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Smallest fullerene-like silicon cage stabilized by a V_2 unit

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We conducted a combined anion photoelectron spectroscopy and density functional theory study on V_2Si_{20} cluster. Our results show that the V_2Si_{20} cluster has an elongated dodecahedron cage structure with a V_2 unit encapsulated inside the cage. It is the smallest fullerene-like silicon cage and can be used as building block to make cluster-assembled materials, such as pearl-chain style nanowires. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4861053]

I. INTRODUCTION

Metal-doped silicon clusters have attracted great attention because of their novel structural features and potential technical applications. Many experimental[1–7] and theoretical[8–19] studies have been devoted to investigate the geometric and electronic properties of metal-doped silicon clusters. Regarding the formation of silicon cage structures, metal-doped Si_{12}, Si_{16}, and Si_{20} clusters are especially interesting. Hexagonal prism (or distorted hexagonal prism) type of structures have been found for metal-doped Si_{12} clusters, such as $Cr@Si_{12}$,[20–22] $Cu@Si_{12}$,[23–25] and $W@Si_{12}$.[26] Frank-Kasper polyhedron type of structures has been identified for metal-doped Si_{16} clusters, $M@Si_{16}$ ($M = Zr$, Sc, Ti, V, and Cr).[27–29] Metal-doped Si_{20} is of great interest because it might be possible to form the smallest fullerene-like silicon cage structure. While it is realistic to stabilize a Si_{12} or Si_{16} cage by doping a single metal atom, it is not easy to achieve the stabilization of a Si_{20} cage in the same way because Si_{20} cage is bigger, therefore, a metal must have a fairly large atomic radius in order to stabilize fullerene-like Si_{20} cage with a single atom. Although it has been proposed by theoretical calculations that the dodecahedron cage Si_{20} cluster can be stabilized by doping with a single metal atom, such as Zr, Ca, Sr, Ba, Pb, or Eu,[30–33] the calculations of Kumar *et al.*[34] showed that dodecahedron $Zr@Si_{20}$ is not stable and the geometry optimization of $Zr@Si_{20}$ leads to the shrinkage of the Si_{20} cage with a Si atom sticking out. Recent theoretical studies of Willand *et al.*[35] suggested that the previously proposed dodecahedron structures of $M@Si_{20}$ are metastable only. Singh *et al.*[36] suggested that Th is the only metal atom that can stabilize fullerene-like Si_{20} cage with icosahedral symmetry because the atomic radii of the other metals are not big enough.

Instead of doping a large metal atom, another possible way to stabilize fullerene-like Si_{20} cage is doping two metal atoms. Indeed, the theoretical studies of Lu *et al.*[37] found that Si_{20} doped with a W_2 unit has an elongated dodecahedron structure. In our previous studies of small silicon clusters doped with two vanadium atoms, we found that the two V atoms are tightly bonded.[38] We suspect that V_2 might be a good candidate for stabilization of fullerene-like Si_{20} cage. Till now, there is no experimental confirmation of endohedral $V_2@Si_{20}$ cluster although a variety of doubly doped silicon clusters were investigated previously by water adsorption experiments[39] and argon physisorption experiments.[40] On the other hand, there are some disagreements between the previous theoretical calculations of V_2Si_{20} cluster. The theoretical studies of Andriotis *et al.*[41] predicted the structure of V_2Si_{20} cluster to be an end-capped stacked hexagonal prism, while Wang *et al.*[42] found a stacked hexagonal prism structure in which two hexagonal prisms share a square side. There was no report of endohedral dodecahedron structure for V_2Si_{20} cluster. In this work, we investigated $V_2Si_{20}{}^{-/0}$ clusters using anion photoelectron spectroscopy and density functional calculations. Our results show that the V_2Si_{20} cluster has an elongated dodecahedron cage structure with a V_2 unit encapsulated inside the cage and the $V_2@Si_{20}$ cluster can be used as building block to make pearl-chain style nanowires.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Experimental method

