Novel nanostructures built from $\text{Zn}_{12}\text{S}_{12}$ cage-like clusters[☆]

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Abstract

A series of nanostructures of Zinc Sulfide (ZnS), including the small Zn_nS_n ($n=1-15$) clusters, the magic cage-like $\text{Zn}_{12}\text{S}_{12}$ and its derivants ($\text{Zn}_{12}\text{S}_{12}$ -based dimers, trimers, nanowires and monolayer) were systematically investigated by using a first-principles bottom-up calculation. The results show that the $\text{Zn}_{12}\text{S}_{12}$ cage-like structure with six isolated four-membered rings (4NRs) and eight six-membered rings (6NRs) has T_h symmetry and a large HOMO-LUMO gap, indicating that the $\text{Zn}_{12}\text{S}_{12}$ cluster would be ideal building blocks for the synthesis of new cluster-assembled materials. Via the aggregation of $\text{Zn}_{12}\text{S}_{12}$, we find that the $\text{Zn}_{12}\text{S}_{12}$ cages can bind into various porous materials with different dimensionality by the most stable bonding H-H₁. Interestingly, all of these cluster-assembled structures are found to be more stable than the individual $\text{Zn}_{12}\text{S}_{12}$ cage and rock salt (RS) phase of ZnS . These fascinating findings will be advantageous for promoting the potential applications of the inorganic ZnS -based nanosystems in the new type of electronic nanodevices and high-performance semiconductor materials.

Keywords: $\text{Zn}_{12}\text{S}_{12}$ building blocks, cluster-assembled nanostructures, first-principles calculations

1. Introduction

II-VI semiconductor nanomaterials have been deeply investigated in recent years due to their unique photophysical properties, which substantially deviate from those of their bulk counterparts. [1] Zinc Sulfide (ZnS) is the most studied II-VI compound. Under an ambient pressure, there are two types of structures for ZnS , i.e. the high temperature phase hexagonal wurtzite (WZ) structure and the low temperature phase cubic zinc-blende (ZB) structure. [2] The wide direct band gaps of ZB- ZnS (3.6 eV) is higher than that of SiC (3.27 eV), ZnO (3.37 eV) and GaN (3.39 eV). [3] Moreover, high exciton binding energies (40 meV) make ZnS particularly suitable for optoelectronic applications. [4] Up to now, ZnS has been broadly applied in light-emitting diodes (LEDs), electroluminescence, flat panel displays, infrared windows, optical sensitizers, laser diodes, biodevices, and so on, [5–10] because of its special properties.

As can now be appreciated, ZnS clusters have been extensively investigated both theoretically and experimentally. [11–29] Various ZnS nanostructures with different dimensionality (for example, the 0-D quantum dots, 1-D nanowires or nanotubes, and 2-D ultrathin films) hold a special interest. [30–44] Offering reduced dimensionality, outstanding materials properties, and the capability for bottom-up assembly, these nanostructures are highly promising nanobuilding blocks for future advanced devices.[45] Herein, we consider the stable clusters as building blocks to construct new novel cluster-assembled nanostructure. As a matter of fact, the interest in such approach of forming new materials using clusters as building blocks, i.e. the approach from the bottom up, has been paid great attention in the past few years. [46–49] Largely inspired

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by the previous works, we used an ab initio calculation to explore the stability and structural and electronic properties of a new family of nanomaterials built from $\text{Zn}_{12}\text{S}_{12}$ clusters with a view to expanding the range of properties and applications of ZnS. The viability of these proposed nanostructures have been assessed via calculating: (1) the thermodynamic and kinetic stability of $\text{Zn}_{12}\text{S}_{12}$ with respect to its competing isomers and other small Zn_nS_n clusters, and (2) the energetics of $\text{Zn}_{12}\text{S}_{12}$ - $\text{Zn}_{12}\text{S}_{12}$ interactions. By determining the binding energy per unit of ZnS, we find the assembled nanowires with energies 0.544 eV-0.583 eV/ZnS below the bulk equilibrium ZBZnS phase. However, considering the synthesized rock salt phase of ZnS (RS-ZnS) lies 0.585 eV/ZnS below the ZB-ZnS phase, the nanowires seem to be attractive synthesis targets.

