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Structure and magnetic properties of cobalt doped Si_n ($n = 2$–14) clusters

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Abstract

The structure and magnetic properties of cobalt doped Si_n ($n = 2$–14) clusters have been systematically studied using density functional theory (DFT). For each cluster size, extensive search of the lowest-energy structure has been conducted by considering a number of structural isomers. The equilibrium site of the Co atom in the ground-state structures of Si_nCo clusters gradually moves from convex, surface, to interior sites as the number of Si atom increases from 2 to 14. Starting from $Si_{10}Co$, Co atom is fully encapsulated by the Si outer cages. The magnetic moment of Co atom in Si_nCo clusters is completely quenched at $n = 7$, due to charge transfer and strong hybridization between 4s and 3d states of Co and 3s and 3p states of Si.

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Keywords: Magnetic property; The lowest-energy structure; Cobalt; Si_n cluster

1. Introduction

The fabrication of cluster-assembled bulk materials and nanostructures demands suitable building blocks that are chemically stable and weakly interact with each other. Silicon clusters are expected to become such a kind of building blocks in light of the extreme importance of silicon-based materials in the semiconducting industry. Unlike hollow cages of carbon fullerene, Si cages are unstable because the fact that sp^2 hybridization is highly unfavorable in silicon. A possible approach to stabilize the Si cage is to introduce a guest atom inside the cage as suggested by recent experimental [1–4] and theoretical works [5–24]. These studies revealed that the encapsulation of a transition metal (TM) atom inside silicon cluster leads to stable Si cages. Hence, the metal-doped silicon clusters can serve as the building blocks for cluster-assembled materials.

In previous experiments, Beck [1] generated TM@Si_n (TM = Cr, Mo and W) clusters using laser vaporization supersonic expansion technique. They found that the doped clusters are more stable towards photofragmentation than the bare Si clusters of the same size. Hiura et al. [2] provided theoretical support for the experimental findings by performing ab initio calculations of a WSi_{12} cluster. Using mass spectrometry, chemical-probe method, and photoelectron spectroscopy, Ohara et al. [3] studied geometric and electronic structures of TM embedded Si clusters (TM = Ti, Hf, Mo, and W). It was revealed that MSi_n is considerably stabilized by the geometry of the encapsulated M@Si_n at $n = 15$–16. Recently, Koyasu and co-workers [4] studied the electronic and geometrical structures of mixed-metal silicon $TMSi_{16}$ (TM = Sc, Ti, and V) clusters using mass spectrometry and photoelectron spectroscopy anionic clusters. They found that neutral $TiSi_{16}$ cluster possesses closed-shell electron configuration with a large gap between highest occupied molecu-

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lar orbital (HOMO) and lowest unoccupied molecule orbital (LUMO).

To further understand the structural and electronic properties of TM-encapsulated Si cage clusters, plenty of first-principles theoretical calculations [5–24] have been done. After studying a number of metal encapsulated Si cage clusters [5], Kumar et al. reported three new classes of metal-encapsulated $M@Si_n$ clusters with high stability and large HOMO-LUMO gap. They found that the size of the outer silicon cage strongly depends on the radius of the interior metal atom. Khanna et al. [12, 13] found that $Si_{12}Cr$ and $Si_{10}Fe$ are more stable than their neighbors. Both $Si_{12}Cr$ and $Si_{10}Fe$ can be explained by the 18-electron rule, that is, each silicon atom denotes one valence electron to the central Cr or Fe atom. Lu and Nagase [14] computed metal-doped silicon clusters $TMSi_n$ (TM = W, Zr, Os, Pt, Co, etc.) and revealed that the formation of endohedral structure strongly depends on the size of the Si_n cluster. Based on the results from first-principles calculations, Froudakis and co-workers interpreted the structure of metal encapsulated Si cages in terms of symmetry and d-band filling [15–18]. Sen and Mitas [20] reported that the hexagonal prism cage of Si_{12} is remarkably stabilized by encapsulation of a TM atom regardless of the type of doping TM atom from 3d, 4d, and 5d series.

