Development of micro-fluidic nitrate-selective sensor based on doped-polypyrrole nanowires

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Abstract

This paper presents a flow-through, nitrate-selective, electrochemical sensor developed by electropolymerization (doping) of polypyrrole nanowire (PPy-NW) electrodes. The flow-through micro-fluidic platform enabled a realistic and controlled testing environment. Cyclic voltammetry, amperometry and flow-through analysis were performed to evaluate the sensor performance for determination of nitrate ions in two sets of calibration solutions (DI water and IAPSO standard seawater). The sensor response was linear over the range from $10\,\mu M$ (0.14 ppm Nitrate-N) to 1 mM (14 ppm Nitrate-N), with a sensitivity of 1.17–$1.65\,nA/\mu M$ and detection limit of $4.5 \pm 1\,\mu M$ or 0.063 ± 0.014 ppm Nitrate-N. The electrochemically doped PPy-NW electrodes show improved selectivity for chloride, sulfate, phosphate and perchlorate ions, without the loss from interfering ions.
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1. Introduction

This work describes the development of a nitrate-selective electrochemical sensor using doped-polypyrrole (PPy) nanowires on a micro-fluidic platform. Determination and estimation of nitrate ion is important for a variety of applications in different fields, including environmental engineering, agriculture, marine cycles, food analysis, water management, biology and medicine [1–4]. In spite of the increase in current understanding of nitrate role within environmental matrices, a substantial degree of uncertainty and speculation still remains. Nitrate is a widespread contaminant of groundwater and surface waters worldwide, because of being in such diverse materials such as fertilizers, foods, livestock feeds, wastewater and drinking water. The extensive use of nitrate fertilizers in agriculture negatively impacts fresh water, ground water and marine ecosystems by simulating the occurrence of eutrophication-algae blooms [2].

The presence of nitrate ions in environment or food samples has potential human health threat, especially in infants, causing "blue-baby syndrome, some forms of cancer and congenital defects [3,4]. Even though, current data are inconclusive, there are causes for concern. A contentious health concern is possible formation of carcinogenic nitrosamines within the acidic conditions of stomach and their subsequent implication in the pathology of gastric cancer. Upon reaching the stomach, nitrite is converted into nitrous acid, which can act as a powerful nitrosating agent [4]. Because of its role in ecosystem dynamics and its potential impact on human health, nitrate level is carefully monitored in municipal water lines, engineered and environmental systems worldwide to prevent exposure of populations to harmful levels. To address these concerns, US EPA and European Community have set limits of nitrate (10 ppm Nitrate-N or 0.71 mM/L [5] and 11.3 mg/L Nitrate-N [6], respectively) in potable water.
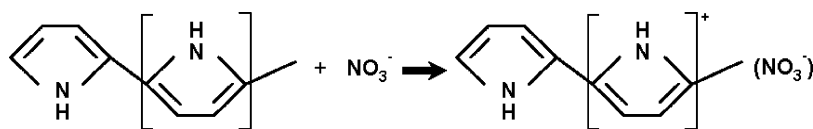
The other significant area, which also forms the basis for nitrate sensors, is ocean research and monitoring. Plant nutrients such as nitrate, phosphate, silicate and ammonia play a key role in controlling ocean, in particular coastal ecosystem. These chemicals are essential nutrients that are required by phytoplankton and benthic plants for growth. In natural ecosystems, all of

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these nutrients are generally the factor that limits the accumulation of plant biomass [3]. The increase flux of nitrates (even few μM) can lead to number of negative impacts on ocean ecosystem. Elevated concentrations of plant nutrients can cause eutrophication or the increased production of plant organic carbon. Further, the increased concentrations may lead to a shift in ecosystem structure [1,3]. Such rapid shifts in ecosystem structure may favor increase in the concentration of phytoplankton that produces toxic compounds such as Harmful Algae Blooms (HAB) or "red-tides" [2].

