Paper

Micro gas preconcentrator made of a film of single-walled carbon nanotubes

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The development of micro gas preconcentrators is crucial for the realization of miniaturized gas chromatography (micro-GC) systems which are expected to open up new applications such as breath analysis. One of the major problems with the reduction in the preconcentrator size by miniaturization is the availability of a sorbent material having high enough concentration factor. Single-walled carbon nanotubes (SWNTs) are one of the promising materials for high adsorption capacity. In this report, a gas preconcentrator having a depth of 40 μm and a volume of 1 μL was microfabricated. The synthesized SWNT films with a thickness of 30 μm were embedded in the micro gas preconcentrators by using the hot water-assisted detachment method. The small size of the fabricated micro gas preconcentrator and the use of SWNTs as the adsorbent material allow for achieving a concentration factor as high as 16000 for 2 ppm octane. This concentration factor value is the highest reported to date for micro gas preconcentrators and sufficient for micro-GC detectors to concentrate trace analytes of interest for breath analysis. It is concluded that micro gas preconcentrators using SWNTs as the adsorbent material have great potential to concentrate compounds.

Keywords : Micro gas preconcentrator, Adsorbent material, Single-walled carbon nanotube, Concentration factor

1. Introduction

Gas chromatography (GC) is the technique of choice for analysis of complex gaseous mixtures. A GC system typically consists of a separation column and a detector. Thanks to advances in microelectromechanical systems (MEMS) technology, miniaturization of GC systems (micro-GC) was made possible [1-2]. Further miniaturization and optimization of the GC components have been actively researched and developed [3-7]. The realization of micro-GC systems will open up new applications such as breath analysis, enabling non-invasive and fast screening/monitoring of infectious diseases. It is known that alkanes are endogenous breath molecules, which are usually associated with a broad range of diseases [8,9]. Alkanes are contained in human breath at very low concentrations in the ppb range and, therefore, are difficult to detect by conventional micro-GC detectors [2,10]. Consequently, preconcentration of alkane analytes is needed.

Several attempts reported in the literature to fabricate micro gas preconcentrators by MEMS technology have resulted in low values of the concentration factor, the conventional figure of merit for preconcentration [11-13]. These micro gas preconcentrators having small inner volumes in the order of μL could not be packed with enough sorbent materials to reach sufficiently high concentration factors [11-16]. In order to enhance the concentration factor, the preconcentrator requires sorbent materials having higher sorption capacity than those of conventional sorbent materials such as Tenax TA and Carbopack. Therefore, one of the major challenges in developing microfabricated preconcentrators is the synthesis of new sorbent materials with high enough sorption capacity for use in microfabricated preconcentrators.

Carbon nanotubes (CNTs) are attractive materials as the adsorbent material of alkanes owing to their chemical and thermal stability, a high surface-to-volume ratio, and a large affinity to the nonpolar compounds [17]. The chemical and thermal stability is required for CNTs to adsorb and desorb various organic compounds. High surface-to-volume ratio yields high adsorption capacity. Previous studies have demonstrated that CNTs have higher adsorption capacity than Carbopack, which is a graphitized carbon [18-20]. Single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) in a conventional steel column have shown good adsorption capacity [18,19]. SWNTs are more suitable as adsorbent material than MWNTs, because SWNTs exhibit a larger aspect ratio and higher effective surface area [18,19]. SWNTs have been also used as an adsorbent material

