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Enhancement of the sensitivity of electrochemical stripping analysis by evaporative concentration using a super-hydrophobic surface

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Abstract

A super-hydrophobic surface was used to concentrate a droplet of sample solution evaporatively for the stripping analysis of heavy metal ions. The system consisted of a working electrode at the center and a Ag/AgCl reference electrode surrounding the working electrode. Except for the sensitive area, a super-hydrophobic layer was formed with polytetrafluoroethylene (PTFE) beads. A droplet of an aqueous sample solution was placed on the sensitive area and concentrated by evaporation. The super-hydrophobic layer effectively pinned the droplet at the edge of the sensitive area. Square-wave anodic stripping voltammetry was conducted for the analysis of Cd^{2+} and Pb^{2+} ions. A significant increase in peak height was observed as the volume of the droplet increased. When a 5-μl-droplet was used, the peaks were 30 times higher than those obtained in the analysis following the conventional procedure without the evaporative concentration. In addition, the peak current increased, and the background current decreased by decreasing the working electrode area.

Keywords: Polytetrafluoroethylene (PTFE); Super-hydrophobicity; Heavy metal; Anodic stripping voltammetry

1. Introduction

With the advent of the 21st Century, environmental pollution caused by heavy metal ions has been attracting more attention. The highest concentrations permitted in soil and water are strictly regulated by laws. Therefore, the demand for portable analysis systems, which can conduct heavy metal detection on the spot, is steadily increasing. To create such a system, electrochemical principles are very promising and realistic because sufficient sensitivity is expected and miniaturization is easy [1]. To detect trace heavy metals electrochemically, anodic stripping voltammetry has been used [2,3]. With this technique, heavy metal ions are first reduced and deposited on the working electrode at a cathodic potential (preconcentration). The deposited heavy metals are then oxidized by scanning the potential to the positive side (stripping). During the process, unique peaks are observed at potentials corresponding to the redox potentials of the respective heavy metals. In addition, the heights of the peaks are in proportion to the concentration of heavy metals. Therefore, heavy metal ions contained in a sample solution can be identified and determined in terms of the position and height of the peaks.

Several portable devices have been fabricated, the main focus being the miniaturization of the working electrode [4–11]. In the stripping analysis, mercury electrodes, including mercury film electrodes and hanging mercury drop electrodes, have traditionally been used as working electrodes. Some of the microfabricated devices have also used mercury electrode arrays [4–7,10]. Although the mercury electrodes are excellent in sensitivity and feature a wide potential window expanding to the negative side, they require careful preparation of pure and clean surfaces to obtain the expected performance. In addition, the use of toxic mercury in environmental monitoring should definitely be avoided. On the other hand, solid metal electrodes are easy to handle and obtained by thin-film or thick-film processes. However, with metal electrodes other than mercury, obtaining sufficient sensitivity has been an issue.

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The sensitivity of the analysis depends on the cleanliness of the working electrode surface, the transport of the analyte ions during the electrochemical preconcentration, the length of time required for the preconcentration, and other conditional parameters. Among them, achieving a completely clean surface is often difficult while ensuring that a patterned organic insulating layer, such as one of polyimide, maintains sufficient adhesion to the substrate. The influence is particularly serious for the heavy metal detection of lower- or sub-ppb levels. Although clean surfaces can be obtained with inorganic insulators by coupling them with a plasma process [4–8,10], the application of organic materials will be an unavoidable requirement in promoting the commercialization of the devices.

A direct solution to the problem will be to enhance the mass transfer during the preconcentration and increase the amount of deposited heavy metals. Actually, when the heavy metals are preconcentrated on the working electrode, the convection of the solution has a significant effect. Although microelectrode arrays can improve the deposition efficiency even in a quiescent solution along with the quality of the stripping voltammogram [12], they do not provide a complete solution to the problem [7]. To solve the problem, we developed a method to concentrate a sample solution evaporatively on a working electrode.