Our paper is organized as follows. In Section 2, the calculational details will be described. In Section 3, we will carry out a systematic investigation on the structures, stabilities, electronic properties of some cluster-assembled materials constructed from $\text{Zn}_{12}\text{S}_{12}$ cage-like clusters so as to deal with some problems in the design theory of cluster assembly. In Section 4, the conclusion remarks will be presented.

2. Methods

All the geometry optimizations and electronic structure calculations were fully carried out with density functional theory (DFT) implemented in the GAUSSIAN03 package. [50] In order to better depict the geometrical features and bonding of the clusters, the B3LYP LANL2DZ [51–53] was employed to characterise the exchange-correlation interaction. **Although the one method-one one-basis-set computational philosophy has been adopted in this paper[60, 61], the reliability of our selected theoretical scheme had been fully tested in our previous works[54–58] and other researchers’ reports on the valence isoelectronic compound clusters.** We get the global minimum structures of small $\text{Zn}_{12}\text{S}_{12}$ ($n=1-15$) cluster by combining the Saunders kick method [49, 62] and DFT local optimization. [29, 63] In the method, all the atoms were placed at the same point initially and then were kicked randomly within a box of chosen dimensions. The kick size varied from 0.2 to 1.0 nm for $\text{Zn}_{12}\text{S}_{12}$ ($n=1-15$). At the DFT/B3LYP/LanL2DZ level, the kick method was run about 800 times until no new minima appeared. Then, we calculate the vibrational frequency for the thermodynamically stable lowest-energy structures and the infrared (IR) spectra simulation result. For the $\text{Zn}_{12}\text{S}_{12}$ -assembled periodic systems, all calculations had been performed by using DMol3 computer code. [64] Generalized Gradient Approximation (GGA) formulated by Perdew, Burke, and Ernzerhof (PBE) was employed to describe the exchange-correlation energy functional. [65] All-electron core treatment and double numerical basis set supplemented with Double numerical plus polarization functions (DNP) were selected. Self-consistent field (SCF) procedures were performed with a convergence criterion of 10^6 a.u. on the energy and electron density. The assembled structures were fully optimized without any symmetry constraints. Periodic boundary conditions were employed in the solid-state calculations, and nanowires were adopted using $1 \times 1 \times 5$ Monkhorst-Pack grids of k points, sheet was adopted using $1 \times 5 \times 5$ Monkhorst-Pack grids of k points. The accuracy and validity of the GGA/PBE and DNP combination for investigating the structures of other II-VI compounds [66–68] had been confirmed by previous study.

3. Results and discussions

3.1. The lowest-energy structures and stabilities of Zn_nS_n ($n=1-15$) small clusters

It is suggested that in the small II-VI semiconductor clusters the cage-like structure $\text{II}_{12}\text{VI}_{12}$ should be a magic cluster. [66–68] To further test this fact, we firstly focus our attention on the lowest-energy structures and stabilities of Zn_nS_n ($n=1-15$) clusters. Using the calculational scheme described in the computational methods, we have explored a number of low-lying isomers and finally determined the lowest-energy state for each cluster size. In Fig.1, the lowest-energy structures and symmetry point groups of Zn_nS_n ($n=2-15$) are presented. One can note that these structures share the following three common features: (1) They are cage-like structures for $n > 4$; (2) Each S (Zn) atom is bonded with three Zn (S) atoms, reflecting the sp^2 feature; (3) For $n \geq 6$, the structures consist of two basic motifs (a four-membered ring 4NR and a six-membered ring 6NR with an alternative arrangement of Zn-S bonds). In fact, these structural features also exist in other valence isoelectronic clusters. [49, 66–68] As we known, the average binding energy (E_b),

Figure 1: The lowest-energy structures and their corresponding symmetry point groups of Zn_nS_n ($n=2-15$) violet balls represent Zn atoms and yellow balls represent S atoms.

