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A poly(dimethylsiloxane)-based electrochemical cell coupled with disposable screen printed edge band ultramicroelectrodes for use in flow injection analysis

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Abstract

We report here the development of an inexpensive poly(dimethylsiloxane) (PDMS)-based electrochemical cell specifically designed for disposable screen printed edge band ultramicroelectrodes (SPUMEs) for use in flow injection analysis (FIA). The SPUME is fabricated with a built-in three-electrode pattern on a non-conducting polypropylene substrate. The edge of the carbon and/or metal-sandwiched films between the insulator layers can serve as a band type ultramicroelectrode. Fabrication of the cell is straightforward; no micromechanical operation is included. Simply by molding of PDMS with a "T" type channel to fix the SPUME in a confined wall-jet-type configuration, the performance characteristic of the proposed cell was evaluated by using the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple. The high velocity jet of solution resulted in a mass transport coefficient up to ca. 0.48 cm/s. The proposed FIA system was applied for the detection of nitrite and the current response was linear up to 700 μM with a detection limit of 0.067 μM ($S/N = 3$). Finally the determination of nitrite in lake and ground waters without the addition of supporting electrolyte was successfully demonstrated.

Keywords: Ultramicroelectrode; Disposable; Screen printed electrode; Nitrite; PDMS

1. Introduction

The application of ultramicroelectrodes (UMEs) has continuously attracted a great deal of attention in various research fields. The advantages include largely increasing in mass transport to the electrode surface, minimizing of *iR* drop even in the absence of supporting electrolyte or in highly resistive non-aqueous media, and facilitating fast response with a steady state current–potential response [1–5]. So far, diverse types of UMEs have been developed for ultratrace analysis [2,6–13]; yet, the fabrication of UMEs normally requires tedious and time-consuming procedures and thus limits their widespread use. Our group recently reported a disposable screen printed edge band ultramicroelectrode (SPUME), which is low-cost (thus disposable), easy for mass production, and flexible in design [14]. This disposable SPUME with an in-built three-electrode configuration was successfully demonstrated for electroanalysis of nitrite by linear scan voltammetry with a detection limit of 0.38 μM ($S/N = 3$) [15]. In continuation of our previous investigation, in this study, we further develop an inexpensive poly(dimethylsiloxane) (PDMS)-based electrochemical cell specifically designed for this disposable SPUME for use in flow injection analysis (FIA). Note that the advantages of hydrodynamic UME include remarkable sensitivity, wide linear calibration range, low dead volume, and fast response time.

PDMS is a soft material widely used in the field of microfabrication [16,17]. The main course of its fabrication includes preparation of the template and curing of the PDMS precursor on it. By taking this material into the construction of a simplified electrochemical cell, it is

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expected that the flexibility of the material can effectively avoid the solution leakage. Micromolding of the material provides an easy way to replicate cells with a high efficiency. Overall, by curing of the PDMS precursor on a designed template, the electrochemical cell fabrication process is simple, cheap, precise, and reproducible.

As mentioned earlier, this disposable SPUME was successfully demonstrated for electroanalysis of nitrite by linear scan voltammetry with a detection limit of 0.38 μM ($S/N = 3$) [15]. For the purpose of comparison, the determination of nitrite is again chosen as the model analyte in this study. The optimization of analytical parameters, such as distance between the SPUME and the wall-jet capillary inlet and flow rate, that can affect the analytical performance in FIA were carefully evaluated. Finally, the proposed system was used in real sample analysis to detect the amount of nitrite in lake and ground waters without the addition of supporting electrolyte. These demonstrations are envisaged to provide a useful electrochemical method as well as a user-friendly setup for electrochemical applications.

2. Experimental

2.1. Reagents and chemicals

Potassium ferricyanide and sodium nitrite were obtained from Sigma (St. Louis, MO, USA). Carbon and silver inks were purchased from Acheson (Tokyo, Japan). Conventional SPE (3 mm in diameter) in three-electrode configuration was obtained from Zensor R&D (Taichung, Taiwan). All the other compounds (ACS-certified reagent grade) were used without further purification. Aqueous solutions were made up of de-ionized water prepared from the Millipore-Q purification system. Natural water samples were collected in a polyethylene bottle from the campus of Chung Hsing University and kept under refrigeration below 4.8 °C and were directly used for detection.

