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\textsuperscript{2+} and Pb\textsuperscript{2+} ions. A significant increase in peak height was observed as the volume of the droplet increased. When a 5-\textmu{}l-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.

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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.
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

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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.
on the reference electrode area in the same manner. The active areas of the electrodes were delineated with an epoxy layer. A AgCl layer was not formed in the fabrication process but, rather, during the deposition of heavy metals. In the Ag/AgCl electrode, the AgCl layer was grown from the edge of the silver pattern into the area protected by the epoxy-insulating layer [15]. The structure has been proven to be very durable even in a concentrated KCl solution. In this study, three types of chips differing in the size of the sensitive area (Types I–III) were prepared. Details of the dimensions are summarized in Table 1.

The sensitive area was surrounded by a super-hydrophobic layer. The wettability of a solid surface depends not only on the nature of the surface but also on microscopic three-dimensional structures. Here, a rough super-hydrophobic surface was realized by depositing PTFE beads. The sensitive area must be exposed to the analyte solution. Therefore, a polydimethylsiloxane cylinder was first attached to the area in order to avoid coverage by the PTFE beads. The diameter of the cylinder was the same as that of the sensitive area. In depositing the PTFE beads, they were floated on distilled-deionized water. The thin layer was carefully transferred to the surface of the chip. After drying at room temperature, the PDMS cylinder was removed. As a result, a super-hydrophobic layer was formed in the area surrounding the sensitive area.

2.3. Measurement procedures

All voltammetric analysis was conducted with an Autolab PGSTAT12 (Eco Chemie, Utrecht, Netherlands) connected to a lap-top computer using an interface. The procedure for detection consisted of three steps: evaporative and electrochemical preconcentrations on the chip and stripping of heavy metals in a solution in a beaker. Although our ultimate goal was to conduct the evaporative concentration and stripping analysis using the electrodes on the same chip, it requires additional technologies, including temperature control, a stirring mechanism, and a more reliable reference electrode. Therefore, at this stage, the two procedures were conducted in different configurations.

First, a sample solution was dropped onto the sensitive area. The droplet was repelled from the surrounding super-hydrophobic layer, and a spherical droplet was formed on the electrode area (Fig. 3). The standard sample solution contained KCl as a supporting electrolyte. In order to reduce the time for evaporation, the chip was placed on a hotplate maintained at 100 °C. As the droplet shrank, not only the analyte ions but also the supporting electrolyte concentrated, and this effect was enhanced in smaller sensitive areas. Therefore, the KCl concentrations were changed for chips with different sensitive areas (Table 1) for a reason to be presented later. During the evaporation of the solution, no potential was applied to the working electrode. When the solution was almost evaporated and spread on the hydrophilic sensitive area as in Fig. 1(c), the evaporation was temporarily stopped by decreasing the temperature, and −1.0 V (vs. on-chip Ag/AgCl) was applied to the working electrode. Although the potential of the Ag/AgCl reference electrode shifted to the negative side as the KCl concentration increased by evaporation, the potential change stopped when KCl was saturated in the droplet. The applied potential was appropriate for the situation. The length of the deposition time was 60 s for all experiments.

Following the preconcentration step, stripping of the deposited metals was performed at 25 °C by using a three-electrode system in a beaker. A commercial platinum plate as an auxiliary electrode and a double junction Ag/AgCl electrode (Horiba 2565A-10T) as a reference electrode were used. The sensitive area of the chip was immersed in an acetate buffer solution containing 0.1 M KNO3 filling the beaker. The working electrode on which heavy metals were deposited was immersed in the solution and poised at −1.0 V. Immediately afterwards, the voltammogram was recorded in a potential range between −1.0 and −0.2 V by applying a square-wave potential (frequency: 200 Hz, potential step: 1.95 mV, amplitude: 25.5 mV). The time required for the entire procedure was approximately 10 min, most of which was spent for the evaporation of the droplet. For comparison, all the procedures were also conducted in a quiescent sample solution in a beaker without the evaporative concentration.
3. Results and discussion

3.1. Surface of the deposited PTFE beads and shape of a droplet

The PTFE beads deposited from the solution surface did not form a uniform monolayer. On the contrary, the film consisted of multi-layers whose thickness varied from place to place. However, the randomness helped form microscopically rough three-dimensional structures and enhance the hydrophobicity [16]. When a droplet was placed on the surface, the contact angle was 167°. A droplet placed on the hydrophilic sensitive area surrounded by the PTFE layer is shown in Fig. 3. Due to the very strong hydrophobicity, the droplet was effectively pinned at the edge of the PTFE layer, although it temporarily spread on the super-hydrophobic area when the droplet was placed there. The contact angle changed when a droplet was placed on a sensitive area of different sizes. With a 1-μl-droplet, the contact angle was 127° on the largest sensitive area (Type I), whereas it increased to 158° on the smallest sensitive area (Type III). Moreover, with a sensitive area of the same size, the contact angle increased as the volume of the solution increased as long as the droplet did not collapse by the gravitational force. This suggests that the method becomes more effective as the area of the sensitive area decreases and the volume of the droplet increases, which was actually the case, as discussed in later sections.