Current methods of detecting nitrate can be classified as direct (e.g. through a reduced nitrogen species, chromatography), or indirect (e.g. spectrophotometry, polarography) [1,7,8]. These methods are either expensive with extensive pretreatment and elaborate equipment, or are not selective [1]. In addition, commercial ion-selective electrodes (ISEs) posses no anion recognition functionalities and respond based on the anion's lipophilicity [9]. They typically respond to ions according to Hofmeister series: large lipophilic anions $> ClO_4^- > SCN^- > I^- > NO_3^- > Br^- > Cl^- > H_2PO_4^-$ [10]. This series implies that commercial nitrate ISEs are more selective to perchlorates and iodides than nitrates. Therefore, it is necessary

polypyrrole films [11]. Another type of recognition element involves metal–ligand interactions. Such interactions have been used in development of phosphate and nitrate-selective electrodes based on organotin, porphyrin or corrin ionophores [12].

The focus of this work is the development of a nitrate-selective and highly sensitive sensor, implemented on a micro-fluidic platform, as illustrated in Fig. 1. The selective chemical recognition towards nitrate is achieved by electrochemical nitrate doping of polypyrrole [13]. Lower detection limit and improved sensitivity is achieved by utilizing polypyrrole nanowires, instead of conventional polypyrrole films [19]. Nanowires, being one-dimensional structures have a large surface-to-volume ratio and lower diffusion resistance, thus enhancing the capture cross-section. Polypyrrole (PPy) is one of the widely studied conducting polymers because of its high conductivity, ease of preparation, flexibility, and stability as ISE [14]. Furthermore, polypyrrole-doped nanowires show high selectivity and rapid reactivity towards the dopant ion and integration ability as sensor elements [13,15]. In its oxidized state, polypyrrole exists as a polyradical cation and at the oxidation stage; nitrate anions are attracted electrostatically into the PPy matrix as dopants or counter ions, as illustrated below [16].

to incorporate selective interactions between ionophores and nitrate using chemical recognition principles. This would enable truly selective nitrate sensor development, one not limited by the Hofmeister series. An example for application of chemical recognition elements in development of selective ISEs is chloride-selective electrodes prepared by doping chloride into

In this work, the selective chemical recognition for nitrate is achieved by electrochemical polymerization (doping) of an appropriate monomer (pyrrole) under controlled conditions to allow generation of selective recognition sites in the PPy layers [11,17,18]. On polymerizing PPy layers in presence of $NaNO_3$, pores that are complimentary to the size of the target nitrate ion
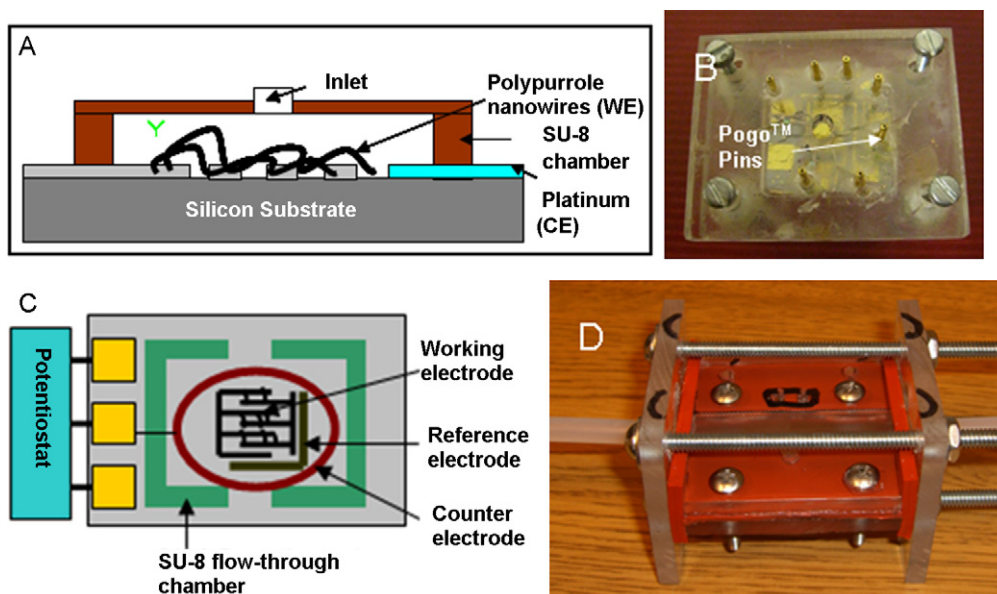

Fig. 1. (A) Illustration of the Electrochemical sensor chip; (B) actual picture of the electrochemical cell; (C) illustration of the flow-through electrochemical test cell; (D) picture of through-flow cell shown with inlet/outlet and Pogo^TM pin connectors.