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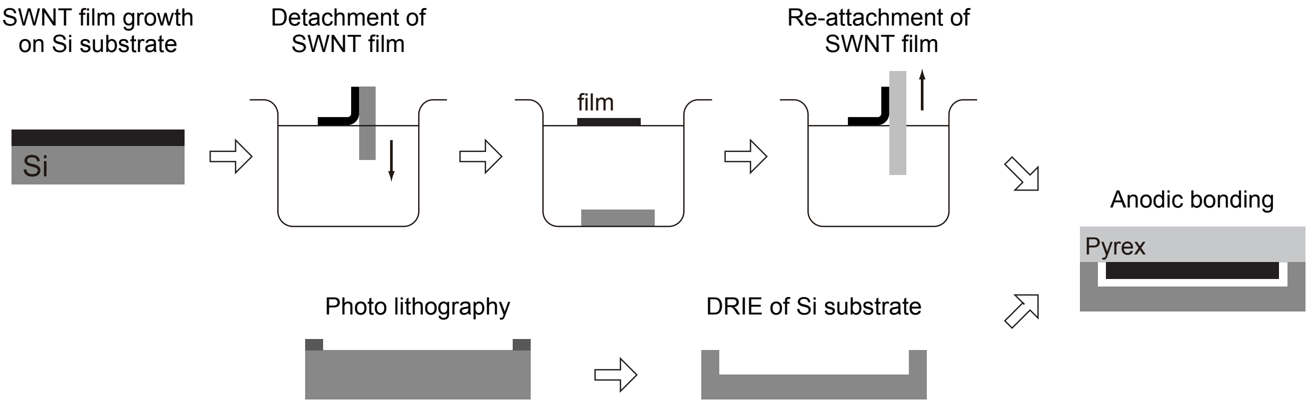

Fig. 1. Fabrication process of the micro gas preconcentrator using an SWNT film. The depth of the Si flow channel was 40 μm, and the volume of the fabricated micro gas preconcentrator was 1 μL.

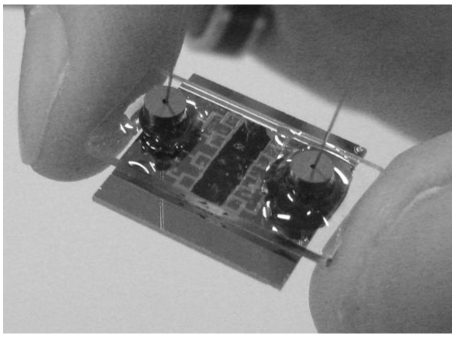

Fig. 2. Photograph of the fabricated micro gas preconcentrator with embedded SWNT film. Deactivated fused silica capillary tubes were connected to the preconcentrator through two holes in the Pyrex glass.

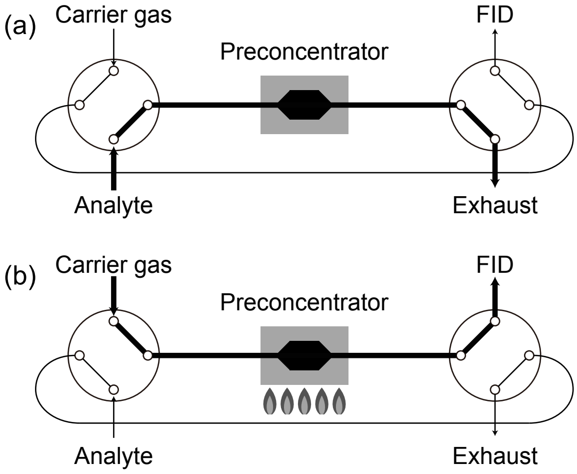

Fig. 3. Schematic of the experimental setup with (a) valves set in the adsorption position and (b) valves set in the desorption position.

in a micro gas preconcentrators, however the concentration factor was not quantitatively evaluated [21]. Therefore, the potential of SWNTs as an adsorbent material for use in micro gas preconcentrator is far from being demonstrated.

The aim of this report is to fabricate a micro gas preconcentrator using SWNTs as an adsorbent material and realize a high concentration factor for an alkane analyte.

2. Experiment

2.1 Fabrication The thickness of the SWNT film we used was 30 μm [15,16]. The SWNT film was obtained by the hot water-assisted detachment method. It is reported that SWNT films can be detached from the substrates on which the films were synthesized, and re-attached to other substrates in hot water above 60ºC [22]. This unique characteristic of SWNT films enabled us to readily embed SWNT films in a micro gas preconcentrator.

The depth of Si channel was designed to 40 μm to reduce the dead volume of the micro gas preconcentrator. With reference to previous works [11-13], the inner volume of a micro gas preconcentrator was designed to be 1 μL. This inner volume is smaller than any of the preconcentrator volumes reported in the literature.

