Visible and Near-infrared Laser Desorption Ionization Mass Spectrometry Using Single Wall Carbon Nanotubes

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We demonstrated detection of PEG 1000 on a surface of single wall carbon nanotubes (SWCNTs) for surface-assisted laser desorption ionization mass spectrometry (SALDI-MS) by irradiating laser pulses with wavelengths of 532 and 1064 nm. We succeeded in observation of molecule-related ion of a coronene with no fragmentation in visible SALDI-MS measurements.

Laser desorption ionization mass spectrometry (LDI-MS) techniques utilizing surface effects from various substrates are generally classified as surface-assisted LDI-MS (SALDI-MS). The SALDI-MS technique has attracted much attention as a soft LDI-MS technique, which can detect sample molecules with no fragmentation. Various materials such as nanoparticles,[1] graphite,[2] and porous silicon[3] have been proposed as a SALDI-MS substrate and they have huge specific surface areas on the substrate. Especially, there are many reports for desorption ionization from porous silicon substrate (DIOS). However, the DIOS technique has a serious disadvantage in that porous silicon is easily oxidized reducing remarkably its surface activity.

Porous silicon substrate has efficient absorbance in the UV region. Generally, most LDI-MS techniques i.e. DIOS usually employ a UV laser (typically N_2 laser) for desorption ionization of analyte molecules. In the case of UV laser irradiation, soft ionization of analyte molecules, which has strong absorbance in UV region, is interfered with fragmentation caused from their photolysis. In order to avoid this problem, it is necessary to eliminate overlap between the absorption wavelength region of analyte molecules and wavelength of irradiating laser. Thus, more effective SALDI-MS material would require the following three properties; sufficient roughness, chemical stability of the surface, and wide absorption wavelength range.

Single wall carbon nanotubes (SWCNTs)[4] are very stable chemically and form bundles due to aggregation. This nano-sized bundle structure can provide sufficient roughness. Although several reports have shown that CNTs generate SALDI effects by irradiation with a 337 nm N_2 laser,[5] there have been no attempts to apply them to visible or near-infrared (IR) SALDI-MS. Previously, visible SALDI using graphite substrate with a black body have been reported.[2] SWCNTs are also black and can efficiently absorb laser energy in a wide wavelength region from UV to near-IR, thus SWCNTs would have sufficient possibility to be effective SALDI material at the laser wavelength regions shown above. That is, SALDI-MS measurements with SWCNTs would be capable of selecting a laser wavelength which does not overlap with the absorbance wavelength of analyte molecules. In this study, we report that a surface of SWCNTs is effective for visible or near-IR SALDI-MS. The SALDI-MS technique employing SWCNTs is performed as a soft ionization technique for analyte molecules which are difficult to ionize softly by irradiating with UV laser.

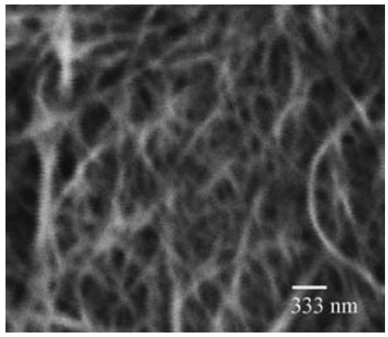

Figure 1. SEM image of the surface of SWCNTs–substrate.

The SWCNTs were suspended in ethanol and sonicated until they were well dispersed and then the suspension was deposited on a SUS plate (SWCNTs substrate). A surface of SWCNTs substrate was observed by scanning electronic microscopy (SEM, Keyence, VE-9800), as shown in Figure 1. The SEM image shows a nano-sized network structure formed by SWCNTs bundles of several tens of nanometers in diameter. Since this nano-sized roughness, like other SALDI substrate surface, has a huge specific surface area, the SWCNTs substrate shows good performance as a SALDI-MS substrate.

For mass spectrometric measurements, we used a laboratory-built linear time-of-flight mass spectrometer (TOF-MS) equipped with a Nd:YAG laser (fundamental wavelength of 1064 nm, second harmonic wavelength of 532 nm, and forth harmonic wavelength of 266 nm). The acceleration voltage for ions was 4 kV and mass spectra were obtained in the positive ion mode. The mass spectra were acquired by accumulating 128 single-shot mass spectra. PEG 1000 samples (1.0 mg) were dissolved in 1.0 mL of methanol. Coronene was prepared at a concentration of 1.0 mM in toluene. Each sample solution (0.50 µL) was deposited on the SWCNTs substrate and dried in air.

