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Flow injection amperometric nitrite sensor based on silver microcubics-poly (acrylic acid)/poly (vinyl alcohol) modified screen printed carbon electrode

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ABSTRACT

This work reports an electrochemical sensor for the nitrite determination by using flow injection amperometry (FI-amp) based on a screen printed carbon electrode (SPCE) modified with silver microcubics-polyacrylic acid/poly vinyl alcohol (AgMCs-PAA/PVA). The AgMCs-PAA was synthesized via a simple chemical reduction method. The prepared AgMCs-PAA/PVA modified SPCE displayed excellent electrocatalytic properties for the oxidation of nitrite and increased the catalytic current response. Under the optimum conditions, the sensitivity of the AgMCs-PAA/PVA/SPCE was 1.6, 4.9 and 1.2 times higher than the bare SPCE, PVA/SPCE, and Ag/PVA/SPCE, respectively. This sensor exhibited a rapid amperometric response to the oxidation of nitrite, which allowed it to be used for the determination of nitrite with a linear range from 2.0 μM to 800.0 μM with a limit of detection and a limit of quantification of 4.5 and 14.9 μM, respectively. This propose nitrite sensor had a high sensitivity (474.14 $\mu AmM^{-1}cm^{-2}$), good repeatability (RSD < 6%, n = 6), stability (RSD = 3%, n = 120) and good accuracy (recovery = 84 $\pm$ 3 to 102 $\pm$ 1%). This method successfully detected nitrite in meat products and the results were consistent with those obtained with the standard spectrometer method. It is possible to apply the proposed method to detect nitrite in other foods and in the environment.

1. Introduction

Nitrite is one of the most food additives widely used in the food meat industry for the purpose of color stability and protection against botulism of meat product [1]. The Codex General Standard for Food Additives (GSFA) approves the use of the nitrite in processed comminuted meat, poultry, and game products not to exceed 80 mg kg^{-1} [2]. Thus, much concern because of excessive ingestion of nitrite from food is imperiling to human health. Nitrite can react with amines and amides to form toxic and carcinogenic nitrosamines in stomach leading to gastric cancer [3,4]. Moreover, it creates shortness of breath and methemoglobinemia resulting from the oxidation of the iron (III) of the hemoglobin in blood by nitrite leading to the formation of methemoglobin which has no oxygen-carrying ability [5,6]. Therefore, the development of a rapid and sensitive determination of nitrite in the food product is very important. Several methods have been reported for the determination of nitrite at trace level, including high performance liquid chromatography [7], ion chromatography[8], capillary electrophoresis[9], spectrophotometry[10], and electrochemical methods[11–15]. Among these methods, electrochemical techniques possess many advantages such as simple operating procedure, inexpensiveness, fast analysis and high sensitivity [16–18]. Especially, the electrochemical sensor coupled with flow injection system is an interesting alternative method due to its main advantages which are high reproducibility, good sensitivity, rapid analysis and high throughput [19–21].

Nowadays, many materials can be used as electrodes in electrochemical sensor such as glassy carbon electrode (GCE)

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[22], carbon paste electrode (CPE) [23,24], gold electrode (AuE) [25] and screen-printed carbon electrodes (SPCEs) [26–28]. Especially, SPCEs are disposable electrodes that are frequently used for production of electrochemical sensor because of their ease-of-use, inexpensiveness and ability to be miniaturized to reduce consumption of sample. Moreover, SPCEs do not need to be polished or pretreated as the typical glassy carbon electrodes [29–31]. However, the limitation of SPCE is the small surface area of working electrode leading to the lack of sensitivity [32]. Therefore, the electrode modification is urgently required.

Recently, noble metals have been widely exploited in fabrication of electrochemical sensors to enhance the sensitivity. Metal particles are attractive material as a catalyst in the electrochemical applications owing to their high catalytic abilities for catalyzing the oxidation of nitrite, large surface active area and high electrical conductivity such as platinum (PtPs) [33], palladium (PdPs) [34], Gold (AuPs) [35,36] and silver (AgPs) [37,38]. In particular, silver particles (AgPs) are attractive for modification of electrode due to their high catalytic activity, easy synthesis and low cost when compared with other metal particles [39]. However, the synthesis of AgPs without stabilizer still has some serious limitations due to the aggregation and low dispersion of AgPs. Different stabilizers for AgPs synthesis have been reported including chitosan[40], carboxymethyl dextrane [41], dextran sulphate [42], poly(l-glutamic acid) [43], Poly(amidoamine) [37], poly(vinylpyrrolidone) [44], poly(vinyl alcohol) [45], poly(acrylamide) [46], poly (ethylene glycol) [47], and Poly(acrylic acid) (PAA) [48,49]. Among these, PAA is an interesting stabilizer because it is water-soluble polyelectrolyte [50]. It also has a single chain structure with carboxylic side chains that can produce poly-acrylate anions with uncoordinated carboxylate groups in aqueous solution which can bind with silver ion (Ag^+) before reduction as AgPs, leading to high stability, good dispersion and reduced aggregation of AgPs [48,49]. Nevertheless, the electrocatalytic performance of metallic particles depends upon their shape [51–53]. Consequently, previous contributions have reported that the electrocatalytic performance of cubic shape of many noble metallic particles is higher than the spherical shape due to their large surface area [53–56].Therefore, Ag in micro-cubic shape (AgMCs) is another interesting candidate as a modified electrode for catalyzing the oxidation of nitrite.

