ray diffraction analysis (XRD) was performed on the surface of the working electrode. The results of XRD analysis are shown in Figure 9. It can be found that there are 5 characteristic peaks in the XRD test pattern, and the comparison material spectrum shows that three of them are characteristic peaks of platinum (Pt), which is the property of the platinum material of the working electrode; the other

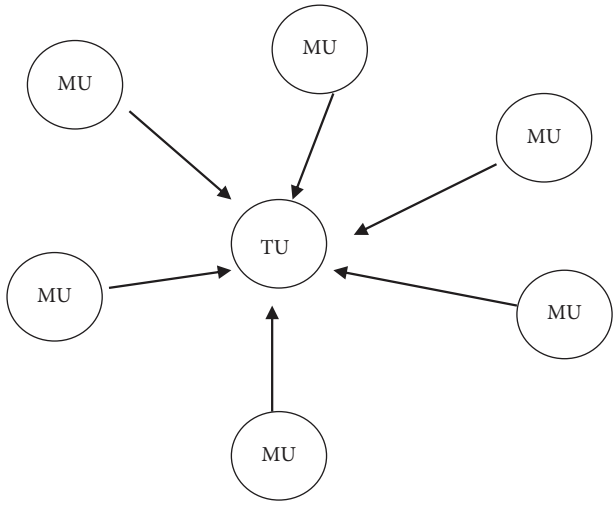


Figure 6: Structure and composition model of the automatic detection system.

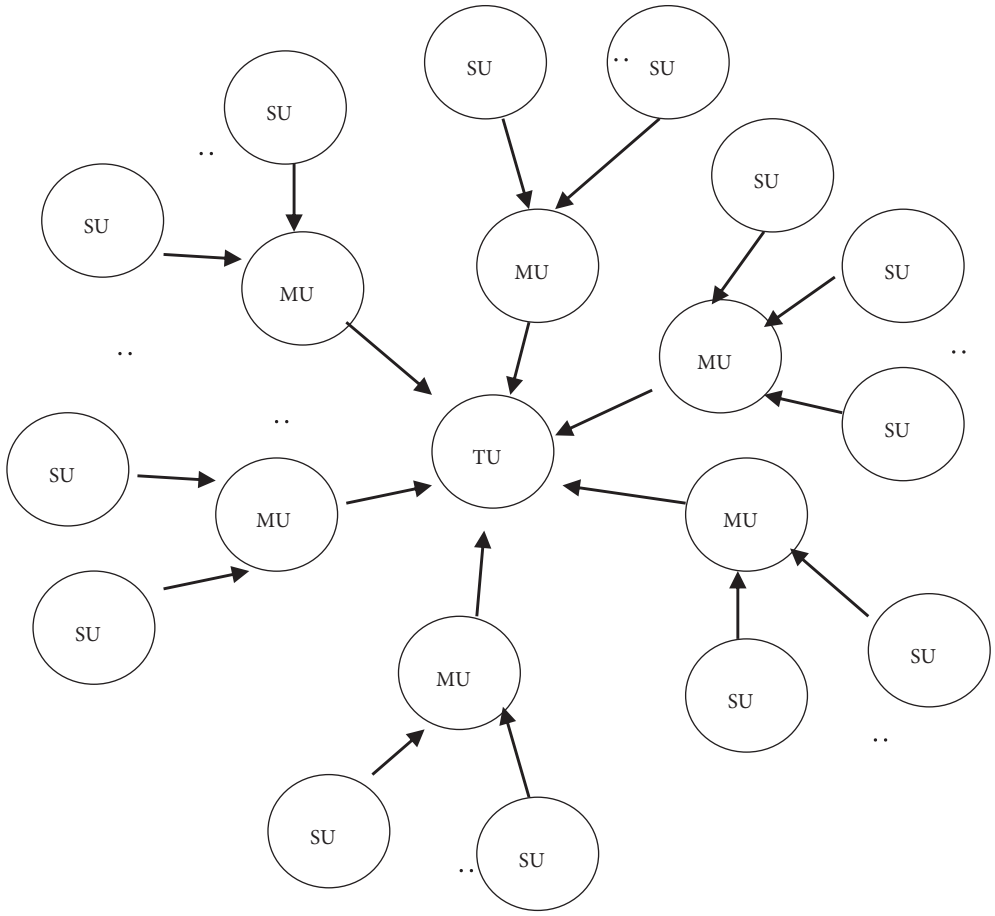
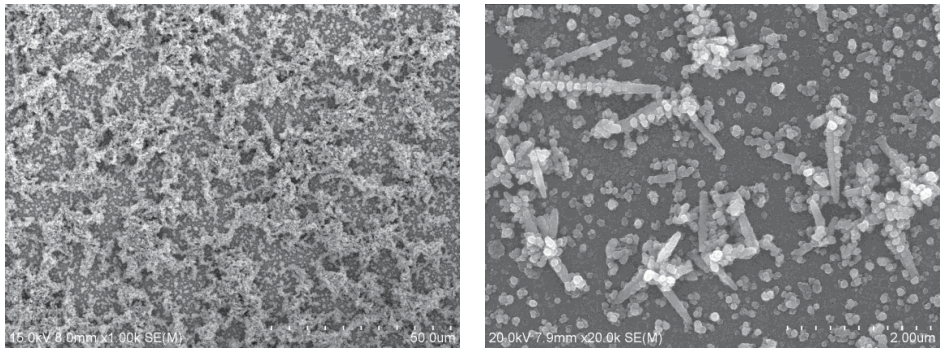


