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Research Article

The Electronic and Structural Properties of Na_xS_y Nanoclusters

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Abstract: In this study, the structural and electronic properties of Na_xS_y (x+y=5) nanoclusters were investigated by density functional theory (DFT). Na-S is a material with potential in battery technologies. Therefore the smallest configurations of Na and S alloys are essential for applications in nanotechnology. Because electronic properties depend on the geometric structure, the minimum energy configurations were presented in detail. The most stable systems were determined as S_5 and NaS_4. The highest HLG value was obtained for the Na_2S_3 nanocluster. HLG values decrease with Na and S atom increase in bare clusters. Adding the S atoms to Na clusters or Na atoms to S clusters reduces the HLG values in general. Ionization potential and electron affinity values of clusters were also presented.

Key words: Nanoclusters, Electronic structure of nanoclusters, Na-S alloy.

Na_xS_y Nanokümelerinin Elektronik ve Yapısal Özellikleri

Öz: Bu çalışmada, Na_xS_y (x+y=5) nanokümelerinin yapısal ve elektronik özellikleri yoğunluk fonksiyonel teorisi (DFT) ile araştırılmıştır. Na-S, pil teknolojilerinde potansiyeli olan bir malzemedir. Bu nedenle Na ve S alaşımlarının en küçük konfigürasyonları nanoteknolojideki uygulamalar için önemlidir. Elektronik özellikler geometrik yapıya bağlı olduğundan minimum enerji konfigürasyonları detaylı olarak sunulmuştur. En kararlı sistemler S_5 ve NaS_4 olarak belirlenmiştir. En yüksek HLG değerine Na_2S_3 nanokümesinin sahip olduğu belirlenmiştir. Saf elementlerden oluşan kümelerde Na ve S atomunun artmasıyla HLG değerlerinin azaldığı görülmüştür. Na kümelerine, S atomlarının veya S kümelerine, Na atomlarının eklenmesi genel olarak HLG değerlerini azalma meydana gelmiştir. Ayrıca kümelerin iyonlaşma potansiyeli ve elektron afinite değerleri de sunulmuştur.

Anahtar kelimeler*:* Nanokümeler, Nanokümelerin elektronik özellikleri, Na-S yapılar.

1. Introduction

Nanoclusters are composed of atoms less than 10 nm (100 Å) in diameter. Because they are an intermediate model between atoms and bulk states, investigations on nanoclusters can help making further developments in nanoscience. They have a wide range of usage areas such as quantum dots [1], quantum devices [2-4], chemical sensors [5], light-emitting diodes [6], catalysts [7-13]. In this view they are potential candidate for next-generation nanotechnology. It is well known that the physical and chemical properties of nanoclusters depend on their size and composition [14]. It has been found that the

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electronic and magnetic properties of nanoclusters can change with their geometric shapes [15]. Therefore it is important to reveal the relationship between geometric and electronic structures of nanoclusters. Some properties of nanoclusters are different from their bulk counterparts. For example, that bulk gold (Au), known to be as inactive as noble gases, shows catalytic properties at nanoscales [16]. Composition is also another factor to change several properties of nanoclusters. Especially bimetallic clusters have different catalytic properties compared to monometallic ones. For example, Cu/Ni alloys are 60 times more active for CO2 activation than pure Cu [17]. Because of all the above, researches on nanoclusters have great importance for nanoscience and nanotechnology.

Computational studies are carried out effectively in examining the geometric, electronic, optical and magnetic properties of different material types since they are cheaper and more detailed than experimental studies. Density Functional Theory (DFT) is one of the most effective methods in computational material studies that are used to investigate the properties of materials on the nanoscale [18-19].

