Extractions of $Ca@C_{60}$ and $Sr@C_{60}$ with Aniline

Yoshihiro Kubozono,* Takako Noto, Takayoshi Ohta, Hironobu Maeda, Setsuo Kashino,
Shuichi Emura,† Shigeyuki Ukita,†† and Toshiaki Sogabe††
Faculty of Science, Okayama University, Okayama 700
†*ISIR, Osaka University, Osaka 567*
††*Research and Development Center, Toyo Tanso Corporation, Ohnohara 769-16*

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Endohedral metallofullerenes, $Ca@C_{60}$ and $Sr@C_{60}$, prepared by the arc-heating of the graphite rods containing CaO and SrO, respectively, have been extracted with aniline under the air atmosphere. The laser desorption time-of-flight (LD-TOF) mass spectra for the extracted solutions exhibit intense peaks due to $M@C_{60}^+$ (M: Ca and Sr) and C_{60}^+ with weak peaks due to the other hallow fullerenes and metallofullerenes.

Since the extraction of $La@C_{82}$ by Chai et al. in 1991,[1] the endohedral metallofullerenes have been extensively studied by many investigators.[2,3] However, most of studies on the endohedral metallofullerenes have been focussed on $M@C_{74}$, $M@C_{80}$ and $M@C_{82}$ (M: metal atoms)[2,3] except for a few studies on $M@C_{60}$.[4-8] The slow progress in studies of $M@C_{60}$ can be attributed to the difficulty of extraction. Although the preparations of $La@C_{60}$,[1] $Y@C_{60}$,[4] $U@C_{60}$,[5] $Ca@C_{60}$,[6,7] $Gd@C_{60}$,[8] $Eu@C_{60}$,[8] $Sm@C_{60}$,[8] $Yb@C_{60}$,[8] $Sr@C_{60}$,[8,9] and $Lu@C_{60}$[8] have been reported, only $Ca@C_{60}$ has successfully been extracted among these.[6,7] Recently, we reported the extraction of $Ca@C_{60}$ with pyridine.[7] However, the extraction was performed under the oxygen-free condition. In the present letter, we report the extraction of $Ca@C_{60}$ and $Sr@C_{60}$ with aniline under the air atmosphere.

The soots containing $Ca@C_{60}$ and $Sr@C_{60}$ were prepared by the arc-heating of the CaO/graphite and SrO/graphite rods, respectively, (Toyo Tanso; CaO and SrO concentrations: 0.3 mol %) at 25 V and 80 A under 100-200 Torr (1 Torr = 133.322 Pa) He atmosphere. The extractions of $Ca@C_{60}$ and $Sr@C_{60}$ were tried for four extraction-solvents of aniline, benzene, toluene (Wako Pure Chemicals; GR) and CS_2 (Ishidzu Seiyaku; GR) under the air atmosphere; the soots were dissolved in the solvents with a supersonic washing machine for 3 h at low temperatures from 0 to 5 °C, and the solutions were passed through 0.1 μm membrane filter (Toso: H-13-5). Mass spectra were measured by a laser desorption time-of-flight (LD-TOF) mass spectrometer (Finnigan: Vision 2000); laser desorption and ionization were done at 337 nm.

The LD-TOF mass spectrum for the soot obtained by the arc-heating of CaO/graphite rod is the same as that reported previously.[7] Figure 1(a) shows the LD-TOF mass spectrum for the soot obtained by the arc-heating of SrO/graphite rod. The peaks in the mass spectrum can be assigned to C_{60}^+, $Sr@C_{60}^+$, C_{70}^+, C_{74}^+, $Sr@C_{70}^+$ and $Sr@C_{74}^+$. In the LD-TOF mass spectrum, the peak due to $Sr@C_{60}^+$ is the most intense in comparison with the other peaks. Consequently, $Sr@C_{60}$ has been prepared effectively by the arc-heating of the SrO/graphite rod.