The experiments were conducted on a home-built apparatus consisting of a laser vaporization cluster source, a time-of-flight mass spectrometer, and a magnetic-bottle photoelectron spectrometer, which has been described in Ref. 38. The V-Si cluster anions were generated in the laser vaporization source by laser ablation of a rotating translating disk target (13 mm diameter, V/Si mole ratio 1:2) with the second harmonic of a nanosecond Nd:YAG laser (Continuum Surelite II-10). The typical laser power used in this work is about 10 mJ/pulse. Helium gas with ~4 atm backing pressure was allowed to expand through a pulsed valve (General Valve Series 9) into the source to cool the formed clusters. The generated cluster anions were mass-analyzed with the time-of-flight mass spectrometer. The cluster anions of interest were selected with a mass gate, decelerated by a momentum decelerator, and crossed with the beam of an Nd:YAG laser (Continuum Surelite II-10, 266 nm) or an excimer laser (ArF: 193 nm) at the photodetachment region. The electrons from

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photodetachment were energy-analyzed by the magnetic-bottle photoelectron spectrometer. The resolution of the magnetic-bottle photoelectron spectrometer was about 40 meV at electron kinetic energy of 1 eV. The photoelectron spectra were calibrated with the spectra of Cu^- and Au^- taken at similar conditions.

B. Theoretical method

All theoretical calculations in this work were performed with the B3LYP hybrid density functional method[43,44] implemented in the Gaussian09 program package.[45] The double-zeta Lanl2DZ basis set was used for both V and Si atoms. All geometry optimizations were conducted without any symmetry constraint. The geometries of the clusters were determined by optimizing the structures at all possible multiplicities. Harmonic vibrational frequencies were calculated to make sure that the structures correspond to the real local minima. The zero-point vibrational energy corrections were included for the relative energies of the isomers.

III. RESULTS AND DISCUSSION

The photoelectron spectra of $V_2Si_{20}^-$ cluster recorded with 266 nm and 193 nm photons are presented in Figure 1. The theoretical simulated spectral lines[46] of dodecahedron $V_2@Si_{20}^-$ (Figure 2, 20A) are also plotted in Figure 1. The adiabatic detachment energy (ADE) and vertical detachment energy (VDE) of $V_2Si_{20}^-$ cluster are estimated to be 3.5 eV and 3.7 eV, respectively, based on its spectrum taken with 266 nm photons. The spectral features in the experimental spectrum are very broad, no clear electronic transition peaks or vibrational structure has been resolved, probably due to the high density of states of the $V_2Si_{20}^-$ cluster; as it can be seen, the simulated spectral lines of dodecahedron $V_2@Si_{20}^-$ are very dense.

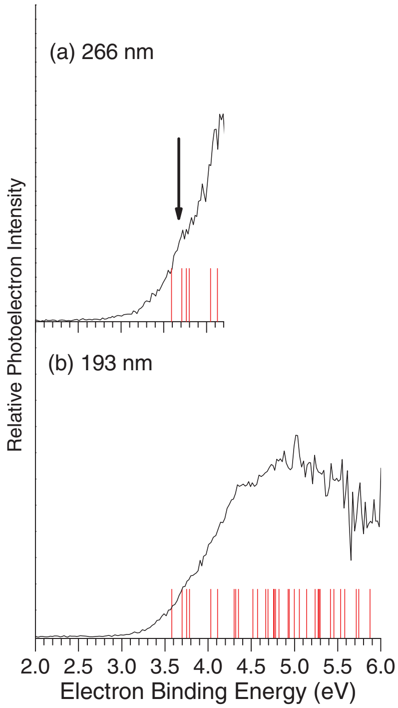
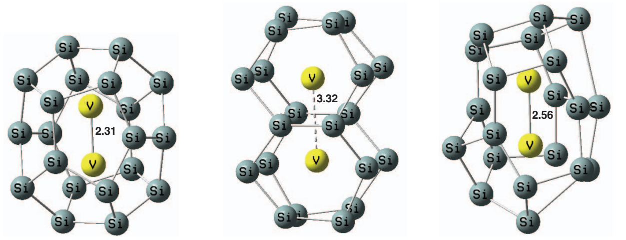