Figure 7: Structure and composition model of the wireless data acquisition system.

two peaks are characteristic peaks of (111) and (200) orientations of copper (Cu), indicating that the modified layer prepared by the potentiostatic deposition method is made of metallic copper rather than its related oxides.

3.2. Electrochemical Detection Performance of the Microsensor for Nitrate Ions. The current response characteristics of the microsensing electrodes modified by constant voltage deposition to different concentrations of nitrate standard



(a) (b)

Figure 8: The SEM image of the surface on the working electrode after electrochemical deposition process with deposition potential −0.3 V and deposition time 160 s. (a) ×1000 times. (b) ×20000 times.

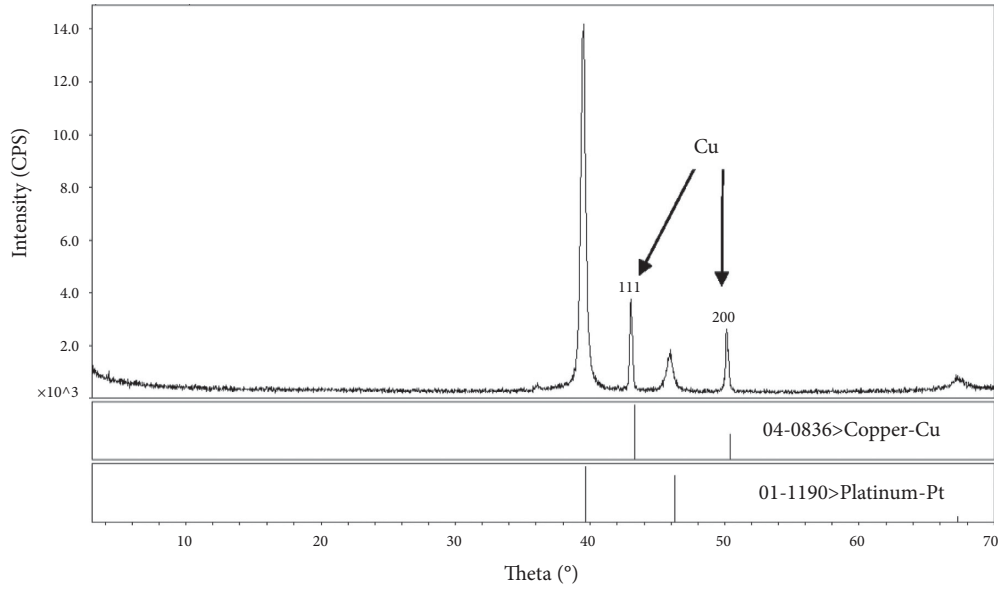


Figure 9: X-ray diffraction analysis of the modified layer material: deposition potential of −0.3 V; deposition time of 160 s.

solutions were analysed by voltage linear scanning. In all experiments, 0.1 mol/L Na_2SO_4 solution with pH = 2.0 was used as the supporting electrolyte, and the microsensor was immersed in the test solution containing different concentrations of NO_3^- for linear scanning test, and the relationship between the concentration of NO_3^- and the reduction peak current was investigated. Figure 10(a) is the linear scan response curve of the microsensor in different concentrations (0.0–3.0 mmol/L) of standard nitrate. It is found that from the figure that the current response signal of the sensor increases with the increasing NO_3^- concentration in the test solution.