2.2. SPUME and cell design

The wall-jet cell assembly as well as the incorporation of the SPUME into the wall-jet electrochemical cell is depicted in Fig. 1. By molding of PDMS with a "T" type channel (depth 1.15 mm and width 1.15 mm) the SPUME not only can be easily fixed but also can prevent the solution leakage from inlet and outlet. Since the capillary within the channel has an inner diameter of 0.5 mm, the insertion as well as the alignment of the SPUME into the flow cell is also very simple. Two polymethylmethcrylate (PMMA) plates were then used to cover and strengthen the wall-jet cell. The system is capable of operating under a high pressure flow system of up to 10 cm^3/s.

The fabrication of the SPUME was the same as reported by our group earlier [14]. In brief, different stencil assemblies were first prepared properly to fabricate the multilayer SPE on a 50 mm × 15 mm polypropylene (PP) base. The layer-by-layer assembly of the built-in three-electrode system contains a stencil format in the order of carbon ink → insulating polymer → silver ink → insulating polymer → silver ink → insulating polymer. The as-prepared SPUME was then cured in an UV radiation source at an intensity of 1.85 mW/cm^2 for 2 h. The tip edge window was suitably sliced to expose the SPUME with a built-in three-electrode pattern. Note that the procedures can allow for preparing versatile three-electrode SPUME suitably in-between the insulating polymeric layers.

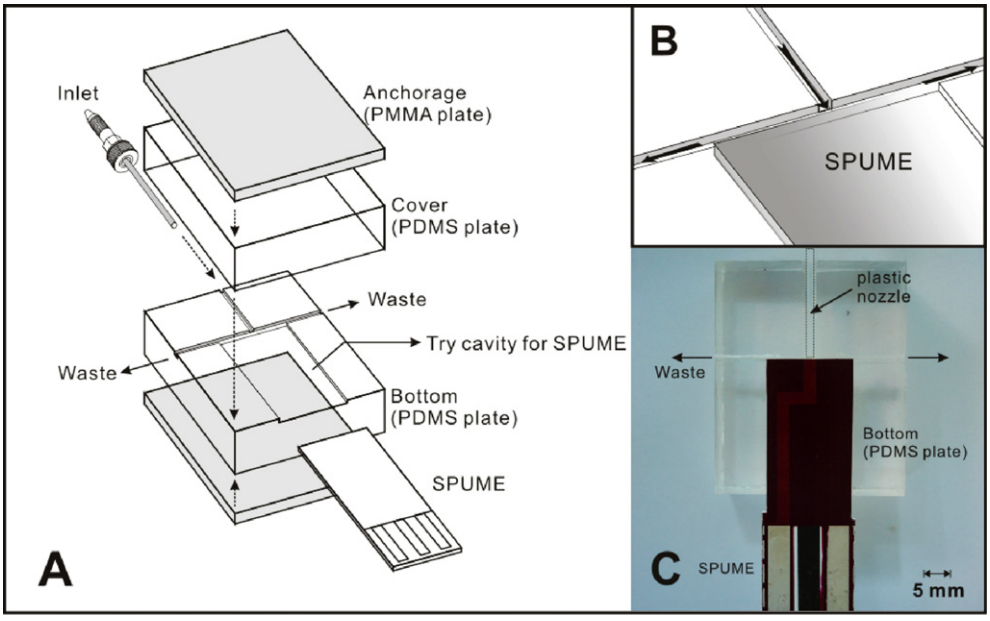

Fig. 1. Scheme and pictorial representation for the proposed electrochemical cell with the SPUME: (A) arrangement of the cell component, (B) magnification of the T-type interface between the injection inlet and the SPUME, (C) photograph of the proposed system.