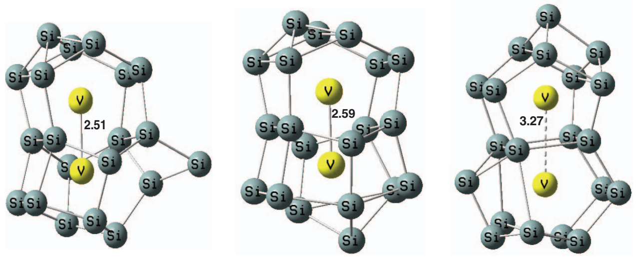
FIG. 1. Photoelectron spectra of $V_2Si_{20}^-$ cluster recorded with 266 nm and 193 nm photons. The red lines are the theoretical simulated spectral lines of dodecahedron $V_2@Si_{20}^-$ (Figure 2, 20A).



20A (C_{2h}, ^2A_g) 0 eV
ADE: 3.47 eV
VDE: 3.52 eV

20B (C_i, ^2A_g) +1.26 eV
ADE: 3.33 eV
VDE: 3.37 eV

20C (C_1, ^4A) +1.48 eV
ADE: 2.43 eV
VDE: 3.70 eV



20D (C_1, ^4A) +1.61 eV
ADE: 3.44 eV
VDE: 3.51 eV

20E (C_1, ^2A) +1.72 eV
ADE: 3.69 eV
VDE: 3.86 eV

20F (C_1, ^4A) +2.43 eV
ADE: 3.40 eV
VDE: 3.71 eV

FIG. 2. Low-lying isomers of $V_2Si_{20}^-$ cluster as well as their relative energies, ADEs and VDEs from density functional calculations. The V–V distances are given in angstrom.

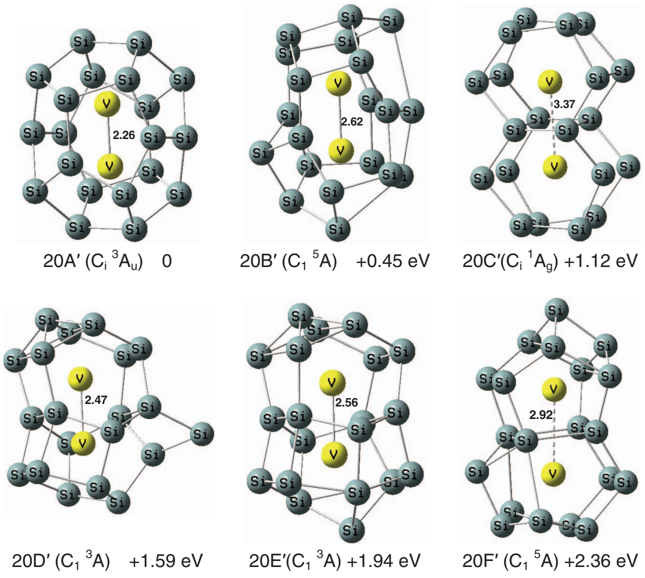
As shown in Figure 2, the most stable structure of $V_2Si_{20}^-$, isomer 20A, is an elongated dodecahedron cage structure with a V_2 unit encapsulated inside the silicon cage. The Cartesian coordinates of isomer 20A and other low-lying isomers can be found in the supplementary material.[47] The Si_{20} cage is composed of twelve pentagonal faces. The V–V distance in the dodecahedron $V_2@Si_{20}$ is about 2.31 Å, which is longer than that of the V_2 dimer (1.77 Å)[48] but shorter than that in metallic vanadium (2.62 Å).[49] This indicates that the V–V interaction inside the cage is very strong. The calculated ADE/VDE of isomer 20A (3.47 eV/3.52 eV) are in reasonable agreement with the experimental measurements (3.5 eV/3.7 eV). This type of endohedral dodecahedron structure has also been reported as the ground state structure of $W_2@Si_{20}$ cluster.[37] It is worth mentioning that we have constructed the initial structure of $V_2Si_{20}^-$ by inserting two V atoms into an I_h dodecahedron Si_{20}, which is composed of 12 regular pentagonal faces. This high symmetric structure with I_h dodecahedron Si_{20} cage was elongated after optimization and finally turned into isomer 20A mentioned above.