Literature studies [6, 21] have shown that applying a voltage to the surface of the copper nanoparticles converts the nitrate into ammonium ions, generating an electric current in the process. The nitrate concentration can be reflected by measuring the current. During the experiment, a total of 10 concentrations were measured and these concentration-current data sets were obtained, and the I–C relationship curve was plotted based on these data. Figure 10(b) is the fitting relationship curve between the corresponding reduction current value in the linear scan curve and the NO_3^- concentration in the test solution when the reduction potential is −600 mV. It is found that there is a good linear relationship between the reduction current value and the NO_3^- concentration value in the concentration range of 0.1–3.0 mmol/L. The result indicates that the detection of nitrate concentration can be realized by measuring the magnitude of the reduction current via the developed miniature electrochemical sensor. The current is related to the rate of the scanning voltage and the area of the working electrode [22]. The functional relationship between the peak current value obtained by linear fitting and the nitrate concentration is

$$y\left[\frac{\mu A}{\text{mmol}L^{-1}}\right] = -0.0249x - 4.9705, \quad R_1^2 = 0.9965. \tag{1}$$

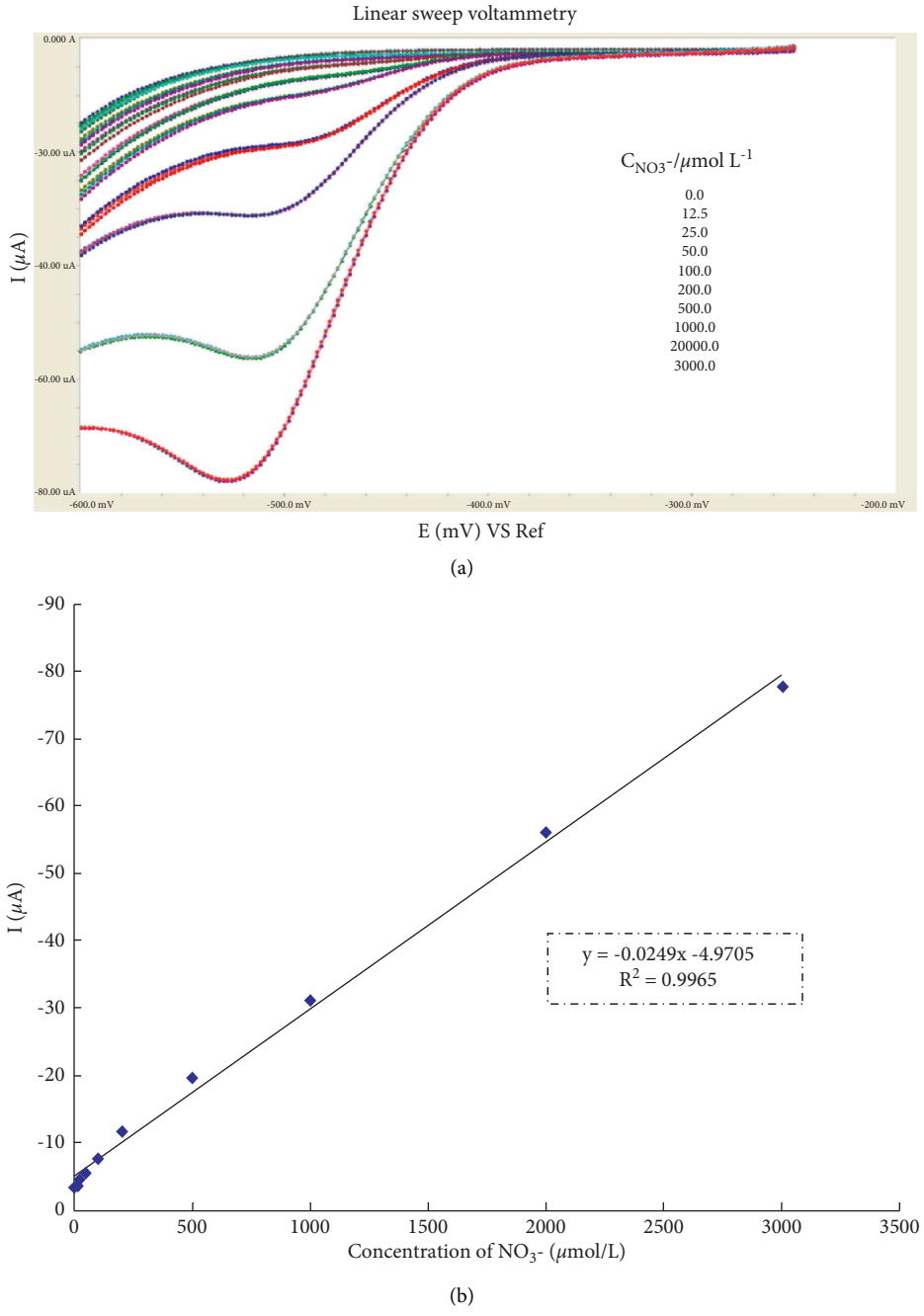


Figure 10: Response curve of the miniature electrochemical sensor. (a) Linear scan curves in different nitrate solution concentrations. (b) Linear fit curve: scan rate of 50 mV/s.

The microsensor modified by the potentiostatic deposition method also demonstrated good repeatability and anti-interference when testing nitrate ions. Except for nitrite ions, the common ions in water did not significantly interfere with the test results [10]. The microsensor was tested three times for each nitrate standard sample, namely, 1.0 mmol/L, 2.0 mmol/L, and 3.0 mmol/L, and the maximum relative standard deviation RSD was less than 5%. The detection limit was 10 μmol/L ($S/N = 3$).

3.3. Reuse of Electrochemical Sensors. The sensor studied in this paper is fabricated by using MEMS technology on silicon substrate. The manufacturing process can be described by sputtering a layer of silicon dioxide insulating layer on which the electrode pattern is etched by light, and then a layer of platinum metal is sputtered by sputtering process, and the final electrodes are made by stripping technique. The sensors are made of working electrode and counter electrode. On the working electrode, the sensitive material of the sensor is

