CHINESE JOURNAL OF ANALYTICAL CHEMISTRY
Volume 46, Issue 2, February 2018
Online English edition of the Chinese language journal

Cite this article as: Chinese J. Anal. Chem., 2018, 46(2): 147–156

REVIEW

Research Progress on Nitrite Electrochemical Sensor

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Abstract: Nitrite has been widely used in industrial and agricultural production and is commonly found in food, drinking water, biology and environment. However, nitrite is a toxic inorganic pollutant that is very harmful to the health of human and other organisms. A variety of strategies have been proposed for nitrite detection in recent years. Among which, electrochemical approaches have gained more and more attention owing to the characteristics of simplicity, speediness, high sensitivity, and low cost, etc. The principle of nitrite electrochemical sensor is recommended in this review. The research progresses of nanocomposite material sensor for electrochemical nitrite detection based on carbon material, metal material, metal organic framework, conducting polymer and enzyme in recent years are also introduced from the perspective of composite electrode modification layer. The construction approaches and sensing performances of modified electrode are put special emphasis. At last, future trends of nitrite electrochemical sensor are discussed.

Key Words: Electrochemical sensor; Nitrite; Nanocomposite electrode; Review

1 Introduction

Nitrite, coming from nitrogenous organic compound of animal waste, organic waste, chemical fertilizer, natural deposition and nitrate biotransformation, is ubiquitous in food, drinking water and environment. Nitrite is an inorganic pollutant that has been proven to be of great threat to human health. As an important precursor, upon interaction with proteins, nitrite can generate highly carcinogenic *N*-nitrosamines[1,2]. A number of medical issues might be caused by excessive consumption of nitrite, such as esophageal cancer and gastric cancer[3], infant methemoglobinemia (blue baby syndrome)[4], spontaneous abortion[5], birth defects in the central nervous system[6], etc. The maximum contaminant level of nitrite, legislated by the U.S. Environmental Protection Agency, is 1 ppm (21.7 μM), and analogous guideline value set by the World Health Organization is 3 ppm[7]. The acceptable daily intake for nitrite is set at 0.06 mg kg^{-1} of body weight by the European Union Scientific Committee for Food[8]. According to the National Standard of the People's Republic of China GB 2760-2014, the maximum allowable level of nitrite as color fixatives and preservatives in food is 0.15 g kg^{-1} [9].

It is necessary to detect the nitrite content in the fields such as food safety supervision, food analysis and water quality identification. Ion chromatography and spectrophotometry are used to test the nitrite concentration in food in GB 5009.33-2016[10]. Meanwhile, diazo coupling spectrometry is applied to determine the nitrite content in drinking natural mineral water according to GB 8538-2016[11]. Diverse analytical techniques have been reported to determine nitrite, such as spectrophotometry (e.g. Griess Reaction)[7,12–14], chemiluminescence[15,16], chromatography[17–19], surface enhanced Raman spectroscopy[20,21], capillary electrophoresis[22–24], fluorescence[25,26], electrochemilumine scence[27], etc. The detection processes of these techniques are generally complex and time consuming. Compared with other techniques, electrochemical methods testing nitrite own many outstanding performances, including simplicity, speediness, high sensitivity and low cost[28–35]. As is known to all that nitrite is

Received 28 September 2017; accepted 12 December 2017
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This work was supported by the the National Natural Science Foundation of China (Nos. 21405147).

DOI: 10.1016/S1872-2040(17)61066-1

electroactive at platinum, gold, copper, glassy carbon and transition metal oxide electrodes. However, to some degree, the utilization of bare electrode for the determination nitrite is restricted on account of the easily poisoned electrode surface, thus decreasing the sensing sensitivity and accuracy[36]. The suitable modification of the electrode surface can not only improve the oxidation response signals of nitrite, but also extend the dynamic range in analytical determinations. A variety of modified electrode layers have been reported, such as carbon material (graphene[37–39], carbon nanotube[40], carbon nanoparticle[41], porous carbon[42], etc), metal material (metal[43,44], metal oxide[44], metal sulfide[32,46], metal nitride nanoparticle[47,48] and nanocluster[49,50], etc), metal organic framework (MOF)[34,35], conducting polymer (CP)[51,52], enzyme[28,53] and various combined composite material[54–57], etc. This review presents the latest developments in nitrite electrochemical sensor reported in recent years.