Visible (532 nm) and near-IR (1064 nm) SALDI mass spectra of PEG 1000 are shown in Figures 2a and 2b respectively. Both spectra of PEG 1000 were obtained with sufficient sensitivity and the series of ion peaks separated by 44 unit were observed. These ion peaks could be attributed to the sodium adduct ions $[M + Na]^+$. A series of ion peaks in both spectra showed clear mass distribution which was similar to standard distribution obtained by conventional matrix-assisted LDI-MS (MALDI). MALDI-MS is a powerful tool for structural characterization of synthetic polymers[6] and biomolecules.[7] However, the selection of suitable matrix is imperative, and the typical matrix which has efficient absorbance at a wavelength of laser irradiation (typically for a 337 nm N_2 laser) is not available for visible or near-IR lasers. Thus, typical MALDI-MS measurements do not befit soft ionization of analyte molecules having strong absorbance in the UV region because of fragmentation caused

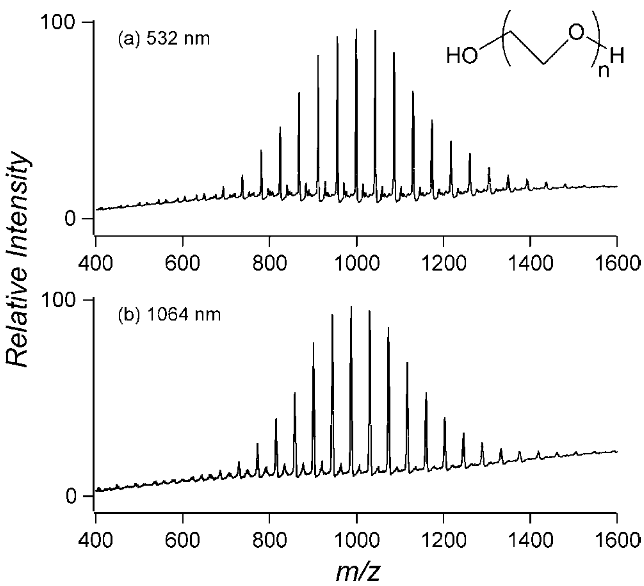

Figure 2. Mass spectra of PEG 1000 acquired using (a) 532 nm visible laser, (b) 1064 nm near-IR laser, with the chemical structure. Both mass spectra were acquired by accumulating 128 single-shot mass spectra.

by their photolysis. In contrast, our SALDI-MS technique enabled simple acquisition of mass spectrum of PEG 1000 by laser irradiation with either wavelength of 532 and 1064 nm though PEG samples did not have strong absorbance in each wavelength. This result suggests that the surface of SWCNTs would assist the desorption ionization of PEG 1000 at these wavelengths. In addition, we attempted detection of analyte molecules which have strong absorbance in UV regions by SALDI-MS measurements.

Figure 3a shows a LDI mass spectrum of coronene by irradiating laser at 266 nm. Coronene is an aromatic compound having strong absorbance in the UV region. Two peaks were observed in the LDI mass spectrum, and the major peak corresponds to molecule-related ion $[M]^+$ of coronene at m/z 300. An observed fragment ion, observed at m/z 276, would be a C2 loss ion ($[M - C2]^+$) derived from photolysis of coronene caused by its strong absorbance in the UV region. In contrast, visible-SALDI mass spectrum of coronene is shown in Figure 3b. Molecule-related ion peak of coronene was observed with no fragmentation. The molecule-related ion of coronene could not be detected in visible LDI-MS measurement. This observation indicates that the amount of ion caused by single- or multiphoton absorption processes was below detection limits and therefore contribution of single- or multiphoton absorption can be excluded under this experimental conditions. These results suggest that the surface of SWCNTs substrate assists the soft laser desorption ionization of coronene by irradiating visible laser. For comparison, in the case of UV SALDI-MS measurement of coronene, not only molecule-related ions but also fragment ions were observed. Consequently, SWCNTs substrate is applicable for the detection of analyte molecules with the strong absorption of UV light by both avoiding UV light and employing visible or near-IR light.

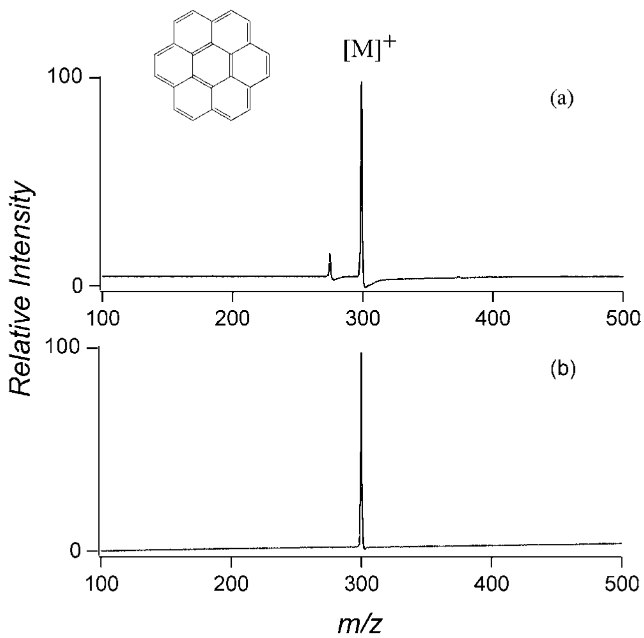

Figure 3. Mass spectra of coronene (a) in LDI-MS at 266 nm, (b) SALDI-MS at 532 nm, with the chemical structure. Both spectra were acquired by accumulating 128 single-shot mass spectra.

In the future, we expect that SALDI-MS employing SWCNTs would enable soft desorption ionization of various kinds of analyte species by eliminating overlap between their absorption wavelength region and wavelength of irradiating laser.

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