Metal-Carbon Binary Clusters as Precursors of Endohedral Metallofullerene and SWNTs

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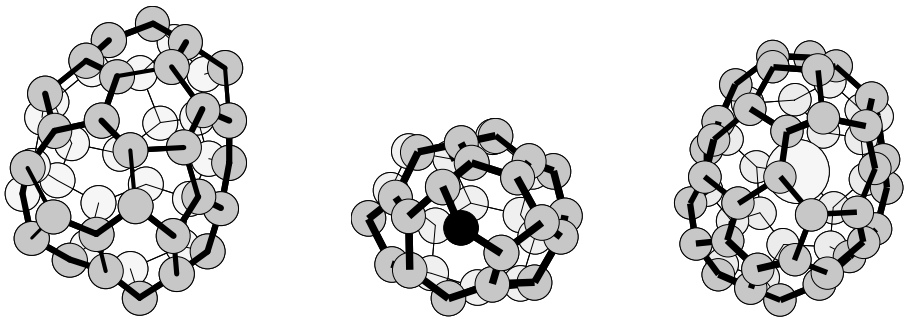
Understanding the formation mechanism of SWNTs and endohedral metallofullerene is very interesting and also very important for the large-scale generation and controlled generation of various possible structures, such as different cage size and different metal species for metallofullerene and various radii and chiralities of SWNTs. Both endohedral metallofullerene and SWNTs are usually generated with arc-discharge method or laser-oven method from carbon material loaded with a few atomic percents of metals. Furthermore, the preferred conditions such as buffer gas pressure and oven temperature are almost common. Then, the different combinations of loaded metal atoms determine the pathway to endohedral metallofullerene or SWNTs. In order to clarify the roles of metal atoms in the formation processes, we have focused on the initial vaporization stage and clustering stage of the samples. The experimental studies with FT-ICR mass spectrometer with laser-vaporization cluster source [1] are compared with molecular dynamics studies of the direct simulation of formation process [2].

Positive and negative metal-carbon binary clusters generated by the laser-vaporization supersonic-expansion cluster beam source were directly injected to the FT-ICR mass spectrometer. Depending on the metal species, the generated cluster distributions were drastically different. The chemical reaction of these clusters with NO was used as the probe of the structure of clusters. LaC_{2n}^-, ScC_{2n}^- and YC_{2n}^- from La-doped, Sc-doped and Ni/Y-doped carbon samples, respectively, were much less reactive to NO compared with pure carbon clusters. On the other hand, NiC_n^- from Ni/Co-doped and Ni/Y-doped materials was much more reactive than pure carbon clusters. Through comparisons with the molecular dynamics simulations, it was speculated that La, Sc and Y were inside the annealed "random-cage" carbon structure shown in Fig. 1 even at small size as $M@C_{44}$. Through experiments of Ni/Co and Ni/Y doped samples for SWNT generation, carbon clusters with Y atom inside the random cage and only a small amount of carbon clusters with a Ni atom were observed. However, a drastic enhancement of even-odd alternations in pure carbon distribution was observed. The efficient generation of "random cage" structures starting from C_{36} might be the important step in the generation mechanism of SWNT.

References

[1] S. Maruyama et al., Fullerene Sci. Tech., 1999, vol. 7, no. 4, pp. 621-639.
[2] Y. Yamaguchi and S. Maruyama, Eur. Phys. J. D, 1999, vol. 9, no. 1-4, pp. 385-388.



(a) C_{48} (b) C_{33} (c) $La@C_{54}$

Fig. 1 Typical random-caged structures picked up from the molecular dynamics simulations. (a) C_{48} without dangling bonds. (b) C_{33} with one dangling bond (in black atom). (c) Even-numbered carbon cluster with La atom inside: $La@C_{54}$.