Today, Li-ion batteries are widely used, but both the low capacity of Li-ion batteries and the decrease in Li resources have led scientists to search for new materials. Sodium-sulfur (Na-S) battery has the potential of electrochemical energy storage devices due to their non-toxic behaviour, low cost and abundance of sodium resources [20-24]. They draw attention due to their high energy density (760 Wh/kg), high storage capacity (1309 mAh/g), long life and efficiency approaching 100% [25-29]. Therefore Sodium-sulfur (Na-S) batteries are viewed as one of the most promising alternative materials for next-generations batteries [30].

In this paper Na_xS_y (x+y=5) nanoclusters were investigated by using density functional theory. It is well known that electronic properties are depend on to structural properties. Therefore geometric structure and structural parameters of Na-S alloy nanoclusters were presented in detail. The electronic structure of these nanoclusters was examined in terms of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and the charge densities of Na-S cluster systems. Ionization potential and electron affinity of clusters were also presented.

2. Material and Method

The geometry optimizations and electronic calculations of the Na_xS_y nanocluster models were carried out using density functional theory (DFT) calculations provided by SIESTA package [31]. Atomic orbital basis sets of Double zeta basis plus polarization (DZP) basis sets and Troullier Martins norm-conserving pseudopotentials were used. The exchange-correlation functionals were used as Perdew-Burke-Ernzerhof (PBE) functional within generalized gradient approximation (GGA) [32]. The calculations have been performed at Gamma point, and mesh cut-off has been taken as 300 Ry. The tolerance value in the density matrix has been used of 10^{-5}. The optimized structures were obtained the was used the conjugate-gradient [33-34] algorithm until Hellmann–Feynman forces on each atom were reduced to less than 0.02 eV/ Å. Spin polarization is included in all calculations.

The cohesive energy (E_c) of the clusters was calculated by the formula below.

$$E_c = \frac{E_{total} - xE_{Na} - yE_S}{x + y} \quad (1)$$

where, E_{total} is the total energy of isolated nanocluster, E_{Na} and E_S are the energies of isolated sodium (Na) and isolated sulfur (S) atoms respectively. x and y are the numbers of Na and S atoms in the nanocluster, respectively.

XCrySDen was also used to plot charge densities[35].

Adiabatic ionization potential (IP) and electron affinity (EA) values were calculated as below.

$$IP = E^{+}_{Na_xS_y} - E_{Na_xS_y} \quad (2)$$

and

$$EA = E_{Na_xS_y} - E^{-}_{Na_xS_y} \quad (3)$$

where E_{NaxSy} and E_{NaxSy} are the total energies of cationic and anionic clusters, E_{NaxSy} is the total energy of neutral system.

3. Results

In this study, we have investigated nanoclusters consisting of Na and S atoms named Na_xS_y (x+y=5). First, we optimized several different initial configurations of each cluster system, then the minimum energy structures were determined as the most stable configurations energetically. These ground state energy structures of each nanocluster systems were presented in Figure 1. Na-Na, S-S, and Na-S dimers were also calculated to analyse bond lengths. Na-Na, S-S, and Na-S dimer bond lengths were obtained as 3.08 Å, 1.94 Å, and 2.43 Å, respectively. These results are consistent with the values given in the literature [36-38]. This is also important for the reliability of the pseudopotentials used in the calculations. The bond lenghts of Na_2 and S_2 dimers were presented as 3.079 and 2.03 Å in the experimental studies. Our results were very close to the literature values, therefore we continued our calculations with these pseudopotentials [39-40].

The calculated cohesive energies (E_c) of these dimers are -0.42 eV, -2.84 eV, and -1.39 eV, respectively. According to these values, the S-S bond is the strongest one among them. Here it is worth noting that while Na-Na dimer is nonmagnetic, S-S and Na-S dimers have magnetic moment values of 2.0 μ_B and 1.0 μ_B.

