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Electronic and magnetic properties of two dimensional cluster-assembled materials based on TM@Si_{12} (TM = 3d transition metal) clusters

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ABSTRACT

Electronic and magnetic properties of two dimensional (2D) cluster-assembled materials based on TM@Si_{12} (TM = 3d transition metal) clusters were systematically investigated by using the density functional method. Taking the hexagonal prism TM @Si_{12} as a building block, we constructed four different kinds of 2D crystal structures, each with a higher stability than the corresponding individual clusters. The hexagonal honeycomb and porous structures are proved to be thermodynamically stable at room temperature by first-principles molecular dynamics simulations, and the honeycomb structure is more favorable in energy than the porous structure. The magnetic coupling properties of the honeycomb and porous structures based on TM@Si_{12} were further studied in detail. The results show that almost all of the hexagonal TM@Si_{12} 2D lattice exhibit a certain degree of magnetic ordering. These studies provide insights into the effective design of 2D spintronic materials.

1. Introduction

Atomic clusters show the rich and unique properties because of quantum size effect [1–3]. One of the long-sought goals of cluster science is to assemble some stable clusters into new materials with the desired properties by a bottom-up ways, these new materials assembled with clusters as building blocks are called cluster assembly materials (CAMs) [4–9]. As CAM building blocks are clusters, meaning that more atoms and arrangements are available to select and assemble to adjust the properties of the material [10]. Many clusters have been confirmed the validity as CAM building blocks [11–13]. Some of the highly stable clusters known as superatoms can mimic the chemical behavior of the elements in the Periodic Table and present an unprecedented potential for assembly of CAMs [14,15]. One-, two-, and three-dimensional CAMs based on As_7 and As_{11} superatoms had been built by using first-principles electronic structure calculations combined with synthesis in experiment [15,16].

In addition to the superatoms mentioned above, transition metal doped silicon (TM@Si_n) clusters are also of great interest in the fields of physics and chemistry because of their unique properties [17–30]. The TM @ Sin clusters have proven to be a promising building block for CAM because of their superatomic properties, and because the nature of the transitional atom itself is considered as promising candidates for spintronic devices [30–32]. As a typical representative of TM@Si_n clusters, TM @Si_{12} clusters with a hexagonal prism structure have been assembled into zero-dimensional (0D) quantum dots [33,34], one-dimensional (1D) nanotubes [35], and two- dimensional (2D) nanoplates [36–39].Previous studies on magnetic properties of TM@Si_n and their CAMs have shown interesting phenomena. Khanna's group theoretically studied the assembly and magnetic properties of the hexagonal prism Cr@Si_{12} cluster, they found that the magnetic moment of the Cr atom is quenched in Cr@Si_{12} monomer by the strong Cr-Si interaction, but when two nonmagnetic Cr@Si_{12} as building units are brought together, the finite magnetic moment appeared in the composite Cr@Si_{12} dimer because of the Cr-Si interaction weakening [33]. Huang et al. studied Si_{12} cage structures doped with different numbers of V atoms, the results show that V@Si_{12}^- adopts a spin singlet and V_2@Si_{12}^- is in a spin doublet state, while V_3@Si_{12}^- with a unique wheel structure exhibits a $4\mu_B$ ferrimagnetism spin state [34]. Singh's research on finite and infinite nanotubes constructed by TM@Si_{12} showed that Fe and Mn-doped nanotubes of finite length exhibit higher local magnetic moments and Co-doping exhibits lower local magnetic moments, whereas

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Ni-doped exhibits non-magnetic properties. In infinite nanotubes, Fe and Mn doping exhibit respectively ferromagnetism and antiferromagnetism [35].

Recently, 2D materials have been considered key ingredients of future nanoelectronic and optoelectronic devices. Besides their exquisite properties, they have the potential to dramatically reduce the size of electronic devices [38–40]. Liu's research group demonstrated by first-principles calculations that the experimentally characterized V@Si_{12} clusters can construct two types of stable single-cluster layer materials (hexagonal porous or honeycomb lattices, respectively) with regularly and separately distributed V atoms. Both the structure and strength of the ferromagnetic coupling of the porous sheet are stable enough to survive at room temperature, which provide a new avenue to achieve 2D silicon-based spintronic nanomaterials for magnetic device applications [41].

The results of the above study are very significant, which inspired us to further explore whether other transition metal-doped Si_{12} hexagonal prism clusters can also form a magnetically ordered 2D sheet material. In this report, we will take the hexagonal prism structure of 3d-TM@Si_{12} (3d-TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni) as building blocks to construct various 2D planar crystal lattices and further investigate their structural stability and electronic properties by using density function theory (DFT) calculation. The 2D lattices we have built have a square lattice, a central rectangular lattice, a hexagonal porous structure and a hexagonal honeycomb structure. Our results show only the two hexagonal structures are proved to be thermodynamically stable, and they show ordered spin arrangements, which can provide a new avenue to achieve 2D silicon-based spintronics nanomaterials.

