Ab Initio Study of Structural and Electronic Properties of (ZnO)$_n$ “Magical” Nanoclusters $n = (34, 60)$

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Abstract

Density functional theory studies of the structural and electronic properties of nanoclusters (ZnO)$_n$ ($n = 34, 60$) in different geometric configurations were conducted. For each cluster, an optimization (relaxation) of structure geometry was performed, and the basic properties of the band structure were investigated. It was established that for the (ZnO)$_{34}$ nanoclusters, the most stable are fullerene-like hollow structures that satisfy the rule of six isolated quadrangles. For the (ZnO)$_{60}$ nanoclusters, different types of isomers, including hollow structures and sodalite-like structures composed from (ZnO)$_{12}$ nanoclusters, were investigated. It was determined that the most energetically favorable structure was sodalite-type structure composed of seven (ZnO)$_{12}$ clusters with common quadrangle edges.

Keywords: Structure, Electronic properties, ZnO nanoclusters, The density functional theory

Background

Wide-gap semiconductors are perspective materials to use in optoelectronic systems, ultraviolet lasers, field emitters, and other devices of new generation. It is said that not only the composition but also the nature of the nanostructures give new properties to the material. Atomic clusters and fullerenes are the building blocks of the new nanostructured materials which are a subject of intensive research with the prospect of applications in optoelectronics. Special interest is given to the clusters of zinc oxide which, with its variety of interesting physical and chemical properties, such as anisotropic crystalline structure, semiconducting properties even with a wide band gap, amphoteric chemical properties, piezoelectric properties, biocompatibility, and high exciton energy, is quite unique [1, 2]. A large number of studies have been devoted to understand its structure, processes of formation and properties, and the behavior of its nanoparticles [3–5]. Thin films and nanostructures based on ZnO, are candidates for creating ultrathin displays, UV emitters and switches [6, 7], and gas sensors [8].

The main methods of studying the electronic properties of atomic clusters are quantum mechanics methods, such as restricted and unrestricted Hartree-Fock method, the density functional theory, and molecular dynamics. To address this problem is to use theoretical methods to study model clusters, particularly in structures that lie between molecular and bulk. Nonetheless, the structure design still allows for many geometric possibilities to exist, and it is challenging to find a true global minimum energy structure.

Numerous theoretical studies of (ZnO)$_n$ clusters have explored optimized geometries for a range of cluster sizes, and a prevalent theoretical observation shows that a fullerene-like structures are more stable in the case for smaller-sized clusters, while a wurzite-like structure shows increased stability for larger clusters [9]. A core-cage structure for (ZnO)$_{34}$ has been proposed as the most stable in [10, 11], while [12] have predicted the hollow cage structures formed by (ZnO)$_2$ squares and (ZnO)$_3$ hexagons. In the case of (ZnO)$_{60}$, the studies [13, 14] revealed an energetically preferred sodalite motif, while nested cage configuration was predicted to be the most stable in [10, 11]. Such differences indicate that there is a strong dependence of the calculated binding energy on the details of the computational framework adopted.

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This paper presents a theoretical investigation of structural and electronic properties of clusters \((\text{ZnO})_n\) \((n = 34, 60)\), within the density functional theory, in different geometric configurations to establish which type of structure is the most energetically favorable.