Starting from dimers, the number of Na and S atoms was increased systematically, and equilibrium structures of nanoclusters were obtained. In the first step, we analyze the geometric structure of each cluster. Na_2S nanocluster has L-shape with an angle of 109.52° in the most stable configuration. It is a nonmagnetic nanocluster. However, when the number of Na atoms increased by one, the system has a magnetic nature with the magnetic moment of 1.0 μ_B. This Na_3S nanocluster has a two-dimensional (2D) shape. The S atom has bonded to the top of the Na atom of the Na_3 block, as shown in Figure 1 in its equilibrium structure. The ground state of the Na_4S nanocluster has a three-dimensional (3D) shape like a pyramid and no magnetic moment. When we compare the cohesive energies (E_c), we found that E_c values decrease with the increase of each Na atom. However, when the S atom is increased, as in NaS_2, NaS_3, and NaS_4, E_c values increase. The most stable structure of NaS_2 has a triangle shape and the magnetic moment of 1.0 μ_B. NaS_3 has a 2D shape and 1.0 μ_B magnetic moment, similar with NaS_2 nanocluster. In the ground state structure of the NaS_4 nanocluster, the Na atom is attached to the pyramid structure formed by the S atoms, and the magnetic moment value of this system is 0.99 μ_B.

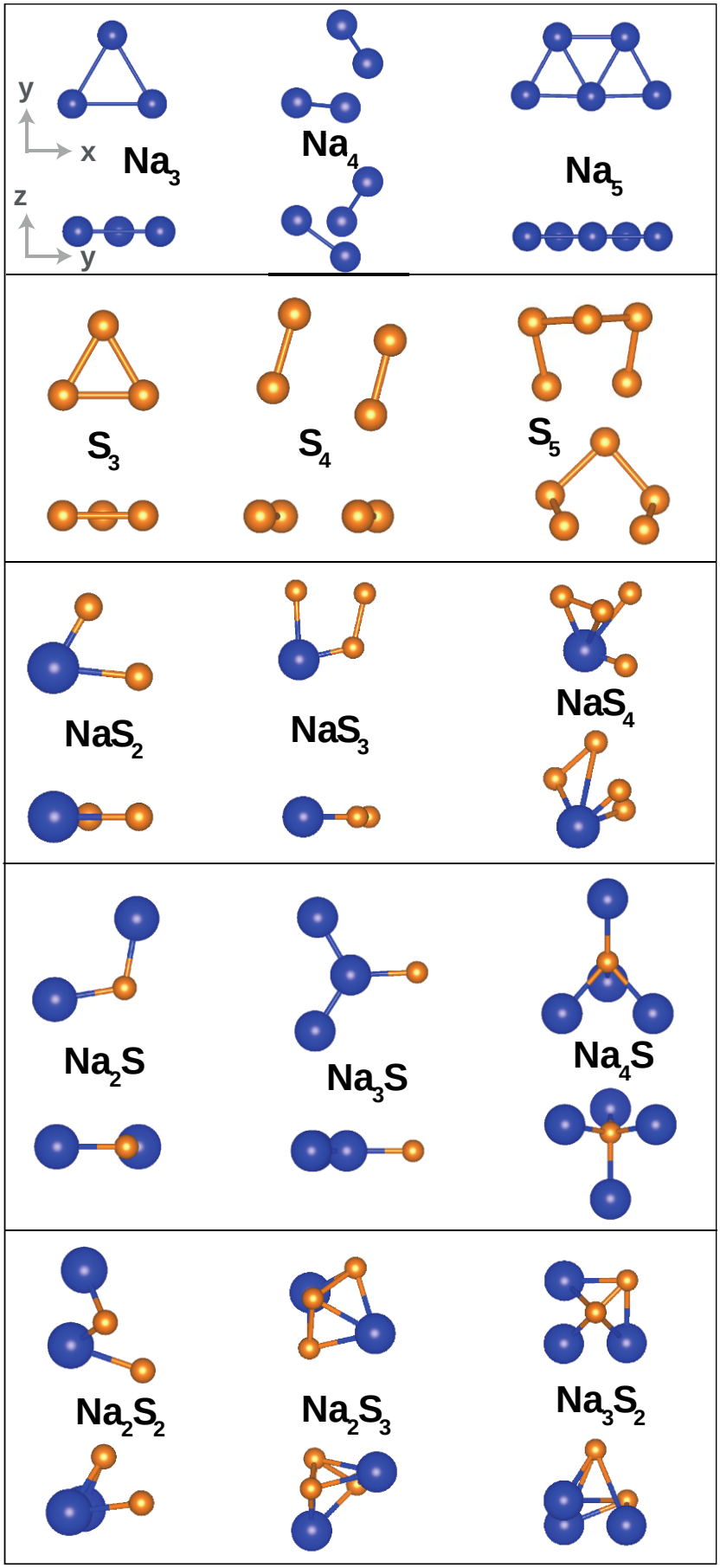

Figure 1. Optimized structures of Na_xS_y systems (x+y=5) from top and side views

For the sake of comparison, pure Na and S nanoclusters were also calculated. Pure Na nanoclusters are the most stable in the nonmagnetic state, and Na-Na bond lengths are higher than that of the dimer. For this reason, charge density plots were drawn to elucidate the presence of bonds between Na atoms (Figure 2). Nanoclustering is confirmed by the charge densities between Na atoms in Na_3 and Na_5 nanoclusters. However, there is no nanoclustering for Na_4. Because there is no charge density between Na_2 dimers, Na_4 prefers to be as Na_2 dimers. This is also confirmed by the excessive distances of Na dimers in Na_4. S_3 and S_5 nanoclusters show high cohesive energy and nonmagnetic behaviour. However, S_4 exhibits a formation in the form of dimers similar to Na_4 . These results agree with the literature [41-43]. In order to investigate paired clusters, 6-atom nanoclusters were also structurally investigated. Na_6 shows a pentagon cluster shape with the average bond length of 3.37 Å However, S_6 is paired as dimers similar to S_4 . In this study, nanoclusters up to 6 atoms were examined and S atoms exist in pairs up to six atoms.