energy gap between HOMO and LUMO (E_g) and second difference of energy (Δ_2E) can effectively reflect the relative stabilities of Zn_nS_n ($n=2-15$) clusters. Here we have calculated the E_b , E_g and Δ_2E as defined below:

$$E_b = E(Zn) + E(S) - \frac{E(Zn_nS_n)}{n} \quad (1)$$

$$E_g = E_{LUMO}(Zn_nS_n) + E_{HOMO}(Zn_nS_n) \quad (2)$$

$$\Delta_2E = E(Zn_{n-1}S_{n-1}) + E(Zn_{n+1}S_{n+1}) - 2E(Zn_nS_n) \quad (3)$$

where $E(Zn)$, $E(S)$, $E(Zn_nS_n)$, $E(Zn_{n+1}S_{n+1})$ and $E(Zn_{n-1}S_{n-1})$ are the total energy of a zinc atom, a sulfur atom, a Zn_nS_n cluster, a $Zn_{n+1}S_{n+1}$ cluster and a $Zn_{n-1}S_{n-1}$ cluster, respectively. The quantity of interest is the change in E_b , E_g and Δ_2E values as the ZnS units are successively increasing. In Fig.2(a), the E_b energies are presented as a function of cluster size n . As shown in the figure, there are three turning-points at $n=3$, 6 and 12. It should be noted that the Δ_2E energies are sensitive to the relative stability of the clusters. As is shown in Fig.2(b), three obvious local maximum peaks can be found at $n=3$, 6 and 12, indicating that the corresponding cluster is more stable than its neighboring clusters. In Fig.2(c), the E_g for the lowest-energy structures of Zn_nS_n ($n=2-15$) are displayed. The distinct maximum appears at $n=4$, as the structure changes from two- to three-dimensions. For the larger clusters ($n=5-15$), their HOMO-LUMO gaps firstly decrease to the minimum value, and then reach to a constant (3.5 eV) with slight fluctuations. Nonetheless, compared with the bandwidth 2.18 eV of ZB-ZnS bulk (see the red line in Fig.2(c)), this constant is still too large, which suggests that the small clusters are far from the bulk ZnS. Moreover, there are two local maxima ($n=6$ and 12) excepting the distinct maximum, and the largest one is found at $n=12$. Generally, the cluster with larger HOMO-LUMO gaps would be more stable and chemically inert. Therefore,

the coincidence between the maximum peaks for $\Delta_2 E$ and local maximum for E_g at $n=12$ suggests that the $\text{Zn}_{12}\text{S}_{12}$ cage is the most stable cluster with six isolated 4-membered ring and 6-membered ring among Zn_nS_n ($n=2-15$), which is in agreement with the previous report. [15, 49, 66–68]

Figure 2: The binding energy(E_b) per ZnS unit(a), second-order difference of total energy ($\Delta_2 E$)(b) and HOMO-LUMO gap(E_g)(c) calculated for Zn_nS_n ($n = 2 - 15$).

3.2. The structures, energetics and electronic properties of $(\text{Zn}_{12}\text{S}_{12})_m$ ($m = 1 - 3$) clusters

In order to examine the possibility that the stable $\text{Zn}_{12}\text{S}_{12}$ cluster could be ideal building block for new nanomaterials, we have further investigated the energetics, structural and electronic properties of $(\text{Zn}_{12}\text{S}_{12})_m$ ($m = 1 - 3$). Firstly, six low-lying isomers are presented for the monomer $\text{Zn}_{12}\text{S}_{12}$ in Fig.3.