Let us suppose that the entire surface, including the sensitive area, is hydrophilic and a droplet of a sample solution is placed there (Fig. 1(a)). In this case, it would be extremely difficult to collect all analyte ions dissolved in the solution because the working electrode can collect ions only in the vicinity of the solution. On the other hand, an aqueous solution takes a spherical shape on a super-hydrophobic surface. If a small hydrophilic sensitive area were surrounded by a super-hydrophobic surface, the analytes in a droplet would concentrate as the sample solution shrinks by evaporation (Fig. 1(b) and (c)). This means that ions that are distant from the electrode would be collected intentionally to the sensitive area. With this method, there is an accompanying advantage, namely, that both the heavy metal ions and the supporting electrolyte are concentrated. Therefore, it is not necessary to add a large amount of supporting electrolyte to the sample solution. Using this technique, a significant increase in the current peaks was observed for Cd^{2+} and Pb^{2+} ions at concentrations of a lower-ppb order. In this report, the details of the technique and the performance of the system will be reported.

2. Experimental

2.1. Reagents and materials

Reagents and materials used for the fabrication and performance characterization were purchased from the following commercial sources: polytetrafluoroethylene (PTFE) beads (diameter: 1 μm) from the Aldrich Chemical Company, Milwaukee, WI, USA, lead (II) acetate trihydrate and cadmium standard solution (99.8 mg/l in 0.1 M nitric acid) from Wako Pure Chemical Industries, Osaka, Japan. An epoxy resin (YL-980) and an epoxy-curing agent (YH-306) were obtained from Sekisui Chemical, Osaka. Standard solutions of Cd^{2+} and Pb^{2+} ions were prepared with a 0.1 M acetate buffer solution (pH 4.0). An appropriate amount of KCl was added, as mentioned later.

2.2. Structure and fabrication of the system

Fig. 2 shows the structure of the chip formed on a glass substrate. Metal patterns were formed by photolithography, including metal deposition by sputtering followed by chemical etching or lift-off. A gold layer was formed to make contact pads and a backbone layer. Chromium was used as an intermediate layer to promote the adhesion of the gold layer to the substrate. Here, bismuth was used for the electrode material. The bismuth-film electrode shows a performance comparable to that of mercury-film electrodes [13,14]. Bismuth was sputter-deposited on the working electrode area by the lift-off process. Silver was patterned

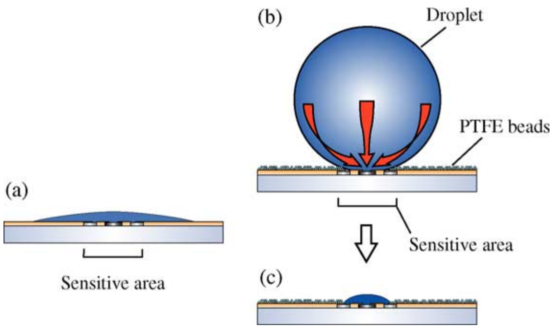

Fig. 1. Evaporative concentration using super-hydrophobicity. (a) Droplet placed on a hydrophilic sensitive area surrounded by a hydrophilic layer. (b) Droplet placed on a hydrophilic sensitive area surrounded by a super-hydrophobic layer. (c) Droplet shrunk after evaporation.

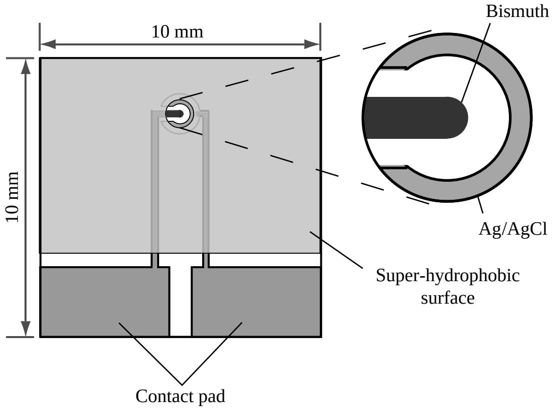

Fig. 2. Structure of the system. A magnified view of the sensitive area is shown in the figure on the right.