**Methods**

Ab initio calculations within density functional were performed, which have been successfully used for studying properties of nanoscale structures such as nanotubes and nanowires [15–18]. For structural models, the optimization
In order to determine the most stable structure for Results and Discussion
in the Monkhorst-Pack k-point set [21]. Integration in the first Brillouin zone was conducted including
d electrons were divided in the basis of atomic orbitals, in-
system will be stable as well. Electronic functions of results say that the cluster model is stable, then the real
paper makes it possible to argue that if calculation re-
compared to the experimental data. Using GGA in this
correlation interaction within local density approxima-
tions. For describing the exchange-correlation energy of the
electronic subsystem, the generalized gradient approxi-
mation (GGA) in a parameterization of Perdew, Burke,
and Ernzerhof was used [20]. It is known that the use of
this approach in the calculation leads to underestimation
of the quantitative value of the binding energy. On the
other hand, an alternative description of the exchange-
correlation interaction within local density approxima-
(In Table 1, the geometry parameters of (ZnO) 34 and
(ZnO)₆₀ nanoclusters are presented. They include
minimal and maximal interatomic distances (d, Å) be-
tween Zn and O atoms in quadrangles and hexagons,
respectively, diameter (distance between the edges of a
cluster D, Å) of the clusters, and range of values for angles in quadrangles and hexagons.
For all clusters, the maximum value of interatomic
distance between Zn and O atoms is set for joint edge
between quadrangle and hexagon. For angle values, we
established that smaller angles correspond to oxygen
atoms and bigger angles correspond to zinc atoms.
In Table 2, we present the properties of electronic spectra of (ZnO) 34 and (ZnO)₆₀ nanoclusters.
In the first column, we have total energy per formula unit of each isomer, second column is the difference bet-
tween total energies with respect to the isomer with low-
est energy separately for (ZnO) 34 and (ZnO)₆₀, third
column is binding energy per formula unit, and band
gap energy is given in the fourth column. Analysis of the
energy values shows that the most energetically favorable
(ZnO) 34 nanoclusters are fullerene-like hollow
structures. All such structures that meet the rule of isolated
quadrangles are close in value of binding energy. The
calculated values are larger than the bulk-binding energy
of ZnO (–7.52 eV per formula unit) as expected due to
surface energy effects. Confirmation of high stability for
these clusters is the higher values of band gap between the
highest occupied molecular orbital (HOMO) and
lowest unoccupied molecular orbital (LUMO) because
such clusters are chemically inert (Fig. 3).

| Isomer          | d, Å in quadrangles | d, Å in hexagons | D, Å   | α, in quadrangles | α, in hexagons |
|-----------------|--------------------|-----------------|-------|------------------|----------------|
| (ZnO)₃₄₋₂₈     | 1.945–1.984        | 1.886–1.984     | 14.827| 84.761–91.960    | 113.612–132.058|
| (ZnO)₃₄₋₄₃     | 1.938–1.994        | 1.881–1.994     | 13.013| 85.315–93.708    | 117.331–122.628|
| (ZnO)₃₄₋₁₅     | 1.938–1.992        | 1.912–1.992     | 13.018| 84.791–93.952    | 107.145–128.283|
| (ZnO)₆₀₋₅₀₋₉₀₋₅₀ | 1.931–2.284       | 1.884–2.284     | 15.659| 83.927–97.183    | 106.583–134.193|
| (ZnO)₆₀₋₂₅      | 1.963–1.968        | 1.896–1.968     | 16.342| 85.782–92.117    | 109.977–129.234|
| (ZnO)₆₀₋₂₄      | 1.964–1.970        | 1.890–1.970     | 16.112| 85.622–92.846    | 110.167–129.060|

In Table 1, the geometry parameters of (ZnO) 34 and
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minimal and maximal interatomic distances (d, Å) be-
tween Zn and O atoms in quadrangles and hexagons,
respectively, diameter (distance between the edges of a
cluster D, Å) of the clusters, and range of values for angles in quadrangles and hexagons.
For all clusters, the maximum value of interatomic
distance between Zn and O atoms is set for joint edge
between quadrangle and hexagon. For angle values, we
established that smaller angles correspond to oxygen
atoms and bigger angles correspond to zinc atoms.

Results and Discussion
In order to determine the most stable structure for “magic” clusters (ZnO)₃₄ (Fig. 1) and (ZnO)₆₀ (Fig. 2),
we examined a number of isomers. Among them were hollow fullerene-like structures and cage structures
which met the rule of six isolated quadrangles.
There were also sodalite-like structures composed of
structural units of (ZnO)₁₂. For each cluster, geometry
optimization was performed and band structure
properties were analyzed.