It is well known that an effective supporting material for the fabrication of the modification electrode is one of the most important factors that influence the performance of the electrocatalysis and stability [57,58]. Poly(vinyl alcohol) (PVA) is one of the interesting supporting materials because it is a biocompatible nontoxic synthetic polymer that has exclusive features, including flexible molecular chains, chemical stability, and ductile nature. Moreover, the excellent film-forming and permeability properties and electrode adhesion capacity of thin PVA films makes it an appropriate matrix for application in electrochemical sensor [59–61]. In this work, PVA was used as a supporting material for the entrapment of AgMCs-PAA to prevent the loss of AgMCs-PAA from the electrode surface.

In this work, a new silver microcubics stabilized by polyacrylic acid (AgMCs-PAA) was prepared by a simple chemical reduction method. This AgMCs-PAA was entrapped into poly (vinyl alcohol) (PVA) film and modified on a screen printed carbon electrode which was incorporated to flow injection ampermetry (FI-Amp) system and developed as novel nitrite sensor. The morphology and electrochemical behavior of the modified electrode (AgMCs-PAA/PVA/SPCE) were characterized and compared with the Ag/PVA/SPCE, PVA/SPCE, and bare SPCE. The effect of important operational parameters on the electrocatalytic performance of AgMCs-PAA/PVA/SPCE for nitrite detection including the amount of AgMCs-PAA/PVA and the concentration of PVA for the modified electrode, and the best operating applied potential, flow rate and sample volume were optimized by varying a single parameter and keeping others constant. Analytical performances such as the linear range, limit of detection, limit of quantitation, stability, repeatability,

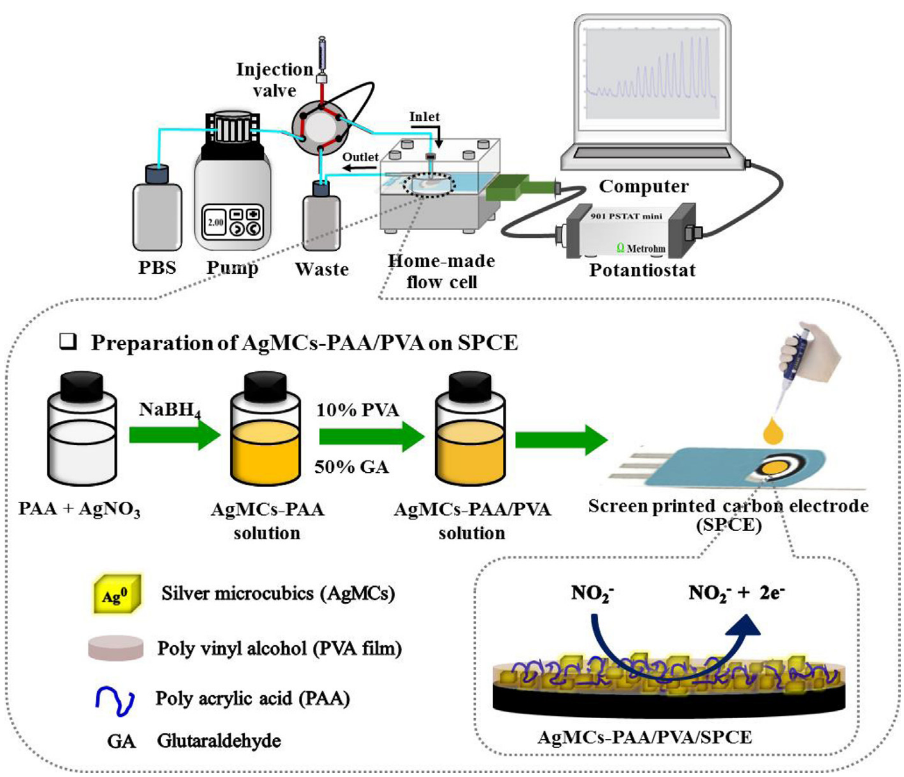

Fig. 1. The flow injection amperometric (FI-Amp) system. Preparation of the AgMCs-PAA/PVA modified SPCE.