A preparation of homogeneous distribution of palladium nanoparticle on poly (acrylic acid)-functionalized graphene oxide modified electrode for formalin oxidation

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ABSTRACT

An excellent electrocatalytic activity, repeatability and stability of electrochemical sensor for formalin detection was fabricated based on a homogeneous distribution of ellipsoidal palladium nanoparticle (PdNPs) on poly (acrylic acid)-functionalized graphene oxide (PAA-GO) modified on a glassy carbon electrode (GCE) (PdNPs-PAA-GO/GCE) with incorporated flow injection amperometry (FI-Amp). Homogeneous distribution of ellipsoidal palladium nanoparticles (PdNPs) were dispersed on PAA-GO via an electroless deposition method. The surface morphology and electrochemical behavior of the PdNPs-PAA-GO/GCE were characterized by transmission electron microscopy, fourier transform infrared spectroscopy, cyclic voltammetry and amperometry. The PdNPs-PAA-GO/GCE exhibited excellent electrocatalytic activity toward formalin oxidation. Then this modified electrode was incorporated with FI-Amp for formalin sensor development. In order to obtain good analytical performances, many parameters such as the amount of PdNPs-PAA-GO, applied potential, flow rate and sample volume were optimized. Under optimal conditions, this sensor provided a wide linear range, 50-50,000 $\mu mol\,L^{-1}$, with high sensitivity ($320\,\mu A\,mmol\,L^{-1}\,cm^{-2}$). The limit of detection and limit of quantitation were $16\,\mu mol\,L^{-1}$ and $53\,\mu mol\,L^{-1}$, respectively. This proposed sensor exhibited good repeatability (RSD $< 3.5\%$), excellence stability (RSD = 1.5%, n = 500) and high sample throughput (60 samples h^{-1}). This method was applied to the determination of formalin in soaked fresh food samples with satisfactory recovery.

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1. Introduction

Formalin, the aqueous solution of formaldehyde (30% to 50% formaldehyde), is normally used in embalming to disinfect and temporarily preserve human and animal remains. It was recently reported contaminated in various common food, including seafood, vegetables, fruits, meat and dried mushrooms etc. [1,2]. Formalin can cause acute and chronic injuries in human such as respiratory problems i.e. asthma, skin irritation as dermatitis and itching from touching [3]. Moreover, ingestion of formalin damages the pharyngeal mucosa, epiglottis, esophagus, and especially gastrointestinal mucosa, with nausea, vomit, bleeding, and perforation [4]. The United States Environmental Protection Agency (EPA) has set the reference dose of formalin to be 0.2 mg/kg bodyweight/day [5]. The International Agency for Research on Cancer (IARC) has also classified formalin as a Group 1 carcinogenic to humans [6]. Therefore, it is very imperative to develop a rapid and reliable sensor for the determination of formalin contamination in fresh food.

There are many formalin-assessment methods that have been developed such as chemiluminescence [7], high performance liquid chromatography [1], gas chromatography-mass spectrometry [8], spectrometry [9,10], and electrochemical [11–13]. Among

these methods, the electrochemical method has been considered as an efficient alternative for the formalin determination. Electrochemical sensor has the advantages of simplicity, cheap instrument, high sensitivity, fast response speed, timesaving, and real time determination [14–16]. Particularly, the electrochemical sensor coupled with flow injection system, i.e., flow injection amperometry (FI-Amp), has been applied in many fields such as clinical diagnosis [17,18], pharmaceutical [19,20], food [21], industry [22,23], forensic science [24] and environmental [25,26]. FI-Amp is probably the most popular detection system used in the development of electrochemical sensor due to its fast response, high throughput, good precision and reproducibility [27,28]. Moreover, the use of FI-Amp system can minimize sample contamination because the sample cannot spend much time at the electrode surface which minimizes the adsorption effect [22,25]. Therefore, FI-Amp system is used as a detection system in this work. Non-enzymatic and enzymatic electrochemical sensors for formalin have been reported. For enzymatic electrochemical sensor, it provides high sensitivity and selectivity. However, the enzyme modified electrode has a serious problem during immobilization process such that the fabrication is complicated and the stability is low causing the poor ability of reproducibility [29,30]. Therefore this research focuses on the development of non-enzymatic electrochemical sensor coupled with flow injection system for determination of formalin.