2. Computational details and theoretical models

The density functional theory (DFT) calculations are carried out using the Vienna ab initio simulation package (VASP)[42–44]. Projector augmented wave pseudopotentials are used to express the ion-electrons interactions, and the plane-wave function with a cut-off energy of 400 eV is adopted [45]. The exchange and correlation interactions are treated within the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerh (PBE)[46,47]. Considering the strong correlation effects of d electrons in transition metals, the structural relaxations and electronic structure calculations are performed with spin-polarized GGA + U method throughout the study. The on-site correlation energy (U) and the exchange energy (J) are respectively chosen to be 4 eV and 1 eV for all transition metal atoms, which have been tested in the previous literature [48].

The Billouin Zone (BZ) is sampled by the Monkhorst-Pack (MP) scheme. For the primitive cell, an $11 \times 11 \times 1$ k-point mesh is used for the optimization of lattice constant, a $9 \times 9 \times 1$ k-point mesh is chosen during the structural relaxations and a denser $11 \times 11 \times 1$ mesh for static calculations. For the 2×2 supercell, the corresponding k-point values are chosen to be $7 \times 7 \times 1$ and $9 \times 9 \times 1$, respectively. In addition, an 18 Å thick vacuum space is found to be large enough to prevent any interactions between the adjacent periodic images of the monolayer. Geometry optimizations were restricted to the convergence thresholds of 10^{-4} eV for energy and 0.01 eV/Å for Hellmann-Feynman force without any symmetry constrains.

In order to determine whether our assembled 2D crystal structures can survive at room temperature, we studied their thermodynamic stability under finite temperature by performing the spin polarized first-principles molecular dynamic (FPMD) simulations [49]. Here, we need to build a larger supercell for FPMD calculations. For example, a 2×2 supercell for the porous and the central rectangle, and a 3×3 supercell for the honeycomb and the square structure. We perform the FPMD simulations with a Nose-Hoover thermostat at 300 K in the canonical NVT ensemble (constant number of atoms N, volume V, and temperature T), and the simulation time is set to 9000 fs.To test the reliability of our methods, we firstly examined the geometric and electronic properties of free-standing 3d-TM@Si_{12} (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni) hexagonal prism clusters and the hexagonal porous 2D sheet of VSi_{12}. The results show that the $TMSi_{12}$ clusters keep their structures, and their magnetic moments are respectively 3 μ_B, 2 μ_B, 1 μ_B, 0μ_B, 1μ_B, 2μ_B, 1μ_B, and 2μ_B from Sc to Ni (Supplementary Table 1), which are well agreed with the results ref. [50]. The results are also further validated by ADF calculation [51]. As for the VSi_{12} cluster-assembled 2D porous sheet, the optimized lattice constant (11.64 Å) is very close to the previous result of 11.49 Å in the literature [41], and its electronic and magnetic properties also obtain the same results as those of the literature[41].

3. Results and discussions

The 2D lattice has four crystal systems and five kinds of bravais lattices. Based on the above ground state structures of the free-standing TM@Si_{12} clusters, we designed four different 2D planar crystal structures for every TM@Si_{12} cluster, and the four 2D crystal structures are respectively hexagonal honeycomb lattice (Fig. 1A), hexagonal porous lattice (Fig. 1B), square lattice (Fig. 1C) and central rectangular lattice (Fig. 1D). In the honeycomb A structure, the connection between the $TMSi_{12}$ clusters is an edge-to-edge contact by Si—Si bond, and a face-to-face contact by Si_4 quadrilateral in the porous B structure. Both connections exist simultaneously in the square C structure, the edge-to-edge connection is in the vertical direction and the face-to-face is in the horizontal direction. The central $TMSi_{12}$ cluster in the D structure is a face-to-face connection with the adjacent four unit clusters. In these assembled 2D crystal structures, the TM atoms are all separated and regularly distributed between the two layers of Si atoms, forming Sandwich-like layered structures.

3.1. 2D self-assembly structures of Cr@Si_{12} clusters

For the above four types of 2D crystal structures, we first optimized their lattice constants a, which corresponds to the lowest point of the E(a) energy curve, and the E(a) curve of the energy with the lattice constant is shown in Fig. 2. As seen from Fig. 2, these four structures are located at the local minimum of the potential energy surface, and the corresponding lattice constants are listed in Table 1.

3.1.1. Geometric structures

Geometric optimization and stability study were carried for each structure, and the optimized geometric parameters of the free $CrSi_{12}$ cluster as well as the four 2D assembly crystal structures are listed in Table 1, including the Cr—Si bond lengths (d_0), the Si—Si bond lengths (d_1) of the hexagonal bottom edge, which are parallel to the 2D plane, and the edge Si—Si bond lengths (d_2) of the hexagonal prism, which are perpendicular to the 2D plane, and the Si-Si bond lengths (d_3) between adjacent clusters.

Compared with the free $CrSi_{12}$ cluster, the bond lengths in the 2D assembly crystal structure are only a small adjustment and relaxation. Almost all the Cr—Si bond and Si—Si bond lengths inside the Cr@Si_{12} cluster are slightly increased, while the Si—Si bond lengths (d_3) between adjacent clusters are slightly smaller than the Si—Si bond lengths inside the cluster, which implies that the atomic arrangement is more loose in the 2D assembly crystal structure and the atomic interaction within the Cr@Si_{12} cluster