These isomers can be classified into three types, i.e., cage-like, ring-like and tube-like geometries. Compared with the ring-like and tube-like structures, the hollow cage possesses energy predominance which is no less than 1.283 eV and 1.848 eV, respectively. The cage structure has eight isolated 6NRs and six 4NRs, and a T_h symmetry with two different Zn-S bond length: the shorter one ($R_s=0.236$ nm) connecting the adjacent 4NRs and the longer one ($R_l=0.245$ nm) in 4NRs. Other most essential parameters of this structure are listed in Table 1. The bond angle in 4NRs is acute at the S atom (80.6°) and obtuse at the Zn atom (96.7°). The corresponding angle in 6NRs is 106.8° and 128.1° , respectively. Additionally, it can be found that the S atoms in both 4NRs and 6NRs are slightly out of the ring planes to form a buckled structure, not like carbon fullerene with an even curvature. Such buckling behavior stems from the fact that the S atom prefers to form a tetrahedral sp^3 hybridization, while the Zn atom tends to form a planar

Figure 3: The structures of different isomers of $\text{Zn}_{12}\text{S}_{12}$ clusters optimized at the DFT/B3LYP/LAN2DZ level, with energy differences compared to the lowest energy T_h cluster. Zn atoms are violet and S atoms are yellow.

Table 1: Bond lengths, bond angles, binding energies (E_b) per ZnS and HOMO-LUMO gaps (E_g) for the lowest-energy monomer, dimer and trimer of $\text{Zn}_{12}\text{S}_{12}$

System	R_s (nm)	R_l (nm)	R_{c-c} (nm)	Zn-S-Zn (deg)	S-Zn-S (deg)	E_b (eV)	E_g (eV)
$\text{Zn}_{12}\text{S}_{12}$	0.236	0.245	---	80.6-106.8	96.7-128.1	5.944	3.986
$(\text{Zn}_{12}\text{S}_{12})_2$	0.236	0.246	0.252	80.8-109	96.5-133.1	6.068	3.831
$(\text{Zn}_{12}\text{S}_{12})_3$	0.236	0.246	0.253	80.8-107.8	95.8-107.8	6.111	3.822

sp^2 hybridization. As mentioned above, the energy gap between HOMO and LUMO for $\text{Zn}_{12}\text{S}_{12}$ has a local maximum (3.986 eV), which means that it possesses high stability and wide-gap semiconductor properties. In brief, high structural symmetry (T_h), large HOMO-LUMO gap and large energy separation (no less than 1.283 eV) between the first and the second lowest-energy isomers further prove that the cage-like $\text{Zn}_{12}\text{S}_{12}$ can be considered as a perfect building block for constructing cluster-assembled materials.

Furthermore, to further understand the interaction between the Zn and S atoms in the $\text{Zn}_{12}\text{S}_{12}$ cage and the features in the electrons states near the Fermi level, we also calculated the density of states projected to different atoms (PDOS) and the distribution of electron density of the HOMO and LUMO, as presented in Fig.4. The mid-gap energy is defined as valid Fermi level, denoted by the arrows in Fig.4. Obviously, the electron states near the LUMO are mainly contributed by the Zn atoms, while those near the HOMO are greatly come from the S atoms. It can be understood by the fact that the charge transfer from the S to the Zn atoms.

Hereafter, we will concentrate on the aggregations of $\text{Zn}_{12}\text{S}_{12}$ clusters. As discussed above, the $\text{Zn}_{12}\text{S}_{12}$ cage has two types of faces (4NRs and 6NRs) and two types of edges (R_l and R_s). Hence, all possible cases of interactions between two $\text{Zn}_{12}\text{S}_{12}$ cages (face to face, face to apex, face to edge, edge to edge, apex to apex and edge to apex) have been took into account. After optimizing, four low-lying structures are characterized (see Fig.5). The most energetically favorable one is 6NR face link (H-H₁, see Fig.5 (d₁)). This is similar to the cases of $\text{In}_{12}\text{As}_{12}$ [49] and $\text{Zn}_{12}\text{O}_{12}$ [66, 67]. The other 6NR face link with D_3 symmetry (H-H₂, see Fig.5(d₂)) is only 0.01eV higher in energy with respect to the H-H₁. Therefore, the two 6NR face links are almost degenerate in energy and can be considered to be the ground state. The third low-lying structure is constructed by 4NR facing 4NR coalescence. This case was found to be the lowest-energy structure for the $\text{Cd}_{12}\text{S}_{12}$ [60] which is different for the case of $\text{Zn}_{12}\text{S}_{12}$, although they hold a similar geometric configurations. The fourth low-lying structure is obtained by Zn-S edge facing Zn-S edge link. It should be noted that in the interaction region of $\text{Zn}_{12}\text{S}_{12}$ dimers, a Zn atom is facing a S atom, forming a Zn-S bond, which verifies

Figure 4: partial density of states (PDOS) of the $\text{Zn}_{12}\text{S}_{12}$ cluster projected to Zn atoms (blue line) and S atoms (red line). The Gaussian width employed in plotting the PDOS is 0.2 eV.

the fact that the II-VI compound nanostructures tend to form a stable motif with II and VI atoms allocated alternatively.