In recent years, the various metal nanoparticles (MNPs) have widely been used as catalyst for the electrochemical sensor in the determination of formalin including silver (Ag) [31], nickel (Ni) [11,32], copper (Cu) [33], platinum (Pt) [13,34], and palladium (Pd) [35]. Pt and Pd are frequently utilized for the electro-oxidation of small organic molecules. Nevertheless, Pd is more interesting because of its inexpensiveness, high electrocatalytic activity, steady-state behavior and resistance to poisoning by carbonaceous species in alkaline solution [36–38]. Nowadays, in order to improve the efficiency of the electrocatalytic activity of MNPs, a lot of studies are carried out on the immobilization of catalytic MNPs on carbon support materials such as single-walled carbon nanotube [13], multi-walled carbon nanotube [39], ordered mesoporous carbon [40] and graphene oxide (GO) [41–43], since they have a high surface area, a high porosity, excellent electrode transfer, and good chemical stability [44–47]. However, the weak interaction between MNPs and carbon support causes the aggregation and low dispersion of MNPs on carbon support, and consequently decreases the active surface area, which leads to a low electrocatalytic activity and poor stability [47–50]. Therefore, it is important to find a strategy for preparation of homogeneous distribution of PdNPs on carbon support to improve the electrocatalytic activity and stability. The surface functionalization of carbon support material (*i.e.,* GO) with polymer is very attractive since the polymer can prevent the aggregation and improve the dispersion of MNPs on the surface of GO. Several polymers have been employed as supporting and stabilizing material for the synthesized MNPs including poly (N-vinyl-2-pyrrolidone) (PVP) [51,52], poly (N-vinylformamide) (PNVF) [53], poly (N-isopropylacrylamide) (PNIPAAm) [54], Polyaniline [42,55] and Poly (acrylic acid) (PAA) [56]. PAA is another interesting candidate for surface functionalization of GO as a supporting material since PAA is an anionic polyelectrolyte which can prevent the restacking of graphene sheets. Moreover, a large number of carboxyl groups in the PAA chains can form coordinate covalent bonds to palladium ions (Pd^{2+}) which can prevent the aggregation and improve the dispersion of PdNPs on GO support, which leads to enhance the electrocatalytic activity and increases the stability [57–59]. To the best of our knowledge, this is the first report on the preparation of the homogeneous distribution of PdNPs on PAA-functionalized GO

(PdNPs-PAA-GO) modified glassy carbon electrode (GCE) with incorporated FI-Amp for the determination of formalin.

In this paper, we report an excellent electrocatalytic activity and stability of electrochemical sensor for formalin detection based on the homogeneous distribution of palladium nanoparticle (PdNPs) on poly (acrylic acid)-functionalized graphene oxide (PAA-GO) modified on a glassy carbon electrode (GCE) (PdNPs-PAA-GO/GCE) with incorporated flow injection amperometry (FI-Amp). PdNPs were dispersed on PAA-GO via an electroless deposition method (Fig. 1A), in which PAA served as a stabilizer and a disperser to deposit PdNPs and sodium borohydride as a reducing agent. The surface morphology of the PdNPs-PAA-GO and PdNPs-GO was characterized by transmission electron microscopy (TEM) and fourier transform infrared spectroscopy (FTIR). The electrocatalytic activity for formalin oxidation by cyclic voltammetry (CV) on the modified electrode, PdNPs-PAA-GO/GCE, was investigated and compared with the PdNPs-GO/GCE, PAA-GO/GCE, PAA/GCE, GO/GCE and GCE (Fig. 1B). The PdNPs-PAA-GO/GCE was then developed by combining FI-Amp for the determination of formalin (Fig. 1C). The parameters optimized for the FI-Amp are amount of PdNPs-PAA-GO, applied potential, flow rate and sample volume. The analytical performance was also investigated including linear range, limit of detection (LOD), limit of quantifications (LOQ), repeatability and stability. Finally, the proposed system was applied for formalin determination in soaked fresh food samples.

2. Experimental

2.1. Reagents and materials

Formalin (HCOH aqueous solution of 37% w/v formaldehyde), Poly-(acrylic acid) and $PdCl_2$ were from Sigma-Aldrich (Louis, USA). Graphene Oxide was from Cheap Tubes (Brattleboro, USA). Potassium hydroxide was from Merck KGaA (Darmstadt, Germany). All chemical solutions were prepared using deionized water (18.2 MΩ.cm) (Barnstead™ EasyPure™ II water purification system, Thermo Fischer Scientific™, USA).

2.2. Instrumentations

The structure and morphology of the modified electrode were characterized by transmission electron microscopy (TEM) (JEM-2010, JEOL, USA), and Fourier Transform Infrared Spectrometer (FT-IR) (EQUINOX 55, Bruker, Germany). All electrochemical experiments were carried out using a µAUTOLAB TYPE III (Metrohm Autolab B.V., The Netherlands) potentiostat-galvanostat with NOVA 1.8 software. The electrochemical measurements were performed with a classical three-electrodes system consisting of the modified electrode as the working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl (saturated KCl) as the reference electrode.

2.3. Procedures

2.3.1. Electrode preparations

2.3.1.1. Preparation of functional GO with PAA (PAA-GO). Thirty milligrams of GO were dispersed in 30 mL of double deionized water using an ultrasonic bath. After that, 20 mL of PAA (15 wt%) was added into complete dispersion solution with continued ultrasonicated for 2 h and then kept overnight at room temperature to get PAA/GO (Fig. 1A(I)) [56].

2.3.1.2. Preparation of PdNPs-PAA-GO composite material. Ten milligrams of PAA-GO were dispersed in 48 mL double deionized