3.2. Basic properties of the thin-film electrode system

In conducting the stripping analysis, the range of the potential window determines the metals that can be deposited and analyzed. Fig. 4 shows the cyclic voltammogram obtained with the bismuth electrode in the background electrolyte solution used in the stripping analysis. Even at −1.1 V, the evolution of hydrogen was not significant, which enables the detection of Cd²⁺ ions. When the potential was scanned to the positive side, the voltammogram was very featureless, and a significant current increase was observed at around −0.1 V accompanying the dissolution of bismuth. This limits the application of this electrode to the detection of heavy metals, such as copper, whose redox potentials are in the positive range [17].

As the evaporation proceeds, the KCl concentration also increases. A problem here is that the AgCl layer dissolves in concentrated KCl solutions forming complex ions, which often leads to the damage of the thin-film Ag/AgCl reference electrode [18]. However, the configuration and the operating condition were preferable for a normal function of the Ag/AgCl electrode. Namely, because of the two-electrode configuration, the Ag/AgCl electrode was always polarized anodically, promoting the growth of the AgCl layer. The Ag/AgCl structure protected by the insulating layer was also effective in providing a stable reference electrode potential in a concentrated KCl solution. This actually settled the potential of the Ag/AgCl electrode in the vicinity of the value expected from the Nernst equation.

3.3. Effect of the evaporative concentration

A simple estimation using the values of the diffusion coefficient of Cd²⁺ (7.2×10⁻⁶ cm²/s) and Pb²⁺ (9.5×10⁻⁶ cm²/s) ions [19] gives the expansion of the diffusion layer as approximately 400 μm for both ions after 60 s supposing that the electrode is macroscopic and planar. Therefore, even within a droplet of 5 μl (diameter: 2.1 mm), only a fraction of these metals is consumed, and it is not impossible to collect all ions in the solution within a realistic timescale for field analyses. To demonstrate this point, heavy metal ions were detected in batch-style measurements in a beaker without the evaporative concentration. In Fig. 5(a), a stripping voltammogram obtained in solutions containing Cd²⁺ and Pb²⁺ ions of 200 ppb is shown. The peak current is very small and barely distinguished from the background current with the indicated current scale. In order to examine the effect of the evaporative concentration, a droplet of sample solution (5 μl) was placed on the sensitive area. In Fig. 5(a), the stripping voltammograms for Cd²⁺ and Pb²⁺ ions of 50, 100, 150, and 200 ppb are also shown. Compared with the data obtained in the batch-style measurement, clear peaks were observed at the respective concentrations, and the peak currents were significantly higher even at lower concentrations. The method was effective to measure much lower concentrations. In the concentration range shown in Fig. 5(b), no peaks were distinguishable in the stripping voltammogram obtained by the conventional batch-style procedure. On the other hand, distinct peaks were observed using the novel method. Linear calibration plots were obtained by plotting the peak current with respect to the concentration (Fig. 6). The slope was 5.7 nA/ppb for Cd²⁺ ions and 7.4 nA/ppb for Pb²⁺ ions. The reproducibility of the data was fairly good.
With the type II chips, the relative standard deviations for the peak currents of Cd\(^{2+}\) and Pb\(^{2+}\) ions were 9.2 and 5.9% at 100 ppb, respectively, but they increased to 14.3 and 13.2% at 10 ppb \((n = 5)\).

The quality of the stripping voltammograms decreased when the internal KCl concentrations were higher than those used for the experiments (Table 1). A possible cause of this phenomenon is the dissolution of silver from the AgCl layer in the reference electrode. During the preconcentration step, the AgCl layer is grown. However, the dissolution of AgCl is promoted as the chloride ions are concentrated in the evaporation process at elevated temperatures [18]. Since the concentration of silver ions or related complex ions is assumed to be much higher than those of Cd\(^{2+}\) and Pb\(^{2+}\) ions, it might affect the deposited heavy metals or change the surface state of the bismuth electrode.