Figure 5: The four isomers structures of $\text{Zn}_{12}\text{S}_{12}$ - $\text{Zn}_{12}\text{S}_{12}$ dimer. Values of ΔE are relative energies with respect to the most stable one. Zn atoms are violet and S atoms are yellow.

On the basis of the most stable dimer (d₁ and d₂ in Fig.5), we optimized all possible structures of $\text{Zn}_{12}\text{S}_{12}$ -trimer at the same theory level. The six low-lying structures are illustrated in Fig.6. The lowest-energy geometry is linear as shown in Fig.6(e₁), in which the $\text{Zn}_{12}\text{S}_{12}$ cages interact with each other by the link of H-H₁. The other linear structure (see Fig.6 (e₂)) with H-H₂ link is 0.032 eV higher in energy, which is almost the degenerate state of e₁. This is different from the cases of $\text{In}_{12}\text{As}_{12}$ [49] and $\text{Zn}_{12}\text{O}_{12}$. [66, 68] Two bent structures, as shown in Fig.6(e₃) and (e₄), are also almost degenerate with only 0.015 eV energy

difference. This may stem from the fact that H-H₁ and H-H₂ have almost the same energy. The other bent and linear structure (see Fig.6 (e₅) and Fig.6 (e₆)) constructed from the 4NR-4NR links are also almost degenerate with only 0.038 eV energy difference. From the results discussed above, one can find that the Zn₁₂S₁₂ cage structures in both dimers and trimers are preserved, and the ZnS bond lengths (R_{c-c}) between Zn₁₂S₁₂ monomers are slightly larger than those in the isolated Zn₁₂S₁₂ cage (see in Table 1).

Figure 6: The six isomers of Zn₁₂S₁₂-based trimer. Values of ΔE are relative energies with respect to the most stable isomer. Zn atoms are violet and S atoms are yellow.

3.3. Thermodynamic stability and spectroscopic fingerprints of the monomer, dimer and trimer of Zn₁₂S₁₂

Fig.7 depicts the IR vibrational spectrum of the monomer, dimer and trimer of Zn₁₂S₁₂, which can help us to find the spectroscopic fingerprints of them. Here, the IR spectrum is broadened by 3 cm⁻¹. For the monomer, we find that the spectrum depicts three obvious peaks at 254 cm⁻¹, 330 cm⁻¹ and 349 cm⁻¹. The spectrum of the dimer is characterized by multiple peaks in the frequency range 222-358 cm⁻¹. The prominent peaks appear at 222 cm⁻¹, 260 cm⁻¹, 329 cm⁻¹ and 350 cm⁻¹, respectively. For the trimer, we founded that there are some sharp peaks at the same range 222-358 cm⁻¹. Several distinguishable peaks appear at 223 cm⁻¹, 260 cm⁻¹, 282 cm⁻¹, 323 cm⁻¹ and 350 cm⁻¹, respectively. Obviously, the strongest peak of these assemblies is slightly dependent on the size of m , and has a red-shift with the increase of cluster size m . These respective spectroscopic fingerprints should provide signatures for future experimental

detections using infrared matrix isolation spectroscopy.

Figure 7: The infrared spectrum for monomer, dimer and trimer of $\text{Zn}_{12}\text{S}_{12}$ cage.