The fabrication sequence of the micro gas preconcentrator using an SWNT film is illustrated in Fig. 1. First, an SWNT film was grown on the surface of a Si substrate by the alcohol catalytic chemical vapor deposition (ACCVD) method [23]. We used molybdenum and cobalt as catalytic metals for the ACCVD process. The catalytic metals were dissolved (at the same weight concentration of 0.01 wt %) in ethanol to form a metal acetate solution. The solution was dip-coated on the Si surface at a constant pull-up speed of 4 cm/min at room temperature. The substrate was then dried in an oven at 400 ˚C for 5 minutes. The ACCVD process was carried out in a quartz tube furnace as follows. The substrate was heated to 800ºC in the furnace with a 300-sccm flow of argon gas containing 3% hydrogen (Ar/H_2 gas), so that the pressure inside the tube was kept at about 40 kPa. When the reaction temperature of 800ºC was reached, the gas flow was stopped, and ethanol vapor was introduced at a pressure of 1.3 kPa for 10 minutes. Second, the synthesized SWNT film on the substrate was detached in hot water and then it was re-attached to a Pyrex glass. The temperature of the water was set to 65ºC. The detached SWNT films on the glass substrate were manually cut into a rectangular piece of 3×9 mm^2. Third, a silicon substrate was patterned by photoresist masking and the pattern was etched using deep reactive ion etching (DRIE) to make a 40-μm-depth flow channel. The width and length of the flow channel were 9 mm and 3.6 mm, respectively. Finally, the Pyrex glass loaded with an SWNT film was sealed on the etched silicon substrate by anodic bonding at 350ºC and 500 V in a nitrogen atmosphere to prevent the oxidation of the SWNTs.

The dead volume without the SWNT film was about 0.3 μL,

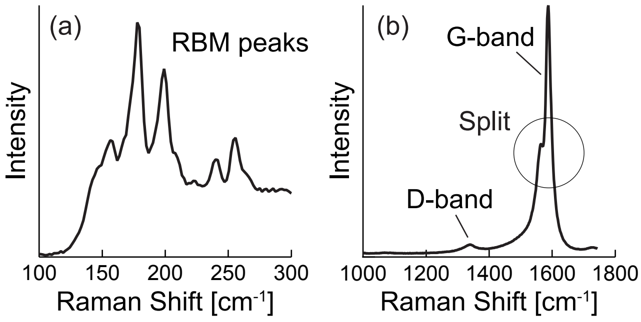

Fig. 4. (a) Low-frequency and (b) high-frequency parts of a representative resonance Raman spectrum of the SWNT film.

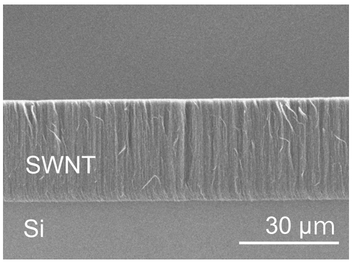

Fig. 5. An FE-SEM image of a cross section of the substrate where an SWNT film was synthesized. The thickness of the SWNT film was 30 μm.

when a 30-μm-thick SWNT film was packed into the fabricated micro gas preconcentrator. The dead volume, which was smaller than those in previous reports [14,16], helps to achieve high concentration factor. The micro gas preconcentrator had two holes (diameter of 1 mm) on a Pyrex glass side for the tubing connection. Two graphite ferrules (internal diameter of 0.5 mm) were used to make ports. They were fixed with a high temperature epoxy adhesive (526N, Aremco Products) on the glass. Deactivated fused silica capillary tubes (internal diameter of 150 μm and outer diameter of 220 μm) were connected to the ports. The connections were sealed with the epoxy adhesive. The completed micro gas preconcentrator is presented in Fig. 2.