### 3.4. Dependence of the peak current on the sample volume

Based on the discussion made in the previous section, the enhancement of sensitivity can be expected as the volume of the sample solution increases. In order to examine this effect, stripping voltammograms were examined with sample solutions of different volumes. In Fig. 7, the ratio of the peak current obtained by the method to those obtained by the batch-style measurement in a beaker without the evaporative concentration was plotted with respect to the sample volume. The ratios for Cd\(^{2+}\) and Pb\(^{2+}\) ions increased as the sample volume increased. With a 5 \(\mu\)l sample solution, the peaks obtained by the novel method were approximately 30 times higher than those obtained by the conventional procedure. Although a longer time is required to evaporate a droplet of a larger volume, the presented results are promising in that the simple method is very effective to increase the sensitivity of the analysis as desired.

### 3.5. Influence of the size of the working electrode

When this method is applied to working electrodes of the different sizes, the amount of deposited heavy metals is supposed to be approximately the same. This is in marked

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**Fig. 5.** Stripping voltammograms obtained by the novel method for a higher range (a) and a lower range (b) of concentration. In (a), beaker refers to the data obtained with the batch-style measurement without the evaporative concentration. The inset shows the magnified graph for the curve beaker. The current axis is expanded ten times. A type-II chip was used. Sample volume: 5 \(\mu\)l.

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The quality of the stripping voltammograms decreased when the internal KCl concentrations were higher than those

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**Fig. 6.** Dependence of the peak current on the concentration of heavy metal ions. ●: Cd\(^{2+}\), ○: Pb\(^{2+}\). A type-II chip was used. Sample volume: 5 \(\mu\)l.

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**Fig. 7.** Dependence of the peak current ratio on the volume of the droplet. The peak current ratio is defined as the peak current obtained by this method relative to the peak current obtained by the batch-style measurement without the evaporative concentration. ●: Cd\(^{2+}\), ○: Pb\(^{2+}\). Concentration: 200 ppb. A type-II chip was used.
contrast with the case without the evaporative concentration, in which the decrease in the working electrode area accompanies the decrease in the peak currents. Furthermore, with smaller working electrodes, the charging current and the other Faradaic background currents will decrease when the deposited heavy metals are stripped [12]. In order to examine this point, stripping voltammograms were obtained for concentrations in a lower ppb range by using working electrodes of the three different areas (Fig. 8). As expected, a noticeable background current was observed with the largest working electrode with the described potential range. However, the background current decreased significantly as the size of the working electrode decreased. Moreover, the peak current increased with smaller working electrodes (Fig. 8). A major cause for the enhancement of the sensitivity will be that the collection efficiency of the heavy metal ions increased in the shrunken solution relative to the size of the diffusion layer as the sensitive area decreased [12].

3.6. Future directions

As mentioned in Section 3.2, detectable heavy metals are limited by the potential window provided by the metal for the working electrode. Although we focused on the detection of Cd$^{2+}$ and Pb$^{2+}$ ions, there are many heavy metal ions whose detection is required. In order to analyze them, a series of working electrodes that have excellent detection performance for specific metals should be used. To this end, the electrode system presented in this work could be arrayed using different working electrode materials.

The application of this method to the analysis of heavy metal ions in dirty real sample solutions requires further study. Many chemicals, including surfactants, may contaminate the working electrode surface and deteriorate the detection sensitivity. In addition, the existence of chelating agents and ions that form precipitates with heavy metal ions affects the amount of detected heavy metals. To this end, a module to remove the undesirable chemicals is required, which is our next issue.

The reduction of the total time for analysis is another issue. As mentioned earlier, most of the analysis time is spent on the evaporation of the droplet. This problem is closely related with the improvement of the sensitivity of detection. If a cleaner well-conditioned working electrode surface is obtained, the detection limit will be lowered further, leading to the reduction of the sample volume and analysis time.

4. Conclusions

This novel method to concentrate a sample solution using the super-hydrophobic surface is effective to significantly increase the sensitivity of heavy metal detection. A droplet placed on a hydrophilic sensitive area surrounded by a super-hydrophobic layer takes a spherical shape. As a result, the droplet shrinks to the sensitive area when it evaporates. The concentrations of ppb order can be easily detected, and the calibration plots are linear. A significant increase in the peak currents is observed as the sample volume increases. Furthermore, the background current decreases, and the quality of the stripping voltammogram is improved by decreasing the working electrode and the total active area. If the method for the formation of the super-hydrophobic layer is optimized, the detection limit will be improved further.

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