Surface Plasmon Resonance Detector for Capillary Chip Electrophoresis

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A novel universal detection system for capillary chip electrophoresis utilizing surface plasmon resonance (SPR) detection was developed. Nafion tube was used as a septum to draw electric current outside the flow without generating any bubble in the capillary channel. Polydimethyl siloxane as a capillary chip could easily attained this setup. We could successfully observe small change in refractive index by SPR under elctroosmotic flow.

In recent years, capillary electrophoresis using micro channel[1] has been studied extensively. The capillary chip electrophoresis has so many advantages over conventional capillary electrophoresis. These advantages are based on the effective dissipation of heat caused by the application of high voltage. However, only poor detection methods are available such as fluorometric measurement[2] or electrochemical method.[3] Though the former method has very high sensitivity, it is not universally applicable. The latter is only sensitive for electrochemically active samples. Light absorption method has not been reported, although the method is rather universal, because of the poor sensitivity caused by the very small light path. We have developed a universal detection system for capillary chip electrophoresis based on surface plasmon resonance (SPR[4-9]). Since SPR detection method responds to the region within the surface plasmon polariton existing in the vicinity of the surface, the sensitivity will be expected to be constant irrespective of the sample amount or the size of the capillary. We have made a SPR detection system for capillary chip electrophoresis. Figure 1 shows a block diagram of the apparatus. The system was mounted on a moving stage equipped with a microscope (Olympus, BX-40) so that we could observe and adjust the relative position for laser beam and micro channel. Monitoring of the sample flow through the micro channel by SPR needs real-time detection system. The detection system was constructed with a He-Ne laser as a light source, of which beam diameter was spread about 3-cm diameter then was focused on the center of the hemispherical prism (made of quartz). The reflective light having a dark band corresponding to SPR angle was monitored by a linear imaging sensor (Hamamatsu Photonics, S-3901-512). Imaging signal of the sensor was digitized with an A/D converter (Hamamatsu Photonics, C-4833) then the digitized data was transferred to a personal computer (NEC, PC9821Bs). Since the image of the reflective light beam was irregular shape, the reference signal shape was recorded at first without any solution, and then the change of the signal shape was obtained by dividing the signal with the reference signal. The SPR resonance angle change was calculated with quadratic fitting method. Thin film of Cr/Au (thickness: 2 nm/ 45 nm) was deposited on the glass plate with vacuum evaporation. Some preliminary experiments showed the following significant results. SPR angle change was successfully obtained using a quartz micro channel[10] of 50×500 μ m (depth × width) under the pumped flow condition. We have confirmed that the sensitivities for different depth micro channels (20 and 50 μ m)

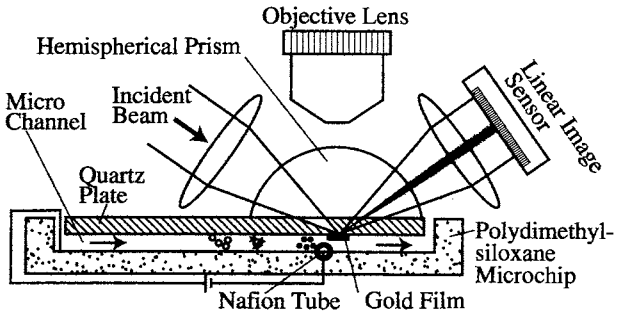

Figure1 Illustration diagram of SPR detection system for microchip CE.