The other isomers of $V_2Si_{20}^-$, 20B, 20C, 20D, 20E, and 20F, are much less stable than isomer 20A (Figure 2). Isomer 20B is composed of two $V@Si_{12}$ hexagonal prisms stacked and sharing a side face. The V–V distance in isomer 20B is calculated to be 3.32 Å, which is quite large compared to that in isomer 20A. Isomer 20B is higher in energy than isomer 20A by 1.26 eV. This type of double hexagonal prisms stacked structure for V_2Si_{20} cluster has also been reported by

Wang *et al.*[42] The theoretical calculations of Antonis *et al.*[41] suggested the structure of V_2Si_{20} as an end-capped stacked hexagonal prism. According to our calculations, however, this structure is unstable and distorted into isomer 20C after optimization. Isomer 20C is an irregular V_2-doped endohedral structure with V–V bond length of 2.56 Å. Isomer 20C is less stable than isomer 20A by 1.48 eV. In addition, we have also found some other local minimum structures such as isomers 20D, 20E, and 20F, which are less stable than isomer 20A by 1.61, 1.72, and 2.43 eV, respectively. Both isomers 20D and 20E are endohedral structures with a V_2 unit encapsulated inside a distorted Si_{20} cage, whose V–V bond lengths are 2.51 Å and 2.59 Å, respectively. Isomer 20F can be considered as two $V@Si_{10}$ pentagonal prisms stacked and sharing a side face and then with two Si_2 units each face-capping one of the prisms. The V–V distance in isomer 20F is about 3.27 Å. Because isomers 20B, 20C, 20D, 20E, and 20F are much less stable than isomer 20A, it is unlikely for them to exist in our experiments.

As shown in Figure 3, the low-lying isomers of V_2Si_{20} neutral are similar to those of the anions except that the relative stabilities of the second and third isomers are switched, where the hexagonal prisms stacked structure becomes the third stable isomer (20C′). Similar to $V_2Si_{20}^-$, the most stable structure of V_2Si_{20} neutral (20A′) is an elongated dodecahedron cage structure with a V_2 unit encapsulated inside the silicon cage. Its V–V bond length (2.26 Å) is slightly shorter than that in the anion (2.31 Å).

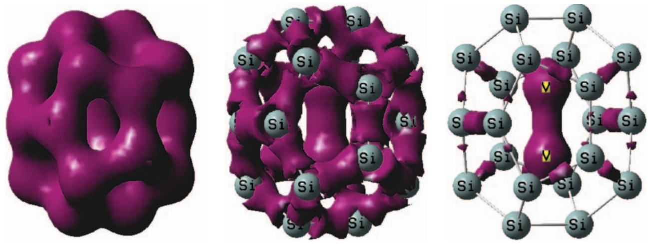
In order to study the bonding nature of $V_2@Si_{20}$, the constant electronic charge densities of the most stable isomer of $V_2@Si_{20}$ (20A′) were analyzed and displayed in Figure 4. The surfaces in the Figures 4(a) and 4(b) show high densities at the V–V and Si–Si bonds, and there is a hollow at the center of each Si_5 pentagon. From Figure 4(c), it is seen that the electron density between the two V atoms is much higher than that between the adjacent Si atoms, suggesting strong bonding between the two V atoms. This is in agreement with our previous investigation on small $V_2Si_n^-$(n = 3–6) clusters[38] which showed that the V-V interaction is very strong, especially in $V_2Si_6^-$. In order for a M_2 (M = metal atom) unit to be able to stabilize a dodecahedron Si_{20} cage, it must have strong M–M bond strength and short M–M bond distance. It is the strong V–V interaction that makes V_2 small enough to be fitted into dodecahedron Si_{20} cage. A M_2 unit with a longer M–M bond would not be a good candidate for stabilizing Si_{20} cage. For example, the Si_{20} dodecahedron cage doped with Zr_2 is an open-cage instead of a closed-cage due to the large Zr–Zr distance.[50]



20A′ (C_i ^3A_u) 0 20B′ (C_1 ^5A) +0.45 eV 20C′(C_i ^1A_g) +1.12 eV

20D′ (C_1 ^3A) +1.59 eV 20E′(C_1 ^3A) +1.94 eV 20F′ (C_1 ^5A) +2.36 eV

FIG. 3. Low-lying isomers of V_2Si_{20} neutral as well as their relative energies from density functional calculations. The V–V distances are given in angstrom.