2.2 Experimental setup To evaluate the concentration factor of the fabricated micro gas preconcentrator, tests of adsorption and desorption of analyte were carried out. Octane, which is one of the alkanes present in human breath [9], was used as an analyte, and clean air was used as a diluted gas. The analyte vapor concentration in the diluted gas was accurately controlled by a gas generation apparatus (Double chamber permeater PD-1B-2, Gastec). The concentration factors of the micro fabricated preconcentrator were measured for 2 ppm octane. The flow rate of the analyte was kept constant at 2 mL/min during adsorption.

The experimental setup given in Fig. 3 was installed inside the oven of a conventional GC system (HP 6890 GC, Agilent). The built-in split/splitless inlet and the built-in flame ionization detector (FID) of the conventional GC system were connected to the setup via the deactivated fused silica transfer tubes (internal diameter of 150 μm and outer diameter of 220 μm). The preconcentrator was heated by a ceramic heater, and the temperature of the preconcentrator was measured with a K-type thermocouple attached to the rear of the preconcentrator.

First, the analyte vapor was introduced into the micro gas preconcentrator in a constant time using two four-port zero-dead-volume valves (step shown in Fig. 3a). The analyte vapor was adsorbed on the SWNTs at the temperature of 25ºC. The adsorption time was varied. Second, the two valves were switched and the micro gas preconcentrator was heated (step shown in Fig. 3b). The desorbed analyte from SWNTs was carried to the detector by the Helium carrier gas. The carrier gas flow rate was kept at a constant 4 mL/min. The peaks for the desorbed analyte were recorded using a data logger with a sampling frequency of 50 Hz and an A/D resolution of 16 bits.

3. Results and discussion

3.1 SWNT film characterization The synthesized SWNT film was characterized by resonance Raman spectroscopy (excitation at 488 nm) and field-emission scanning electron microscopy (FE-SEM), before the detachment of the SWNT film. Resonance Raman spectroscopy is used to estimate the SWNT diameters and characterize their crystalline quality. Figure 4 shows a typical resonance Raman spectrum. The low-frequency part of the spectrum is magnified in Fig. 4a, revealing radial breathing mode (RBM) peaks, which is strong evidence of SWNTs growth. These peaks indicate that the tube diameters of SWNTs were between 1 and 2 nm, although only the SWNTs that were resonant with the excitation laser were detected. The split of the G-band peaks around 1590 cm^{-1} is also unique to SWNTs. This is highlighted in Fig. 4b, where the high-frequency part of the spectrum is plotted. G-band peaks originate from in-plane vibrations of graphitic lattices, and D-band peaks originate from defects in graphitic structures. The ratio of the G-band intensity to the D-band intensity was more than 20, indicating the growth of high-quality SWNTs.

The thickness of the synthesized SWNT film was measured by FE-SEM. An FE-SEM image of a cross section of the silicon substrate with the SWNT film is shown in Fig. 5. Using several images at several locations of the cross section, we confirmed that the SWNT film on the silicon substrate has a uniform thickness of 30 μm.

3.2 Evaluation of concentration factor The concentration factor (f_c) is defined by expression (1).

$$f_\mathrm{c} = \frac{C_\mathrm{d}}{C_\mathrm{o}} \quad \cdots\cdots (1)$$

where C_d is the concentration of the analyte adsorbed by the micro gas preconcentrator and C_o is the concentration of the analyte generated by the gas generation apparatus. C_d was calculated from dividing V_d (the volume of the adsorbed analyte) by V_in (the inner volume of the micro gas preconcentrator). V_d was obtained by the desorption peak area corresponding to the calibration curve. The calibration curve was determined by injecting known sample volumes into the conventional GC instrument and assuming that the intensity of the FID signal is proportional to the number of ionized molecules. Figure 6 shows a measured desorption peak from the preconcentrator after 2 ppm octane was adsorbed for 180 min. Upon switching the valves, the FID signal was recorded and the temperature ramped up to 170ºC.