Figure 1(b) shows the LD-TOF mass spectrum for the solution extracted from the soot containing Ca-endohedral fullerenes with aniline. The main five peaks due to C_{60}^+, $Ca@C_{60}^+$, C_{70}^+, C_{74}^+ and C_{78}^+ have been observed. The

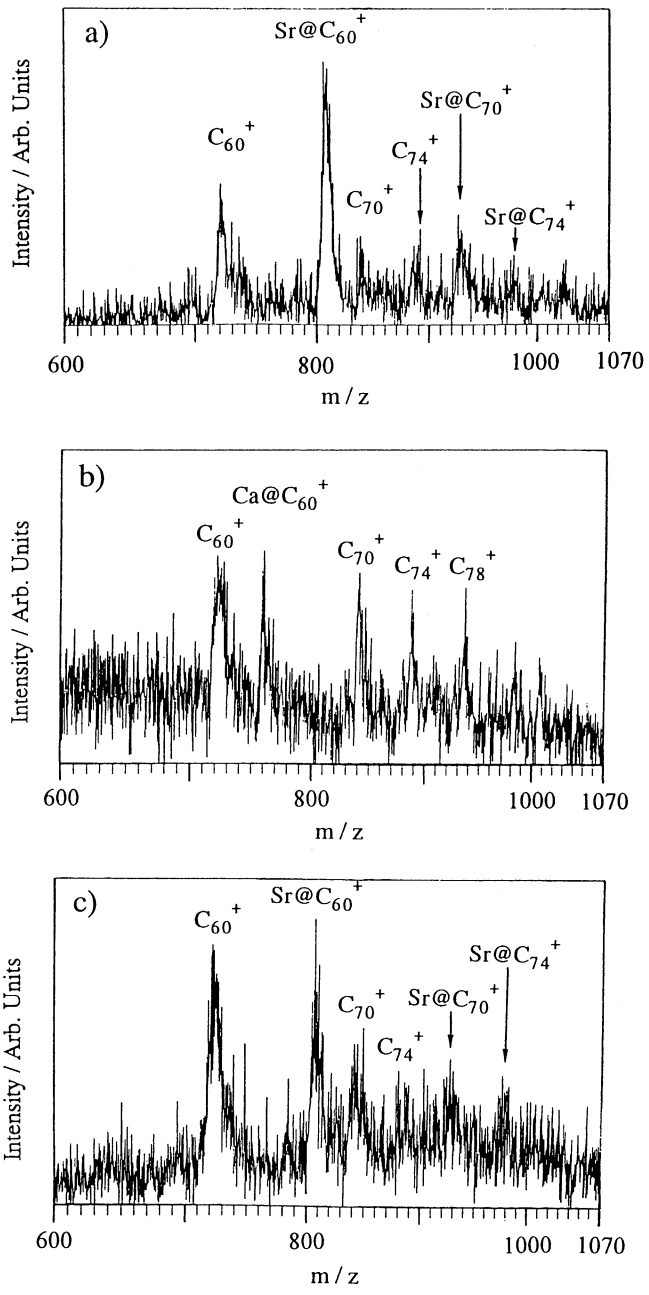

Figure 1. LD-TOF mass spectra for (a) the soot obtained by the arc-heating of SrO/graphite rod, (b) the aniline-extracted solution from the soot containing Ca-endohedral fullerenes, and (c) the aniline-extracted solution from the soot containing Sr-endohedral fullerenes.

spectrum is similar to that for the solution extracted with pyridine.[7] No peaks due to Ca-endohedral metallofullerenes have been observed in the LD-TOF mass spectra for the solutions extracted with the other solvents.

Figure 1(c) shows the LD-TOF mass spectrum for the solution extracted from the soot containing Sr-endohedral fullerenes with aniline. Two intense peaks due to C_{60}^+ and $Sr@C_{60}^+$, and four weak peaks due to C_{70}^+, C_{74}^+, $Sr@C_{70}^+$ and $Sr@C_{74}^+$ have been observed in this spectrum. The relative intensity of the peaks due to C_{60}^+ to that due to $Sr@C_{60}^+$ increases in the LD-TOF mass spectrum for the extracted solution in comparison with that for the soot. The results indicate that the solubility of C_{60} is very high also in aniline. However, the peak due to $Sr@C_{60}^+$ has still been observed with the same intensity as that due to C_{60}^+. No peaks due to Sr-endohedral metallofullerenes have been observed in the LD-TOF mass spectra for the solutions extracted with the other solvents as in the case of $Ca@C_{60}$. Consequently, we have concluded that aniline is an effective extraction-solvent for $Ca@C_{60}$ and $Sr@C_{60}$. The present results will make a contribution to confirm the structure of $M@C_{60}$, including whether the metal atoms are incorporated into the cages.

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