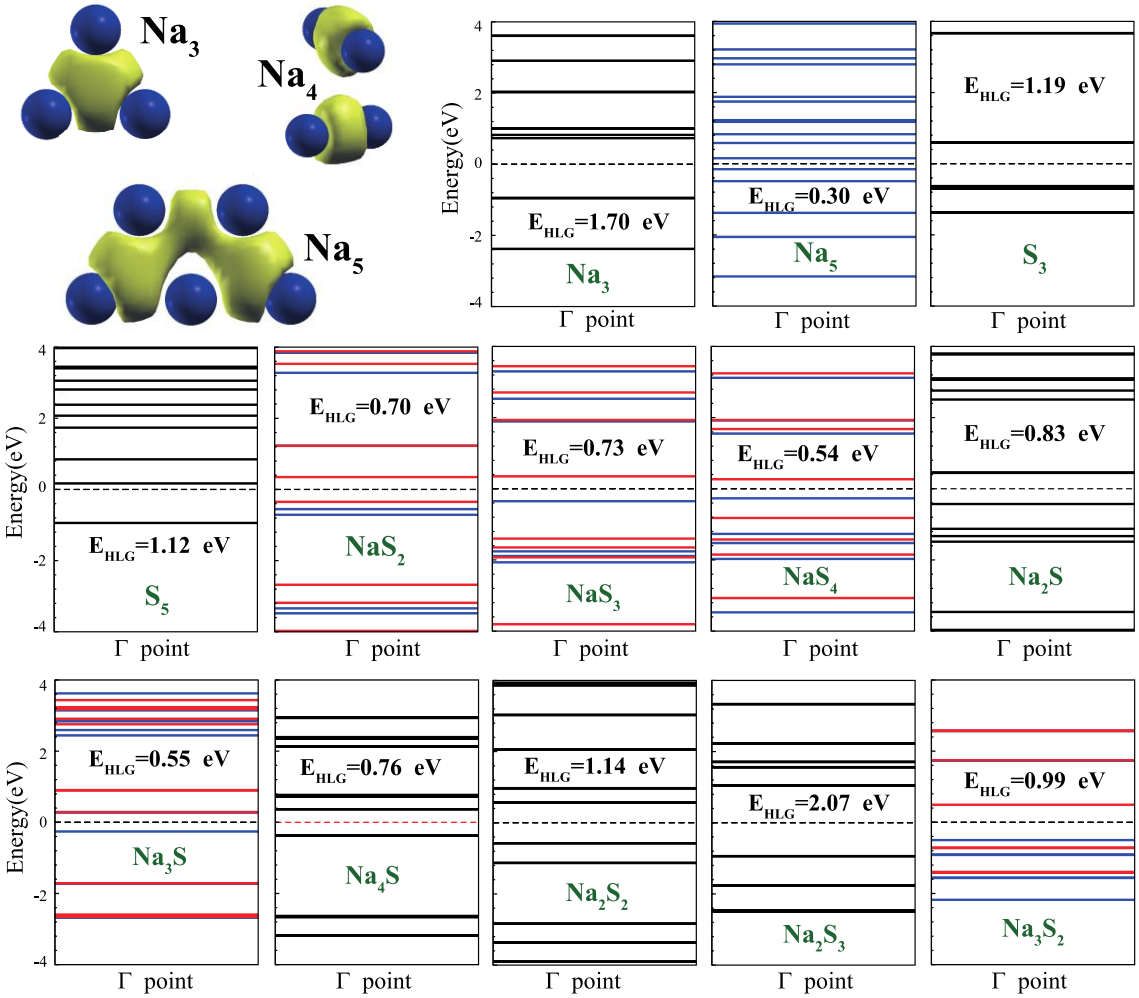

Figure 2. The energy level diagrams of the most stable nanoclusters. Fermi energies were set to zero. The red and blue lines indicate spin up and spin down states, respectively. Spin up and down levels overlap up to 7.2 eV in Na_5 nanocluster.

Na_2S_2 nanocluster has a 3D shape and nonmagnetic behaviour. When one Na atom is added to this structure, the new system Na_3S_2 has a 1.0 μ_B magnetic moment. However, when S atom is added instead of the Na atom, nonmagnetic behaviour continues. The most stable nanoclusters considered in this study are S_5 and NaS_4 energetically.

The HOMO LUMO gap (HLG) is an important parameter related to electronic and photonic properties. The higher HLG indicates higher electronic stability [44]. Therefore HLG values of Na_xS_y systems were also investigated according to the cluster size and composition. The HLG diagrams of the most stable nanoclusters are presented in Figure 2. The highest HLG value was obtained for the Na_2S_3 nanocluster, which means that among the nanoclusters considered in this study, Na_2S_3 needs the most significant energy required for excitation of the system. It can be seen from Table 1 that HLG values decrease with the increase of Na atoms in pure Na_x clusters.

Similarly, the HLG values of S_x clusters decrease with the increase in the number of S atoms. Moreover, addition of S atoms to Na clusters reduces the HLG values generally. The opposite case shows the same result. In other words, adding Na atom to S_x nanoclusters also decreases HLG values and thus decreases the electronic stability of systems. On the other hand, the lowest HLG was found in the Na_5 cluster, which means that Na_5 is the most active nanocluster chemically in the considered systems.

Furthermore, ionization potential (IP) and electron affinity (EA) of Na_xS_y nanoclusters were investigated. Here IP is the energy required to remove an electron from the nanoclusters. EA presents the amount of energy released when an electron is added to a neutral system in order to form a negatively charged nanocluster. A larger IP value indicates more stable structure electronically. However, less value of EA means greater electronic stability. The highest IP values were calculated in S_5, NaS_4 and S_2, which are confirmed by having high cohesive energies. As expected, these clusters show low EA values.