polymerized on the working electrode by a electrochemical analysis instrument to form a nitrate-sensitive sensor. When a new sensitive material needs to be polymerized, most of the sensitive materials are dissolved by concentrated nitric acid, and the oxygen plasma is used to strike the metal surface for removing the sensitive material completely, so that the sensor can be used repeatedly. At the same time, the sensor is designed to be used more frequently by unusing with gold wire and insulating glue.

4. Conclusion

In this paper, a microelectrochemical sensing electrode was fabricated by micromachining technology. Combined with electrochemical potentiostatic deposition technology, it prepared a copper-sensitive film with a branch-like structure on the surface of the platinum working electrode. The electrocatalytic reduction characteristics of copper were used to nitrate ions in an acidic solution and realized the detection of nitrate concentration in the solution. Good detection sensitivity and linearity were obtained in the standard concentration range of 0.0 mmol/L to 3.0 mmol/L. At the same time, a new package-free microsensor system was developed, using STM32f103 microcontroller as the controller and HX711 as the signal converter to build an automatic nitrate detection system, realizing the advantages of miniaturization of detection, fast response, and less detection reagent consumption. The new structure was adopted, which can avoid the defects caused by the golden wire connection between the traditional sensor and the external circuit, and prolong the reliability, stability, and life of the sensor. It has high value to realize the development of low cost and portable nitrate detector for environmental monitoring and food safety detection. It also makes sense that a distributed detection system was built, and a main processing unit was used to collect the automatic detection units with sensors around them, and the collected data were transmitted to the nearby signal transmission unit to realize real-time data transmission. Because the electrode system adopts MEMS technology for mass production, its cost is lower than the existing sensors, which greatly reduces the cost of the whole system, and the consistency and reliability of the electrode system can be guaranteed.

Data Availability

All data included in this study are available upon request to the corresponding author.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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