A molecular dynamics study on the formation of
metallofullerene
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The growth process of metal-containing fullerenes is studied by using the molecular dynamics method similar to our simulations of prefect C_{60} and C_{70} formation [1,2]. In order to model the metal-carbon potential function appropriate for the MD simulation, the binding energy and charge state of various forms of small clusters MC_n (M: La, Sc, Ni) were calculated with the density functional theory based on the Becke's three-parameter exchange functional with the Lee-Yang-Parr correlation (B3LYP). A multi-body potential function was constructed as a function of coordinate number of a metal atom, where the Coulomb and the Morse terms were separately described considering the charge transfer from a metal atom to carbon atoms. The differences of the La-C, Sc-C and Ni-C interactions are qualitatively expressed as strongly ionic, weakly ionic and non-ionic, respectively.

The clustering processes starting from randomly distributed 500 carbon and 5 metal atoms in a 342Å cubic cell were simulated under the controlled temperature condition, where the translational, rotational and vibrational temperatures of clusters were kept nearly equilibrium at T_c=3000K. Fig. 1 and 2 show the growth processes of typical metal attached carbon clusters, where the vertical position and horizontal length denote the size and the existing time of clusters, respectively.

When La atoms were applied as the additional metal, short carbon chains surrounded the La atom for the cluster smaller than LaC_5, and the La atom attached on the monocyclic carbon ring for LaC_{6-15} as shown in Fig. 1. The host monocyclic ring changed to a poly-cyclic ring and the La atom attached on it around LaC_{17}, where the Coulomb attractive force induced curvature to the host poly-cyclic ring. The host annealed to a curved graphite-like sheet when it grew as large as LaC_{19}, and extended the structure until about LaC_{35}, resulted in the formation of a stable open-cap structure, and kept growing with closing the open-cap structure.

Another clustering process using Sc atoms was simulated under the same condition. The structures of the host carbon clusters were not affected a lot compared to those in La-C system because of the weaker Coulomb force. The cluster annealed to the 3-dimensional open cage structure around ScC_{40}, where the Sc atom moved around open edge, and finally, the Sc atom slipped into the caged structure just before closing at around $Sc@C_{54}$ and stably encapsulated inside the cage.

Nickel atoms, which is not experimentally assigned to be encapsulated in the fullerene cage so far, were also applied as shown in Fig. 2. The growth process is very similar to that for Sc attached cluster. Although, even at the final stage, the Ni atom preferred to attach at the large defect of the caged structure such as large rings of more than 7 or 8 membered, and frequently moved in and out of the carbon cage.

1. Y. Yamaguchi and S. Maruyama, *Chem. Phys. Lett.*, **286**, 336 (1998)
2. S. Maruyama and Y. Yamaguchi, *Chem. Phys. Lett.*, **286**, 343 (1998).
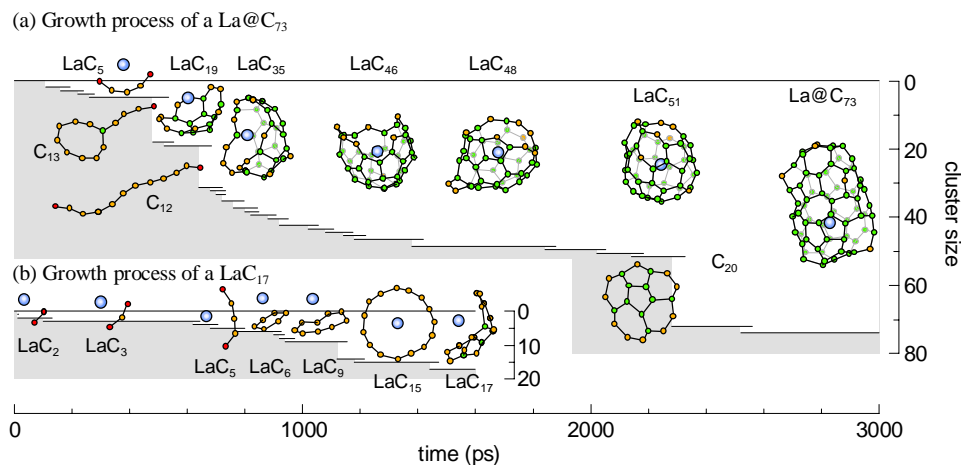
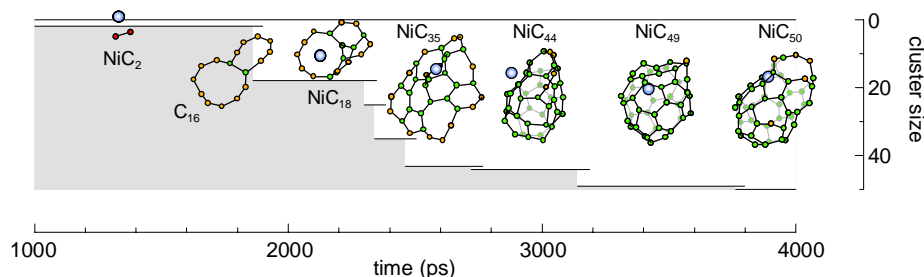Fig. 1. Growth process of La attached clusters: (a) La@C_{73} and (b) La@C_{17}.

Fig. 2. Growth process of a Ni attached cluster NiC$_{50}$.