


Abstract

Development of a Potentiometric Nitrate Ion Microsensor Improved Using Conductive Polymer Doped with Carbon Nanotubes as a Transducing Layer [†]

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Abstract: An all-integrated on-chip electrochemical microcell ($10 \times 11 \text{ mm}^2$) is developed using silicon technology. The potentiometric nitrate ion detection is based on the functionalization of the working microelectrode array with a polymer membrane in fluoropolysiloxane (FPSX) containing ionophore tetradodecylammoniumnitrate (TDDAN) and ionic additive potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB) to form an all-solid-state ion selective electrode (ISE). The addition of an ion-to-electron transducing layer between the platinum working electrode and the polymer membrane helped to improve the sensor performances, especially the response time, the sensitivity, and the stability. Composites formed with two conductive polymers were compared: Polyethylenedioxythiophène (PEDOT) and Polypyrrole (PPy), doped with Poly(styrene sulfonate) or double-walled carbon nanotubes (DWCNTs).

Keywords: potentiometric sensor; all-solid-state ion selective electrode; nitrate; carbon nanotubes; conductive polymers; polymeric membrane; ionophores



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1. Introduction

With the development of industries and intensive agriculture, the use of fertilizers is responsible for the rejection of increasingly large amounts of nitrates in surface water. Although nitrates have an essential role in the nitrogen cycle, in too large of an amount nitrate can be a strong contaminant as it can disturb ecosystems and be harmful to human health. This work aims to develop a low-cost, easy-to-produce, and miniaturized sensor to directly detect in situ nitrate concentrations.

2. Materials and Methods

2.1. Microsensor Geometry

The microsensor was fabricated using a photolithography process. It is composed of a platinum working microelectrode array (5×5 microelectrodes of 10 um^2 diameter that are each interconnected), a silver/silver chloride quasi-reference electrode, and a platinum counter electrode (Figure 1) [1].

2.2. Working Microelectrode Array Functionalization

Transducing layer (Figure 2): The platinum microelectrode array was functionalized by electro-polymerization of an aqueous solution containing the conductive monomer (EDOT or Py) and the dopant (NaPSS or oxidized DWCNTs) [2]. The compositions are given in Table 1. The electro-polymerizations were all carried out through chronopotentiometry

at a current density of 1 mA/cm² across 360 s (PEDOT:PSS), 180 s (PEDOT:DWCNTs), and 75 s (PPy:DWCNTs).

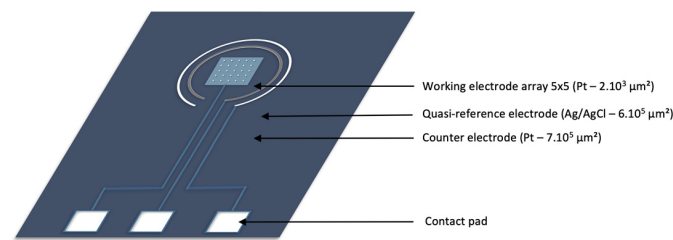


Figure 1. Ultra-microelectrode array integrated on silicon wafer.

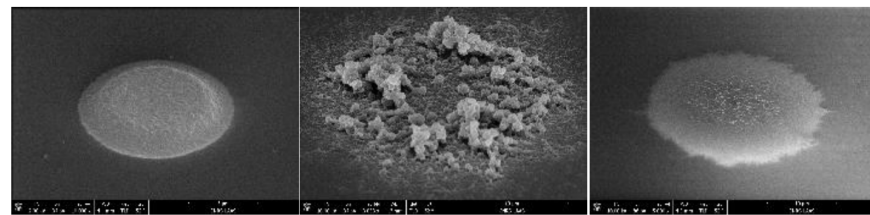


Figure 2. SEM images respectively of PEDOT:PSS, PEDOT:DWCNT, and PPy:CNT deposits on an ultramicroelectrode of the array.

