Smallest fullerene-like silicon cage stabilized by a V₂ unit

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We conducted a combined anion photoelectron spectroscopy and density functional theory study on V₂Si₂₀ cluster. Our results show that the V₂Si₂₀ cluster has an elongated dodecahedron cage structure with a V₂ 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.

I. INTRODUCTION

Metal-doped silicon clusters have attracted great attention because of their novel structural features and potential technical applications. Many experimental and theoretical 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 Si₁₂, Si₁₆, and Si₂₀ clusters are especially interesting. Hexagonal prism (or distorted hexagonal prism) type of structures have been found for metal-doped Si₁₂ clusters, such as Cr@Si₁₂, 20–22 Cu@Si₁₂, 23–25 and W@Si₁₂. 26 Frank-Kasper polyhedron type of structures has been identified for metal-doped Si₁₆ clusters, M@Si₁₆ (M = Zr, Sc, Ti, V, and Cr). 27–29 Metal-doped Si₂₀ 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 Si₁₂ or Si₁₆ cage by doping a single metal atom, it is not easy to achieve the stabilization of a Si₂₀ cage in the same way because Si₂₀ is bigger, therefore, a metal must have a fairly large atomic radius in order to stabilize fullerene-like Si₂₀ cage with a single atom. Although it has been proposed by theoretical calculations that the dodecahedron cage Si₂₀ 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@Si₂₀ is not stable and the geometry optimization of Zr@Si₂₀ leads to the shrinkage of the Si₂₀ cage with a Si atom sticking out. Recent theoretical studies of Willand et al. 35 suggested that the previously proposed dodecahedron structures of M@Si₂₀ are metastable only. Singh et al. 36 suggested that Th is the only metal atom that can stabilize fullerene-like Si₂₀ 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 Si₂₀ cage is doping two metal atoms. Indeed, the theoretical studies of Lu et al. 37 found that Si₂₀ doped with a W₂ 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 V₂ might be a good candidate for stabilization of fullerene-like Si₂₀ cage. Till now, there is no experimental confirmation of endohedral V₂@Si₂₀ 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 V₂Si₂₀ cluster. The theoretical studies of Andriotis et al. 41 predicted the structure of V₂Si₂₀ 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 V₂Si₂₀ cluster. In this work, we investigated V₂Si₂₀ clusters using anion photoelectron spectroscopy and density functional calculations. Our results show that the V₂Si₂₀ cluster has an elongated dodecahedron cage structure with a V₂ unit encapsulated inside the cage and the V₂@Si₂₀ 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\textsuperscript{43, 44} implemented in the Gaussian09 program package.\textsuperscript{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\textsubscript{2}Si\textsubscript{20}$^-$ cluster recorded with 266 nm and 193 nm photons are presented in Figure 1. The theoretical simulated spectral lines\textsuperscript{46} of dodecahedron V\textsubscript{2}@Si\textsubscript{20}$^-$ (Figure 2, 20A) are also plotted in Figure 1. The adiabatic detachment energy (ADE) and vertical detachment energy (VDE) of V\textsubscript{2}Si\textsubscript{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\textsubscript{2}Si\textsubscript{20}$^-$ cluster; as it can be seen, the simulated spectral lines of dodecahedron V\textsubscript{2}@Si\textsubscript{20}$^-$ are very dense.

As shown in Figure 2, the most stable structure of V\textsubscript{2}Si\textsubscript{20}$^-$, isomer 20A, is an elongated dodecahedron cage structure with a V\textsubscript{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.\textsuperscript{47} The Si\textsubscript{20} cage is composed of twelve pentagonal faces. The V–V distance in the dodecahedron V\textsubscript{2}@Si\textsubscript{20} is about 2.31 Å, which is longer than that of the V\textsubscript{2} dimer (1.77 Å)\textsuperscript{48} but shorter than that in metallic vanadium (2.62 Å).\textsuperscript{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\textsubscript{2}@Si\textsubscript{20} cluster.\textsuperscript{37} It is worth mentioning that we have constructed the initial structure of V\textsubscript{2}Si\textsubscript{20}$^-$ by inserting two V atoms into an Ih dodecahedron Si\textsubscript{20}, which is composed of 12 regular pentagonal faces. This high symmetric structure with Ih dodecahedron Si\textsubscript{20} cage was elongated after optimization and finally turned into isomer 20A mentioned above.

The other isomers of V\textsubscript{2}Si\textsubscript{20}$^-$, 20B, 20C, 20D, 20E, and 20F, are much less stable than isomer 20A (Figure 2). Isomer 20B is composed of two V@Si\textsubscript{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\textsubscript{2}Si\textsubscript{20} cluster has also been reported by...
Wang et al.\textsuperscript{42} The theoretical calculations of Antonis et al.\textsuperscript{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 $V_2Si_{20}$\textsuperscript{−}, 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 $V_2@Si_{10}$, the constant electronic charge densities of the most stable isomer of $V_2@Si_{10}$ (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 bond-

![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.](Image)

![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.](Image)
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. 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 $Si_{20}$ but also makes it an ideal building block for quasi-one-dimensional nanowires.

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