Based on the vibration frequencies, we also got the free energies by using quasi-harmonic approximation: [61]

$$F(T) = E_0 + \frac{1}{2} \sum_i hf_i + K_B T \sum_i \ln[1 - \exp(-\frac{hf_i}{K_B T})] \quad (4)$$

where E_0 is the total energy, and $f_i (i = 1, 2, \dots, (72m-6); m = 1, 2, 3)$ are the vibrational frequencies of the $(\text{Zn}_{12}\text{S}_{12})_m (m=1,2,3)$. The calculated free energies versus temperatures from 0 to 1000 K for these clusters have been presented in Fig.8. Amazingly, it has been found that the free energy per ZnS unit of the trimer is always lower than that of both monomer and dimer, and the dimer always lower than the monomer for the same temperature. These facts mean that in these clusters, the $\text{Zn}_{12}\text{S}_{12}$ trimer is more stable than others. The average binding energies at 0 K (see Table 1) also hold the same energy order. This is very similar to the cases of cage-like $\text{In}_{12}\text{As}_{12}$. [49] Thus, one can conclude that if the magic cluster $\text{Zn}_{12}\text{S}_{12}$ is inherent stable and can be synthesized, it will be easier to archive the assemblies $(\text{Zn}_{12}\text{S}_{12})_m$ in experiment.

3.4. cluster-assembled nanowires and nanosheet

As discussed above, Fig.5 has been showed the four lowest-energy structures of $\text{Zn}_{12}\text{S}_{12}$ dimers. We find that the 6NR face link is the most stable one. This suggests that in the energetically favorable $\text{Zn}_{12}\text{S}_{12}$ materials, the cluster-interaction will take the 6NRs way. So some cluster-assembled periodic nanomaterials can be constructed by using the $\text{Zn}_{12}\text{S}_{12}$ clusters. For one-dimensional nanowires, two types of structures, dumbbell-like and zigzag-like (Fig.9(a) and (b)), have been characterized. Note that the two nanowires are

Figure 8: Free energy of the $\text{Zn}_{12}\text{S}_{12}$ -based assemblies as function of temperature.

almost energetically degenerate with each other. The different energy is only 0.039 eV/ ZnS . For the two-dimensional frameworks, a graphenelike cluster-sheet has been characterized. On the cluster-sheet, there are two kinds of pores (Fig.9(c)). The diameter of them is 0.454 nm for the smaller one, 0.989 nm for the larger one which is surrounded by six $\text{Zn}_{12}\text{S}_{12}$ cage. Such structural feature may make this sheet a particularly promising molecular sieve membrane. Furthermore, some essential parameters of those nanomaterials are summarized in Table 2. From the structural data, one can see that the $\text{Zn}_{12}\text{S}_{12}$ cage structure in all the assembled frameworks is well preserved.

Figure 9: The supercells of periodic systems assembled by $\text{Zn}_{12}\text{S}_{12}$ cages: (a) $1 \times 1 \times 5$ nanowire (I) exhibited dumbbell-shaped chain structure, (b) $1 \times 1 \times 5$ nanowire (II) exhibited zigzag-shaped chain structure, (c) $1 \times 5 \times 5$ graphene-like sheet.

It is necessary to assess the viability of these proposed nanostructures. Therefore, we have calculated the binding energies for them. As is listed in Table 2, the binding energies increase with the increase of

dimensionality, and all of them are large than that of the isolated building block. Specifically, the order of stability is that the graphene-like sheet is the most stable one, then followed by nanowire (I), nanowire (II), trimer, dimer. This further affirm that if the $\text{Zn}_{12}\text{S}_{12}$ have been synthesized in experiment, it would be easier to synthesize the assembled nanomaterials. In order to compare, we have also calculated the binding energies of ZB-ZnS RS-ZnS phase. It can be see that the two types of nanowires hold binding energies 0.544 eV or 0.583 eV/ZnS below ZB-ZnS. Considering the synthesized RS-ZnS phase lies 0.585 eV/ ZnS below ZB-ZnS , the energetic expense of forming such nanowires does not seem prohibitive.