Table 1. The cohesive energy, minimum bond lengths, magnetic moments, HOMO-LUMO gaps, HOMO level, LUMO level, electron affinity and ionization potential values of E_{NaxSy} nanoclusters.

Nanoclusters	E_c(eV)	d(Å)	μ(μ_B)	E_{HLG}(eV)	E_{up}(eV)	E_{down}(eV)	EA(eV)	IP(eV)
NaS	-1.39	d_{Na-S}=2.43	1.00	1.50	1.50	2.5	1.17	5.50
Na_2S	-1.84	d_{Na-Na}=3.90 d_{Na-S}=2.39	0.00	0.83	-	-	0.58	4.21
Na_3S	-1.75	d_{Na-Na}=2.46 d_{Na-S}=2.31	0.99	0.55	0.54	1.98	0.68	2.34
Na_4S	-1.67	d_{Na-S}=2.20	0.00	0.76	-	-	0.62	2.45
NaS_2	-2.62	d_{Na-S}=2.26 d_{S-S}=2.52	1.00	0.70	0.70	1.79	0.73	5.12
NaS_3	-3.06	d_{Na-S}=2.55 d_{S-S}=2.05	1.00	0.72	2.25	1.75	1.12	5.26
NaS_4	-3.21	d_{Na-S}=2.56 d_{S-S}=2.56	0.99	0.54	0.81	1.10	2.04	5.8
Na_2S_2	-2.50	d_{Na-S}=2.51 d_{S-S}=2.51 d_{Na-Na}=2.51	0.00	1.14	-	-	0.63	3.72
Na_3S_2	-2.39	d_{Na-S}=2.55 d_{S-S}=2.56 d_{Na-Na}=2.55	1.00	0.99	2.23	1.20	1.44	2.83
Na_2S_3	-2.95	d_{Na-S}=2.58 d_{S-S}=2.16	0.00	2.07	-	-	0.13	4.49
Na_2	-0.42	d_{Na-Na}=3.08	0.00	1.75	-	-	-0.69	2.95
Na_3	-0.60	d_{Na-Na}=3.46	0.00	1.7	-	-	-0.12	1.61
Na_5	-0.61	d_{Na-Na}=3.44	0.99	0.30	0.30	2.56	-2.11	2.66
S_2	-2.84	d_{S-S}=1.94	2.00	1.33	4.74	3.55	0.80	7.50
S_3	-3.06	d_{S-S}=2.14	0.00	1.23	-	-	1.83	6.98
S_5	-3.48	d_{S-S}=2.08	0.00	1.12	-	-	1.19	7.17

4. Conclusion and Comment

In this study, the calculations have been carried out to gain insights into the electronic and structural properties of Na_xS_y nanoclusters. The most stable Na_xS_y nanoclusters were determined among possible initial geometries. It has been found that the cohesive energies increase depending on the number of Na and S atoms in the clusters. NaS_4 cluster has the highest cohesive energy in binary structures. The NaS dimer has the lowest cohesive energy among alloy systems. However, S_5 and Na_2 have the highest and lowest cohesive energy values, respectively, in the systems considered in this study.

Similarly, it was determined that HLG values which is a parameter related with chemical stability of systems also changed depending on the nanocluster combination. It was observed that Na_2S_3 and NaS_4 nanoclusters have the highest and the lowest HLG values, respectively, among binary systems. IP and EA values of the stable nanoclusters were also calculated. The highest IP and EA values were calculated for NaS_4 among binary nanoclusters.

Author Statement

Ese Akpinar: Investigation, Original Draft Writing, Review and Editing, Visualization.

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Conflict of Interest

As the authors of this study, we declare that we do not have any conflict of interest statement.

Ethics Committee Approval and Informed Consent

As the authors of this study, we declare that we do not have any ethics committee approval and/or informed consent statement.

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