2 Principle of nitrite electrochemical sensor

The nitrite electrochemical sensor, as with similar conventional electrochemical sensors, is composed of two parts: immobilized sensing element (identification system) and transducer (conversion system), and the schematic diagram of nitrite electrochemical sensor is shown in Fig.1. Firstly, the modified layer with electroactive and catalytic function is fastened to the electrode surface to form sensing element. Nitrite is catalyzed and oxidized into nitrate by the modified layer on the sensing element, and the response parameters on the electrode surface are transformed into sensing signals produced by conducting system. After that, the sensing signals are received by transducer that known as conversion system, and translated into the measurable electrochemical signals. The electrochemical signals are outputted after the secondary amplification through electronic system, and then displayed and recorded by the instrument afterwards. Owing to the proportional relationship between the secondary amplified electrochemical signals and the nitrite concentration within a certain range, quantitative analysis of nitrite can be realized on the basis of the linearity.

3 Electrode modification material

Electrode modification material is crucial component for the sensing element of nitrite electrochemical sensor, which can dramatically increase the response signals on the electrode surface, reduce the overpotential of nitrite, broaden the determination dynamic range, and improve the detection sensitivity and specificity. Carbon material, possessing good conductivity, can be served as the substrate for loading metal nanoparticles and conducting polymers with electrocatalytic activity. As a result, the catalytic performance of the composite is further increased via synergistic effect. Both MOF with ultrahigh porosity and surface area, and enzyme with specific catalytic function can be used as electrode modification material to fabricate nitrite electrochemical sensor.

3.1 Carbon material

Graphene is a new type of two-dimensional carbon nanomaterial with a series of advantages, such as large surface area, high conductivity and excellent catalytic activity, etc., The nanocomposites of metal[56,57], metal oxide[29,58,59], polymer[60,61], MOF[35,54], enzyme[62,63], etc, compositing with graphene, together with nitrogen doped graphene[38,39] have been reported to be applied to fabricate nitrite electrochemical sensor. Chen *et al*[39] prepared nitrogen-doped reduced graphene oxide (NrGO), and then modified it on the surface of glassy carbon electrode (GCE) to fabricate a facile nitrite electrochemical sensor with a lot of merits, such as long-term stability, resistance to catalyst poisoning and good catalytic activity, etc. NrGO exhibited a good electrocatalytic activity toward oxidation of nitrite with the relatively low oxidation potential (0.68 V). The fabricated sensor showed a low detection limit of 0.2 μM, and had promising applications to the determination of nitrite in pickled garlic and river water.

Because of the high specific surface area, metal and metal oxide nanoparticles exhibit higher catalytic activity compared to bulk materials. When composited with graphene, the nanocomposite modified electrode might present higher specific surface area and catalytic activity, as well as better biocompatibility. Zou *et al*[56] prepared 3D flower-like graphene (f-GE) through an efficient electrochemical approach, and then the Au nanoparticles were reduced on the graphene surface to form Au/f-GE composite by potentiostatic

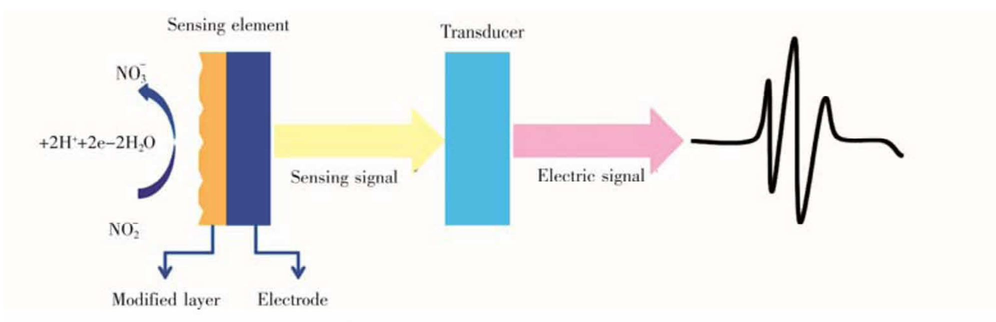

Fig.1 Schematic diagram of nitrite electrochemical sensor