MATRIX-FREE LASER DESORPTION/IONIZATION OF PEPTIDES ON VERTICALLY ALLIGNED CARBON NANOTUBE ARRAYS

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Use of matrices in laser desorption/ionization(LDI) greatly improved the ionization efficiency of various biological and synthetic polymers molecules and gave birth to matrix-assisted laser desorption/ionization(MALDI), of which contribution to the advances of science has been appreciated by Nobel Prize in 2002. Although the matrix made it possible to desorb and ionize of various biomolecules with laser, low mass analytes are not easily analysed because of the interference of the mass signals of the matrix itself. Recently several approaches have been tried to avoid using matrix in laser desorption/ionization of relatively small biomolecules. One of the most successful examples is the desorption/ionization on porous silicon(DIOS)[1] that works as the sample plate. A shortcoming of DIOS is that the performance of the newly fabricated porous silicon deteriorates with time. In search for good substrates for matrix-free LDI, we found that vertically aligned carbon nanotube arrays show a comparable performance to porous silicon and more importantly is stable in air.

The vertically aligned carbon nanotube arrays(CNTa) were fabricated on silicon wafers by either plasma-enhanced or thermal CVD method. The grown nanotubes were several tens nanometers in diameter and several hundred nanometer to a few micron in length. The analyte samples dissolved in water were dropped on vertically aligned CNTa and dried in air. The silicon wafer piece with CNTa and analytes on it was attached to a stainless steel sample plate for MALDI and mass spectra of the analytes deposited on CNTa were obtained with a commercial MALDI-TOF mass spectrometer(Applied Biosystems Voyager DE-STR) equipped with a 337 nm N_2 laser. With the vertically aligned CNTa, several small peptides with masses from 900 to 1,500Da gave excellent quality of spectra, demonstrating that vertically grown CNTa can be used as the substrate for matrix-free LDI. The LDI on the vertically aligned CNTa was successfully applied for Insulin of which mass is about 5,730Da. In addition, it showed nearly the same performance when tested in a long-time storage of a month in air after fabrication.

Since the vertically aligned CNTa can be easily fabricated in various patterns on silicon substrate by well-established semiconductor fabrication technology[2] and can be stored for a long time without any decay of performance, it may be a good substrate for matrix-free LDI. We are currently testing the performance of this substrate for other biological and synthetic molecules. At this point, the working mechanism of the vertically aligned CNTa in matrix-free LDI is not understood yet.

1. J. Wei, J. M. Buriak, and G. Siuzdak, *Nature*, 399, 243 (1999).
2. S. Fan, M. G. Chaplline, N. R. Franklin, T. W. Tombler, A. M. Cassel, and H. Dai, *Science*, 283, 512 (1999).