The variation of the concentration factor with the adsorption time is shown in Fig. 7. The highest concentration factor obtained for 2 ppm octane was 16000. This value is the highest reported to date for micro gas preconcentrators and sufficiently large for

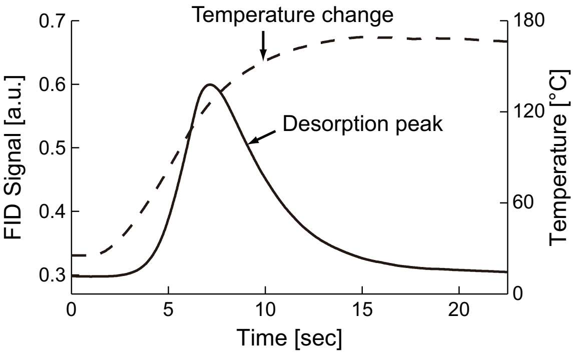

Fig. 6. The desorption peak from the micro gas preconcentrator filled with an SWNT film. Adsorption was done with 2 ppm octane for a duration of 180 min.

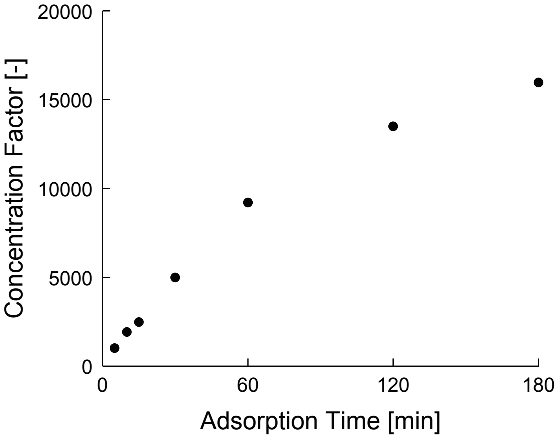

Fig. 7. The concentration factor as a function of the adsorption duration for 2 ppm octane.

micro-GC preconcentrators to concentrate trace analytes of interest to breath analysis. To our knowledge, the highest concentration factor reported in the literature is 10000 [13]. The small volume of the fabricated micro gas preconcentrator and the use of SWNTs as the adsorbent material allow for achieving such a high concentration factor.

In a previous report using Carbopack X sorbent material, the concentration factor of 300 was achieved using 400 μg of Carbopack X packed in 9 μL [16]. In this report, 30 μg of SWNTs was packed in 1 μL, assuming a density of SWNT films grown by the ACCVD method of 0.041 g/cm^3 [24]. Although the ratios between the carbon weight and the inner volume of the preconcentrator are almost the same for the two studies, the higher concentration factor of the SWNTs is strong evidence for superior adsorption capacity of the SWNTs.

The concentration factor was found to increase steadily until 60 minutes of adsorption, at which time the concentration factor started saturating. This relatively long time to reach saturation is explained by the far from ideal flow of the analyte in the preconcentrator. It is considered that most analyte flowed through the gap between the SWNT film and the flow channel. This caused the slow diffusion of the analyte into the SWNT film, which is responsible for the long adsorption time. To shorten the adsorption time, synthesizing SWNTs directly on the etched Si flow channel is needed.

4. Conclusion

We proposed the use of SWNT film as an adsorbent material for microfabricated preconcentrators. An SWNT film having thickness of 30 μm was used as a high performance adsorbent material and embedded into a microfabricated gas preconcentrator having depth of 40 μm and inner volume of 1 μL. Evaluation of the concentration factor of the micro gas preconcentrator revealed that the highest concentration factor reported to date of 16000 for 2 ppm octane was achieved. It is demonstrated that the SWNT film based micro gas preconcentrators have great potential for achieving ultra-high preconcentration of alkanes.

Acknowledgments

This research was supported by CREST (JST) and the Global Center for Excellence for Mechanical Systems Innovation (MEXT). A part of this work was conducted in the Center for Nano Lithography & Analysis, The University of Tokyo. The photolithography masks were fabricated by using the ADVANTEST EB lithography apparatus, F5112+VD01, at the VLSI Design and Education Centre (VDEC) of The University of Tokyo.

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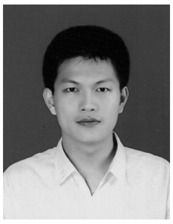

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