In Fig.10, the partial density of states (PDOS) of the periodic assembled materials, as well as that of the

Table 2: Bond lengths, bond angles, binding energies (E_b) per ZnS and bandgaps(HOMO-LUMO gaps) relative to the ground state ZB-ZnS for the $\text{Zn}_{12}\text{S}_{12}$ cluster and it's assembled nanomaterials($E_g/E_{g,ZB}$)

System	R_s (nm)	R_l (nm)	R_{c-c} (nm)	Zn-S-Zn (deg)	S-Zn-S (deg)	E_b (eV)	$E_g/E_{g,ZB}$ (eV)
$\text{Zn}_{12}\text{S}_{12}$ (B3LYP)	0.236	0.245	---	80.6-106.8	96.7-128.1	5.944	1.70
$\text{Zn}_{12}\text{S}_{12}$ (PBE)	0.227	0.235	---	76.5-100.3	97.5-130.5	6.434	1.48
Nanowire(I)	0.227	0.245	0.250	79.1-117.7	95.0-129.3	6.450	1.32
Nanowire(II)	0.233	0.228	0.241	77.1-119.8	97.2-139.6	6.498	1.24
sheet	0.233	0.226	0.246	81.9-123.6	94.5-144.0	6.400	1.10
ZB-ZnS	0.236	0.236	---	109.5	109.5	7.033	1
RS-ZnS	0.251	---	---	90.0	90.0	6.448	---

Figure 10: The total and partial density of states of ZB-ZnS and $\text{Zn}_{12}\text{S}_{12}$ -based nanostructures. The vertical line indicates the Fermi level.

ZB-ZnS phase, have been demonstrated. As is shown, the PDOS of all these have similar characteristics.

The states of the valence bands near Fermi level are mainly come from Zn 3p and S 3p electrons, and few from Zn 4s and S 3s. Therefore, the interaction between the Zn and S atoms is mainly come from p-p hybridization.

4. Conclusions

In summary, a series of cluster-assembled nanomaterials based on $\text{Zn}_{12}\text{S}_{12}$ clusters has been studied systematically by using a first-principles bottom-up approach. We began this work by trying to confirm the lowest-energy structures of Zn_nS_n ($n=115$) clusters and $\text{Zn}_{12}\text{S}_{12}$ cluster-assemblies. It is found that $\text{Zn}_{12}\text{S}_{12}$ is highly stable in a hollow cage with six isolated 4MRs and eight 6MRs. This novel $\text{Zn}_{12}\text{S}_{12}$ cage, which have high symmetries (T_h symmetry) and a large HOMO-LUMO gap, can be indicated as an ideal building block for synthesizing cluster-assembled nanomaterials. In our work, All possible $\text{Zn}_{12}\text{S}_{12}$ - $\text{Zn}_{12}\text{S}_{12}$ interactions have been considered. From the viewpoint of binding energy, it is found that the two almost degenerate structures with 6MR face link are energetically preferred to the others. The calculated IR spectra of $\text{Zn}_{12}\text{S}_{12}$ assemblies show that the strongest peak has a redshift with the increasing number of $\text{Zn}_{12}\text{S}_{12}$ cages, which can be useful to identify structures and sizes for future experimental detections using infrared matrix isolation spectroscopy.

With the characterized dimers and trimers, a novel family of periodic ZnS nanomaterials, such as $\text{Zn}_{12}\text{S}_{12}$ -based nanowires and sheet, have been characterized. They are energetically more stable than individual $\text{Zn}_{12}\text{S}_{12}$ cage and even RS-ZnS phase. In all of these assembled materials, the cage structure of $\text{Zn}_{12}\text{S}_{12}$ is well preserved. Because of the novel porous character of the nanosheet, it could be used for heterogeneous catalysis, molecular transport, gas storage, and so forth. On the basis of these results, we hope that our predictive study will promote more experimental efforts into investigating these novel cluster-assembled materials built from $\text{Zn}_{12}\text{S}_{12}$.

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The $\text{Zn}_{12}\text{S}_{12}$ cages can bind into various porous materials with different dimensionality by the most stable bonding H-H1. Remarkably, all of these assembled-materials are more stable than the individual cage and rock salt (RS) phase of ZnS.