The binding energy of ZnO cluster as per formula unit was calculated using the formula [22]:

\[ E_b = E(\text{Zn}) + E(\text{O}) - 1/n * E_n, \]

where \( n \) is the number of ZnO molecules in a cluster, \( E(\text{Zn}) \) and \( E(\text{O}) \) the basic energy states of atoms of Zn and O, and \( E_n \) the total energy of a (ZnO)_n cluster.

| Isomer          | \( E_{\text{total/ZnO}}, \text{eV} \) | \( \Delta E/\text{ZnO}, \text{eV} \) | \( E_b/\text{ZnO}, \text{eV} \) | \( E_g, \text{eV} \) |
|-----------------|---------------------------------|----------------|-----------------|----------------|
| (ZnO)₃₄₋₂₈     | −50461.66                       | 0              | −6.764          | 2.275          |
| (ZnO)₃₄₋₄₃     | −50461.64                       | 0.02           | −6.748          | 2.151          |
| (ZnO)₃₄₋₁₅     | −50461.62                       | 0.04           | −6.724          | 2.048          |
| (ZnO)₆₀₋₅₀₋₉₀₋₅₀ | −50461.54                     | 0.12           | −6.645          | 1.124          |
| (ZnO)₆₀₋₂₅      | −50461.744                      | 0              | −6.847          | 1.93           |
| (ZnO)₆₀₋₂₄      | −50461.734                      | 0.01           | −6.836          | 2.184          |
| (ZnO)₆₀₋₂₅      | −50461.732                      | 0.012          | −6.835          | 2.4            |
| (ZnO)₆₀₋₂₄      | −50461.699                      | 0.045          | −6.802          | 0.982          |
In the case of \((\text{ZnO})_{60}\) nanoclusters, we confirmed that the most stable among them is the sodalite structure which is built from 7 \((\text{ZnO})_{12}\) nanoclusters with joint quadrangle edges. In previous studies [23], it was shown that the \((\text{ZnO})_{12}\) cage-like structure (truncated octahedron) proved to be very stable compared to other small \((\text{ZnO})_{n}\), suggesting that it can be used as a building block for creating ZnO nanostructures. The values for HOMO and LUMO for sodalite, as well as the other \((\text{ZnO})_{60}\) structural isomers, are presented in Fig. 4.

In Fig. 5, partial densities of states from the contributions of different orbital components for each \((\text{ZnO})_{34}\) nanocluster for valence band (left) and conduction band (right) are presented. Graphs I, III, and V demonstrate s, p, and d states of Zn atoms; graphs II, IV, and VI correspond to s and p states of O atoms.

The valence band of each cluster between \(-7.0\) and \(-4.0\) eV consist mainly from 3d states of Zn and O 2p states. The bands between \(-4.0\) and 0 eV are composed from O 2p states, Zn 3d states, and in smaller scale, Zn 3p and 3s states. The conduction band, on the other hand, between 1 and 5 eV consists mainly from Zn 4s and O 2p and O 2s states.

Figure 6 shows partial densities of states from the contributions of different orbital components for each \((\text{ZnO})_{60}\) nanocluster for valence band (left) and conduction band (right). Graphs I, III, and V show s, p, and d states of Zn atoms, and graphs II, IV, and VI correspond to s and p states of O atoms.

The valence band of each cluster between \(-7.0\) and \(-4.0\) eV, like in the case with \((\text{ZnO})_{34}\) nanoclusters, is composed from 3d states of Zn and O 2p states. The bands between \(-4.0\) and 0 eV consist mainly from O 2p states, Zn 3d states, and in smaller scale, Zn 3p and 3s states. The conduction band between 1 and 5 eV consists mainly from Zn 4s and O 2p and O 2s states.
Conclusions
Density functional theory studies of the structural and electronic properties of \((\text{ZnO})_n\) \((n = 34, 60)\) nanoclusters were performed. Optimization of structure geometry, as well as the band structure research, was performed. It was established that for the \((\text{ZnO})_{34}\) nanoclusters, the most stable are the fullerene-like hollow structures that satisfy the rule of six isolated quadrangles. For the \((\text{ZnO})_{60}\) nanoclusters, different types of isomers, including hollow structures and sodalite-like structures composed...
from (ZnO)$_{12}$ nanoclusters, were investigated. It was determined that the most energetically favorable structure was the sodalite-type structure composed of seven (ZnO)$_{12}$ clusters with common quadrangle edges.

**Authors’ Contribution**

All the authors took part in solving the problem under study. They read and approved the final manuscript.

**Competing Interests**

The authors declare that they have no competing interests.

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