

Nanowire formation by means of coalescence of small gold clusters encapsulated inside carbon nanotubes

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We report the atomistic molecular dynamics study of the stable configurations of small icosahedral Au clusters (Au₁₃, Au₅₅, and Au₁₄₇) encapsulated inside single wall carbon nanotubes (CNTs). The interactions between carbon atoms and between Au atoms were described by the many-body Brenner potential and the Finnis-Sinclair potential, respectively. A Lennard-Jones (L-J) potential was used to describe the C-Au interaction.

In the first step, the stability of single clusters in CNTs was examined and the binding energies of Au₁₃ and Au₅₅ clusters to CNTs with different radii were estimated. The results are given in Table I.

Table I: Binding energies (in eV) of Au₁₃ and Au₅₅ clusters in CNTs with different radii

Tube	(7,7)	(8,8)	(9,9)	(12,12)	(13,13)	(15,15)
Au ₁₃	Unstable	3.35	3.28	3.25	3.22	3.18
Au ₅₅	-----	-----	-----	7.35	7.30	7.27

All binding energies shown are positive. In this case, the filling of SWNTs with clusters is an exothermic process. Moreover we found that the largest binding energies appear in the cases of (8,8) CNTs for Au₁₃ and (12,12) CNTs for Au₅₅. In these cases, as well as for Au₁₄₇ cluster in (15,15) CNTs, the distances between tubes and cluster surfaces are close to the equilibrium distance of the L-J potential, 0.3nm.

In the second step, the coalescence of two clusters in CNTs was studied. Two Au₁₃ clusters in a (8,8) CNTs coalesce spontaneously and form a nanowire segment at room temperature. The initial 5-fold icosahedral symmetry turns into a 7-fold symmetrical wire as shown in fig. 1.

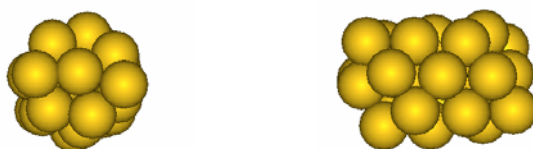


Fig.1. Snapshot of a 7-fold nanowire segment resulting from the coalescence of two Au₁₃ clusters. Views parallel and perpendicular to the axis of the (8,8) CNTs are displayed. The CNTs is not shown.

Two Au₅₅ clusters in a (12,12) CNTs were also found to coalesce spontaneously at room temperature. In contrast with the case of Au₁₃ coalescence, the nanowire segment has two 5-fold symmetric caps. However after raising the temperature up to more than 600K the caps disappear and the symmetry changes to 6-fold (fig. 2).

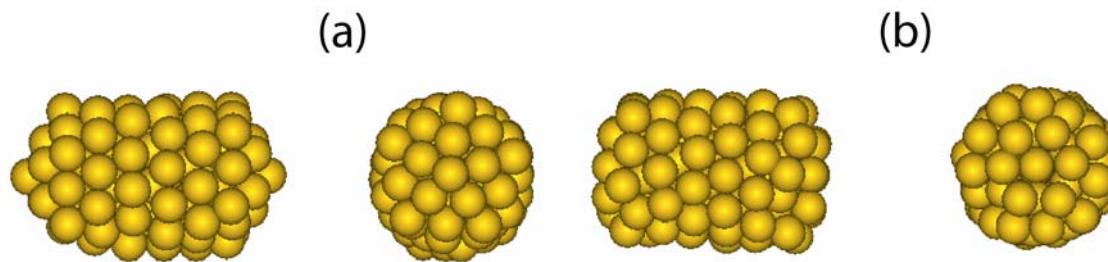


Fig.2: Snapshots of a nanowire segment resulting from the coalescence between two Au_{55} clusters in a (12,12) CNTs. a) 5-fold segment at room temperature; b) 6-fold segment after heating at 600K.

This structure was found better stable than 5-fold by a quenched annealing method. Like the smaller clusters, two Au_{147} clusters were also found to coalesce spontaneously at 300K. Similarly to Au_{55} , they also formed a nanowire segment with two icosahedral caps. After heating and cooling down the system, the caps disappeared also, but the wire segment turned fcc.

These results illustrate that, similarly to filling, coalescence is also exothermic.

In order to identify the main factors governing structural evolution, we analyzed the change in potential energies. It was found that the energy changes are mainly taken over by Au-Au interactions. On the other hand, the disappearing of caps minimizes the surface to volume ratio of the wires, which are not constrained to 5-fold symmetry anymore. This allows the fcc character to appear in the Au_{147} case. The effect of CNTs with appropriate radii is to make coalescence a one dimensional process. The Au system evolves to its minimal energy configuration with this constraint. Indeed, in large tubes, coalescence was found to become three dimensional and a competition between the formation of wires and the deformation of tubes occurs. Finally we encapsulated Au_{13} and Au_{55} clusters one by one into CNTs with different radii. This allowed to show that inserting a set of Au_{55} clusters induces a deformation of the larger than (12,12) CNTs. When inserting Au_{13} clusters in larger than (8,8) tubes, then latter are no deformed but the clusters form a nanowire which matches the confined inner space of CNTs. In this case, a nanowire with the same 6-fold structure as with Au_{55} clusters is formed at room temperature without the use of an annealing treatment. These results suggest that a viable way to fabricate nanowires with controlled diameters and structure is to encapsulate small metal clusters inside the appropriate CNTs.