Recently we reported a theoretical study of the equilibrium geometries of cobalt atoms encapsulated in Si_n ($n = 1$–13) clusters via directly doping the cobalt atoms into the ground-state structures of Si_n clusters [23]. The usage of the structures of pure Si clusters as the initial structures of the metal-doped Si clusters has its limitation. Only limited amount of structural isomers were considered for each size. Hence, some low-lying structural isomers and even the ground-state structures might be missing in the geometry search. In cluster physics, one of the most fundamental problems is to determine the ground-state geometry of a cluster. To improve our previous calculation, in this Letter we conducted an extensive search for the lowest-energy configurations of Si_nCo ($n = 2$–14) clusters by including a considerable amount of possible structural isomers for each cluster size, similar to our recent research on Si_nFe clusters [24]. The size-dependent growth behavior and magnetic properties of the Si_nCo clusters were discussed and compared with the properties of pure Si_n clusters.

2. Theoretical methods

The electronic structures and magnetic properties of Si_nCo ($n = 2$–14) clusters were computed using all-electron density functional theory (DFT) implemented in the DMol package [25]. We used the spin-polarized generalized gradient approximation (GGA) with PW91 functional [26] for the exchange-correlation interaction and the double numerical basis set that includes d-polarization functions (DND) [25]. Self-consistent field (SCF) calculations were done with a convergence criterion of 10^{-6} Hartree on the total energy. The density mixing criteria for charge and spin were taken as 0.02 and 0.05 respectively. The direct inversion in an iterative subspace (DIIS) approach was used to speed up the SCF convergence. A 0.002 Hartree smearing was applied to the molecular orbital occupation. In the geometry optimization, the converge thresholds were set to 0.002 Hartree/Å for the forces, 0.005 Å for the displacement and 10^{-5} Hartree for the energy change. We started with the lowest spin multiplicity for the Si_nCo clusters (that is doublet for odd-electron systems and singlet for even-electron systems), spin-unrestricted calculations were then performed for all allowable spin multiplicities. The on-site charges and local magnetic moment were evaluated via Mulliken population analysis [27].

3. Structures of clusters

Fig. 1 gives the ground-state structures and some low-lying metastable isomers obtained for Si_nCo ($n = 2$–14) clusters in this work. The relative energy of a structural isomer from the ground state is also labeled below the structural plot of Fig. 1. The lowest-energy structures for pure Si_n clusters are also plotted in Fig. 1 for the purpose of comparison, which was reported in our recent work [23]. The lowest-energy configurations of pure Si_n and Si_nCo clusters are summarized in Table 1.

For the smallest clusters with $n \leqslant 4$, both Si_n and Si_nCo clusters adopt planar structures as their lowest-energy geome-

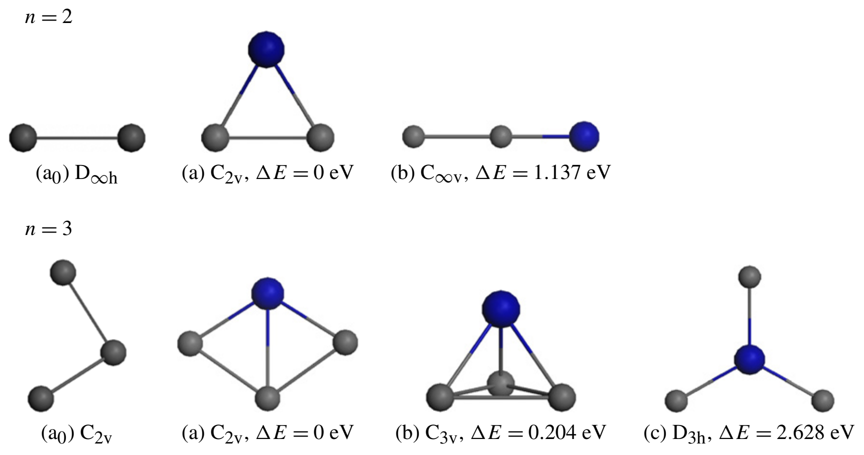

Fig. 1. The lowest-energy and low-lying structures of Si_nCo ($n = 2$–14) clusters and ground-state structures of pure Si_n ($n = 2$–14) clusters. The differences of total binding energies of an isomer from the most favorable isomer are given below the structure for each size.