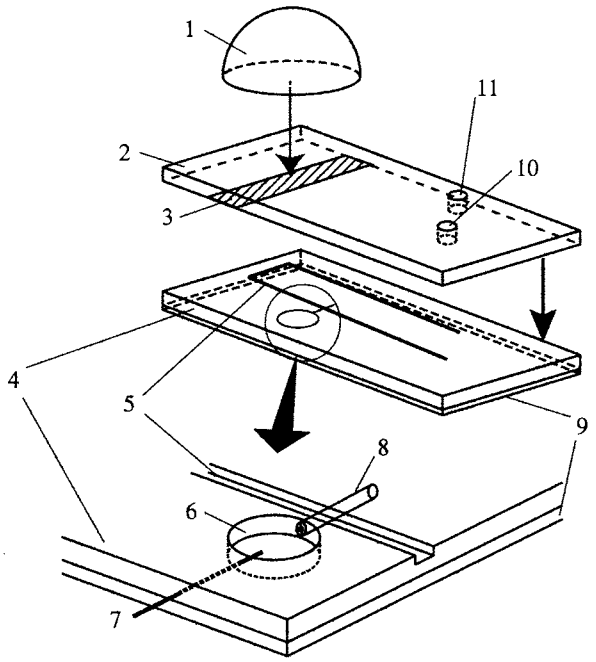

Figure 2 Schematic diagram for SPR detection system and PDMS/quartz composite microchip equiped with Nafion tube as a septum.
1: Hemispherical quartz prism, 2: Quartz plate, 3: Cr/Au (2 nm/45 nm), 4: PDMS microchannel chip, 5: Channel, 6: Reservoir, 7: Pt wire (cathode), 8: Nafion tube, 9: Silicone sheet, 10: Reservoir (anode), 11: Outlet.

were almost identical. The metal thin film for the generation of SPR was eluted out from the glass surface when high voltage was applied to the micro channel. That was due to the polarization of the metal thin film followed by the electrolysis. To overcome the phenomenon, we have devised a new design for microchip. Figure 2 shows the external view for the microchip utilizing Nafion tube as a septum. Nafion tube was placed on capillary flow pass to draw the electric current outside the flow to the cathode without generating any bubble in the capillary channel. Since the metal thin film was placed outside the electric field, sample in the capillary was extruded by electroosmotic flow to reach the metal thin film generating SPR angle change. To attain this arrangement, we used polydimethyl siloxane (PDMS) for the capillary chip material.[11] The PDMS chip was pressed to a quartz plate with thin Cr/Au film to form micro channel between PDMS chip and the quartz plate. Using the instrumental setup, we could successfully measure the SPR electropherogram for ethanol (Figure 3). Initially (time zero) the SPR resonance angle was observed and then slight change of resonance angle was observed due to the decrease of the refractive index caused by heat generation for the application of high voltage (1000 V). After the equilibrium

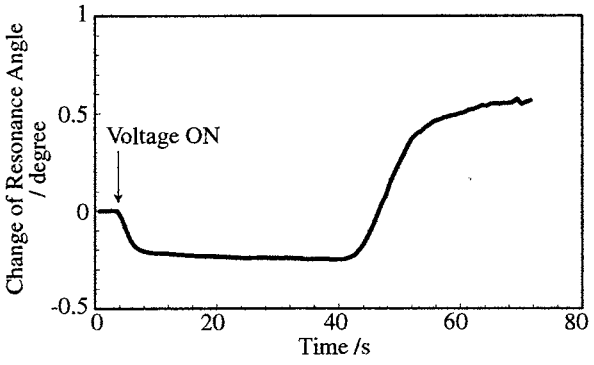

Figure 3 SPR detection of ethanol in the CE microchip under electroosmotic flow.

of the refractive index, increase in the refractive index due to the appearance of ethanol at the detection position was observed. And after 60 s, original buffer solution (50 mM Tris/ borate buffer, pH 8.5) was replaced by ethanol buffer solution showing a plateau SPR angle. The plateau peak was confirmed as follows: 1) Time lag from the application of high voltage to appearance of ethanol was identical to the previous experiment with dye solution. 2) The resonance angle change between buffer solution and ethanol solution was also identical to the batch method. From these results, it has been demonstrated that the SPR detection for capillary chip electrophoresis was possible and that the method was a universal detection method for capillary electrophoresis. Introduction of small amount of sample by crisscross flow pass and improvement of optical system are now undergoing in our laboratory.

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