The stability of silicon cage nanostructures

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Abstract— The aim of this study is to compare the stability of silicon cage nanostructures to carbon fullerenes by means of *ab initio* molecular dynamics simulations, thus determine viable geometries for silicon cage nanostructures. In this work, the stabilities of the $Ti@Si_{16}$ Frank-Kasper polyhedron that is experimentally observed, and a hydrogenated silicone fullerene $Si_{20}H_{20}$, which is suggested to be the most stable Si cage of 20 Si atoms, are compared to the least stable carbon fullerene of C_{20}. We first determined the optimum geometries of these cages, and later performed molecular dynamics simulations for the collision of these cages in order to determine the likelihood of their survival under the excitations that should exist in the synthesis conditions of these nanostructures. We find that $Si_{20}H_{20}$ and $Ti@Si_{16}$ cages are much more prone to structural deformations than C_{20} fullerene under thermal excitations, which explains the experimental difficulty of the synthesis of Si cages against the ease of the synthesis of carbon fullerene cages.

The novel properties and technological applications of carbon fullerenes motivate the researchers to find similar structures of silicon. Although there are many theoretical studies claiming that fullerene geometry is possible for silicon, there is no experimental evidence up to date. On the other hand, it is experimentally shown that the nano-clusters of silicon have the structure of a Frank-Kasper polyhedron[1].

In order to understand the difficulty of experimentally obtaining the Si counterparts of the carbon fullerenes, we not only calculated the cohesive energies of the optimized atomic structures, but also performed *ab initio* molecular dynamics simulations. We note the importance of dynamical effects in assessing the stability of these nanostructures. The atomic structures of a C_{20} fullerene, and $Si_{20}H_{20}$ hydrogenated fullerene, which is suggested to the most stable Si fullerene, and $Ti@Si_{16}$ Frank-Kasper polyhedron, which is experimentally observed, are shown in Fig. 1.

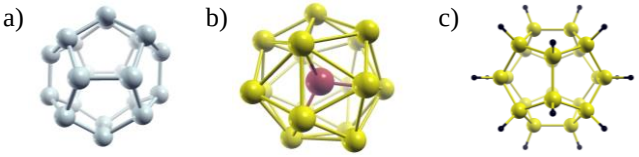

Fig. 1: The ball-and-stick models for the cage structures used in this study. a) The least stable carbon fullerene: C_{20}. b) Experimentally observed Si16Ti Frank-Kasper Polyhedron. (c) $Si_{20}H_{20}$ hydrogenated fullerene.

For a cluster to be stable and isolated, the bonding between other clusters in the environment should be weak. In the synthesis processes the clusters should interact and collide with each other under the thermal excitations. Therefore, we consider a cluster can only be regarded as stable only if it survives the collisions with the other clusters in the environment. We consider head-on collisions of the cage structures in our *ab initio* molecular dynamic calculations using the SIESTA code.[2]

We monitor the potential energy of the system of the two cages that have equal speeds with velocities in the opposite directions at the beginning of our simulations. The cages then experience a head-on collision in our simulations. We monitor both the atomic structure and the potential energy of the system, which is shown in Fig. 2. The potential energy zero is taken as the total potential energy of the 2 clusters that do not interact initially. We repeat our simulations for various initial speed values to determine the threshold for the destruction of the cage structure. Below the threshold speed values, the cages bounces back without any structural damage,

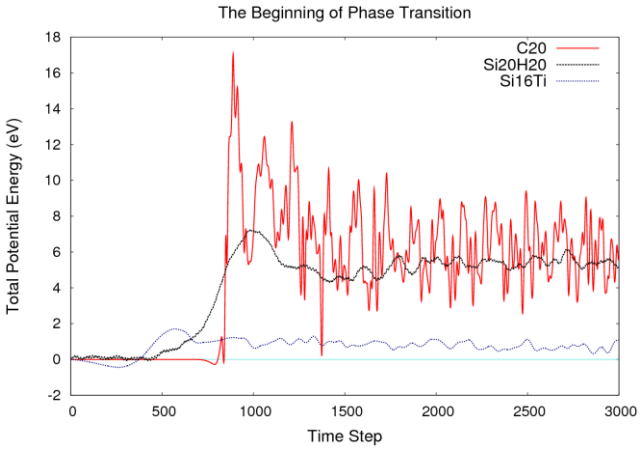

Fig. 2: The potential energy profile during the collisions of 2 identical cages.

and a following cooling of the bounced-back cages recover the initial shape the structure. We find the threshold energies of ~21 eV for C_{20}, ~12 eV for $Si_{20}H_{20}$, and ~2.5 eV for $Ti@Si_{16}$.

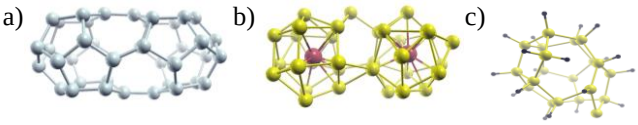

Fig. 3: The final structures after the elastic collisions of identical cages. a) Two C_{20} cages merge into a C40 cage. b) Two $Ti@Si_{16}$ cages stuck to each other. c) $Si_{20}H_{20}$ fullerene cages open up.

Since the lifetimes of these clusters are exponentially proportional to these threshold energies, even the least stable carbon fullerene C_{20}, is several times more stable than the theoretically proposed most stable silicon fullerene. The final structures of inelastic collisions are depicted in Fig. 3. Our results in Fig. 3 indicate that the carbon fullerenes change into a new cage while the silicon structures result in either blown-up structures or severely distorted cages.

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