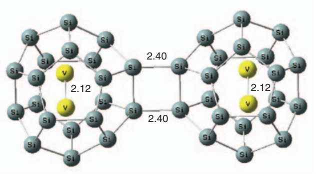


(a) 0.04 a.u. (b) 0.055 a.u. (c) 0.07 a.u.

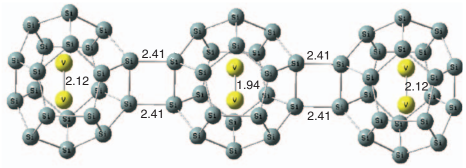
FIG. 4. Constant electronic charge density surfaces of V_2Si_{20} neutral. (a) The charge density equals 0.04 a.u. (b) The charge density equals 0.055 a.u. (c) The charge density equals 0.07 a.u.

People are very interested in cluster-assembled materials.[51,52] A few attempts have been made by theoreticians to investigate the formation of cluster-assembled materials using metal-doped silicon clusters as building blocks.[34,53–55] Since $V_2@Si_{20}$ has a fullerene-like structure, it would be interesting to investigate whether it is possible to make cluster-assembled materials using this smallest fullerence-like silicon cage as building block. Motivated by this, we calculated the structures of $(V_2@Si_{20})_n$ (n = 2–4) and present them in Figure 5. It can be seen that the $V_2@Si_{20}$ units can be connected to form pearl-chain structures with two Si–Si bonds between each pair of neighboring $V_2@Si_{20}$ units. The bond lengths of Si–Si bonds between the $V_2@Si_{20}$ clusters are approximately 2.4 Å, indicating they are assembled tightly via covalent bonds. The V–V bonds in the $V_2@Si_{20}$ units are perpendicular to the $(V_2@Si_{20})_n$ chain and shortened slightly due to the cluster assembling. The shape of $V_2@Si_{20}$ clusters in the middle of the pearl-chains is more similar to the ideal dodecahedron structure than the bare $V_2@Si_{20}$ cluster is. This implies that the formation of pearl-chains can stabilize $V_2@Si_{20}$ dodecahedron cage rather than destabilizing it, therefore, $V_2@Si_{20}$ cluster is a very good building block for cluster-assembled materials.

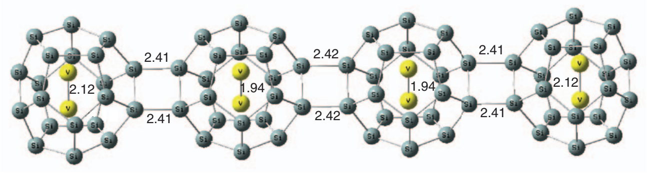
In addition to the pearl-chain structures of $(V_2@Si_{20})_n$, we have also considered many other structures during the optimizations, such as having two dodecahedron $V_2@Si_{20}$ joined at edges with two V_2 dimers in the same line and having two dodecahedron $V_2@Si_{20}$ connected via their pentagon faces. These tried structures were all distorted significantly after optimizations. Even so, the energies of the distorted structures are much higher than that of the pearl-chain structure. This further confirms that the pearl-chain structures of $(V_2@Si_{20})_n$ are very stable.



(a) $(V_2@Si_{20})_2$



(b) $(V_2@Si_{20})_3$



(c) $(V_2@Si_{20})_4$

FIG. 5. Optimized geometries of $(V_2@Si_{20})_n$ (n = 2–4) clusters. The V–V and Si–Si bond lengths are given in angstrom.

It is well known that silicon clusters prefer to form diamond-like structures through sp^3 hybridization, which prevents their unlimited growth via the one-dimensional pattern. Theoretical calculations suggest that the one-dimensional growth of pure silicon clusters is limited to cluster size smaller than 70 atoms.[56] The pearl-chain structure of $(V_2@Si_{20})_n$ found in this work demonstrates that doping of V_2 not only can stabilize the fullerene-like cage structure of Si_{20} cluster but also makes it an ideal building block for quasi-one-dimensional nanowires.

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