Table 1. Electropolymerization solution compositions.

| Composite | Monomer | Dopant |
|--------------|------------|----------------|
| PEDOT:PSS | EDOT 10 mM | NaPSS 34 mM |
| PEDOT:DWCNTs | EDOT 10 mM | DWCNTs 1 mg/mL |
| PPy:DWCNTs | Py 150 mM | DWCNTs 1 mg/mL |

Ion-sensitive membrane. The fabrication process of the nitrate-ion-sensitive membrane involved 134 mg FPSX, 6.00 mg TDDAN, and 4.16 mg KFTPB dissolved in 1 mL tetrahydrofuran (THF). The solution was drop-casted on the microelectrode array (2 μL). The deposit was left to dry for 72 h before use.

3. Discussion

The transducing layer improved the response time and the stability of the sensor because it helped to remove the water layer between the electrode and the membrane [3]. The DWCNTs greatly increased the sensitivity, similarly to a Nernstian response (Figure 3, Table 2). The sensors with a conductive polymer doped with carbon nanotubes showed good selectivity performances against principal surface water interfering ions (Table 3) and largely acceptable stability for rapid in situ measurement. Better performances were obtained with a PEDOT:DWCNT deposit as the transducing layer.

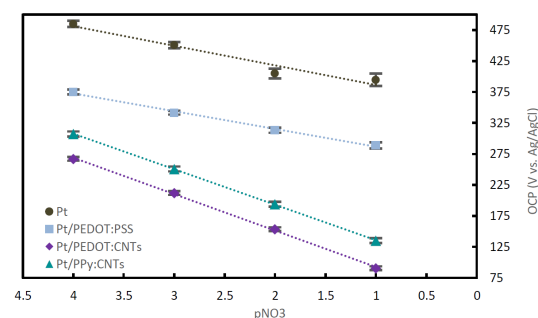


Figure 3. Open circuit potential value of the different nitrate ion sensors with pNO₃.

Table 2. Sensitivity, limit of detection, and stability of the sensors.

| Transducing Layer | Sensitivity Slope | Limit of Detection | Long-Term Drift |
|-------------------|--------------------------|----------------------|-----------------|
| Without | 40.1 mV/pNO ₃ | 1.10 ^{−4} M | n/a |
| PEDOT:PSS | 28.7 mV/pNO ₃ | 1.10 ^{−4} M | n/a |
| PEDOT:DWCNTs | 57.3 mV/pNO ₃ | 1.10 ^{−5} M | ±0.1 mV/h |
| PPy:DWCNTs | 57.4 mV/pNO ₃ | 1.10 ^{−5} M | ±0.05 mV/h |

Table 3. Selectivity coefficient obtained by FIM method with 1.10^{−2} M interfering ion concentration.

| Transducing Layer | Interfering Ion | Log (K) |
|-------------------|-------------------------------|---------|
| PEDOT:DWCNTs | Cl [−] | 2.65 |
| | HCO ₃ [−] | 2.8 |
| | SO ₄ ^{2−} | 4.1 |
| PPy:DWCNTs | Cl [−] | 2.2 |
| | HCO ₃ [−] | 2.8 |
| | SO ₄ ^{2−} | 3.9 |

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References

1. Christophe, C.; Belaïdi, F.S.; Launay, J.; Gros, P.; Questel, E.; Temple-Boyer, P. Elaboration of integrated microelectrodes for the detection of antioxidant species. *Sens. Actuators B Chem.* **2013**, *177*, 350–356. [[CrossRef](#)]
2. Zhu, J.; Li, X.; Quin, Y.; Zhang, Y. Single-piece SC-ISE with polymer-carbon nanotube composites. *Sens. Actuators B Chem.* **2010**, *148*, 166–172. [[CrossRef](#)]
3. Fibbioli, M.; Morf, W.E.; Badertscher, M.; De Rooij, N.F. Potential Drifts of SC-ISE due to zero-current ion fluxes through the sensor membrane. *Electroanalysis* **2007**, *12*, 1286–1292. [[CrossRef](#)]

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