Commun. Comput. Phys.
doi: 10.4208/cicp.101209.260110a

Vol. **8**, No. 2, pp. 289-303
August 2010

Theoretical Study on Structural Stability of Alloy Cages: A Case of Silicon-Doped Heterofullerenes

Xiaofeng Fan[1,*], Zexuan Zhu[1], Lei Liu[1], Zexiang Shen[1] and Jer-Lai Kuo[1,2]

[1] *School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore.*

[2] *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, 10617, Taiwan.*

Received 10 December 2009; Accepted (in revised version) 26 January 2010

Communicated by Michel A. Van Hove

Available online 12 March 2010

Abstract. Structural stability and Si-substitution pattern in fullerene cage of $C_{60-n}Si_n$ are thoroughly investigated by integrating density functional calculations with a color-bond graph (CBG) model. We find that the parameterized CBG model with genetic algorithms can efficiently scan the large configuration space of alloy and therefore identify the low-energy region within the first-principles accuracy. Low-energy (stable) structures of $C_{60-n}Si_n$ in carbon-rich region ($1 \leq n \leq 30$) were identified and the silicon atoms are found to tend to aggregate in the fullerene cage. The mixing energy of these low-energy structures is $\sim$ 35 meV/atom and insensitive to the Si concentration. We expect that these alloy fullerene cages can be synthesized experimentally at elevated temperatures.

PACS: 71.15.Mb, 82.33.Fg, 71.15.Nc, 36.40.Qv, 73.61.Wp, 61.46.Bc

Key words: Structure of alloy cluster, density functional calculations, fullerene Alloys $C_{60-n}Si_n$ Heterofullerenes, genetic algorithms.

1 Introduction

Nano-sized clusters have gained considerable attention for their peculiar geometry-induced optical, electronic, magnetic and catalytic properties [1–4]. As a special case of

---

[*] Corresponding author. *Email addresses:* `xffan@ntu.edu.sg` (X. Fan), `zhuzexuan@pmail.ntu.edu.sg` (Z. Zhu), `LiuLei@ntu.edu.sg` (L. Liu), `zexiang@ntu.edu.sg` (Z. Shen), `jlkuo@pub.iams.sinica.edu.tw` (J.-L. Kuo)

©2010 Global-Science Press

nanoclusters, cage-like carbon fullerenes have rapidly become an active area of research [5–10], since the discovery of fullerene C_{60} [11–13]. Due to the stable sp^2-hybridized carbon bonds, these cage-like molecules have been considered as a building block for new nano-structured materials with novel properties [9,12,14,15]. The exohedral and endohedral doping of metal atoms on C_{60} have led to the well known superconductivity of fullerides [16,17].

The substitutional doping is also expected to enable tailoring and functionalizing of the fullerene molecules [18–24]. Recently, doping carbon cages with silicon has been actively explored [21,25–28]. Although having the same number of valence electron as carbon, silicon is known to prefer sp^3-hybridization. If silicon atoms can be substitutionally doped in the carbon cages, the reactivity of Si sites will offer a new path toward the polymerization of fullerenes [21]. So far, the successful synthesis of $C_{60-n}Si_n$ ($n=1,3$) has been reported [21,25,29,30]. While from photofragmentation experiments [31] it is speculated that up to 12 silicon atoms can be substituted in a fullerene without destroying its structure, clear experimental evidence for $C_{2N-n}Si_n$ ($n>3$) still has not been obtained [28]. Thus, the systematic theoretical study on this multi-component system will be helpful and timely to illuminate its fundamental properties, such as the stability, morphology, electronic behavior, and basic features of chemical bonding.

To study alloy clusters, the first challenge is finding their ground state and low-energy structures. For the binary alloy clusters (A_nB_m), the number of combinatorial possibilities (2^{n+m}) due to different arrangement of A- and B- type atoms increases exponentially with the size of alloy clusters [2]. This makes it almost impossible to find the lowest energy structures of alloy cluster with high-level quantum calculation. For $C_{60-n}Si_n$ cages, searching systematically the ground states in rich carbon region is still a formidable task, even though the geometric structures are assumed established. By intuitively and empirically choosing the configurations, the structural and electronic properties of some "low-energy" states with different number of substitutional atoms (silicon) have been studied in a series of density function theory calculations [27,32–37]. However, without an effective searching method it makes the theoretical studies blindfold to some extent and less comprehensive on the binding characteristics between silicon and carbon atoms on the cage structures.

In this work, we intend to fill up the gaps in the existing theoretical framework for exploring the stability of cage-like alloy structures. Using the alloy fullerene $C_{60-n}Si_n$ as a paradigm, the complexity of the question is illustrated. A parameterized model about total energy based on first-principles calculations is established with a few randomly chosen structures. Then the initial model is used to guide a systematic search powered by genetic algorithms (GA). The low-energy structures are identified to improve the accuracy of the model. This procedure is reiterated to assure the validity of our predictions. Lastly, the selected low-energy states of $C_{60-n}Si_n$ were examined in details to understand their structural stability and electronic properties.