First principle study of structure and electronic properties of $(ZnO)_n$ (n= 96, 120) nanoclusters

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Introduction

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. 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 wurtzite-like structure shows increased stability for larger clusters [1]. In our previous studies we determined structural and electronic properties of $(ZnO)_{12}$ nanoclusters as well as "magic" nanoclusters $(ZnO)_n$, n=(34, 60) [2, 3]. In this study we investigate which type of structure is the most favourable for $(ZnO)_{96}$ and $(ZnO)_{120}$ nanoclusters as well as determine their electronic properties.

Methods of calculation

Ab initio calculations within density functional were performed, which have been successfully used for studying properties of nanoscale structures such as nanotubes and nanowires. For structural models, the optimization (relaxation) of the geometry (finding the equilibrium of ions coordinates, in which the full electronic energy of the system is minimal) was carried. Optimization was calculated using the effective algorithm of delocalized internal coordinates. The convergence of the relaxation procedures deemed reached when the magnitude of forces acting on atoms was less than 0.05 eV/Å.

For describing the exchange-correlation energy of the electronic subsystem, the generalized gradient approximation with Hubbard corrections (GGA)+U in a parameterization of Perdew, Burke, and Ernzerhof was used. Unfortunately, for strongly correlated materials including ZnO, standard DFT with GGA (PBE) functional will underestimate the bandgap. To accurately describe the electronic spectrum, two Hubbard corrections were selected the studied objects: for d-orbitals Zn (Ud) and p-orbitals O (Up). Electronic functions of electrons were divided in the basis of atomic orbitals, including d-orbitals. Core electrons had been described using effective potential with regard to relativistic corrections. Integration in the first Brillouin zone was conducted in the Monkhorst-Pack k-point set.

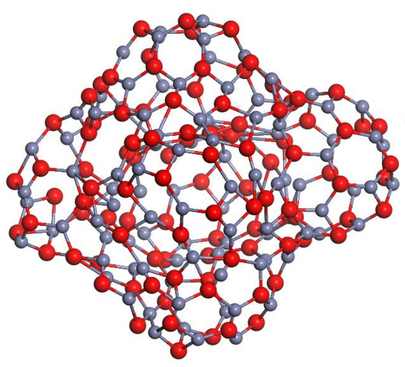
Results

In order to determine the most stable structure for nanoclusters $(ZnO)_{96}$ (Fig. 1) and $(ZnO)_{120}$ (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.

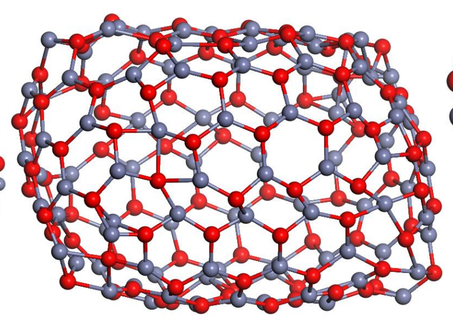
The binding energy of ZnO cluster as per formulaunit was calculated using the formula:

$$E_b = E(Zn) + E(O) - 1/n*E_n,$$

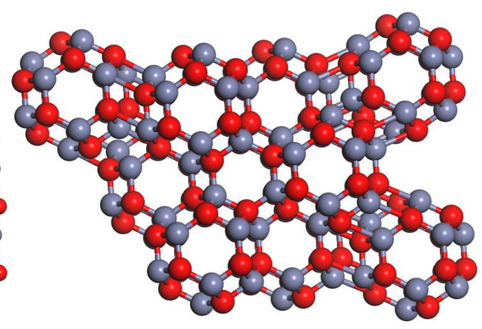
where n is the number of ZnO molecules in a cluster, E(Zn) and E(O) the basic energy states of atoms of Zn and O, and E_n the total energy of a $(ZnO)_n$ n=(96, 120) nanocluster.



$(ZnO)_{96}$-A

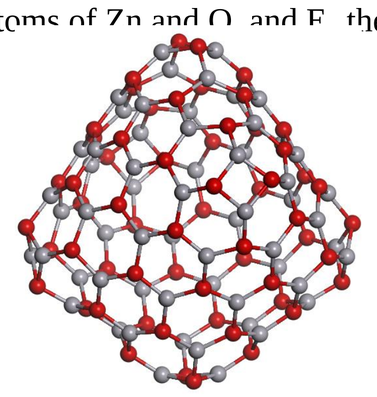


$(ZnO)_{96}$-B

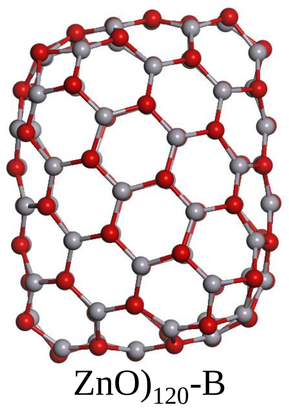


$(ZnO)_{96}$-sodalite

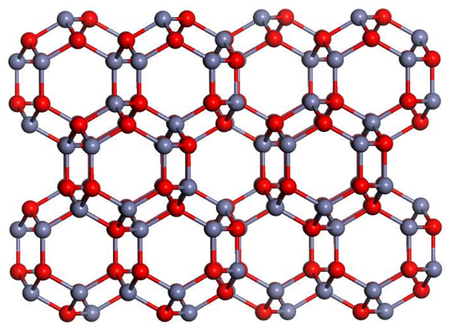
Fig.1 Optimized sturctures of $(ZnO)_{96}$ nanoclusters



ZnO)$_{120}$-A



ZnO)$_{120}$-B



$(ZnO)_{120}$-sodalite

Fig.2 Optimized sturctures of $(ZnO)_{120}$ nanoclusters

In Table 1, the geometry parameters of $(ZnO)_{96}$ and $(ZnO)_{120}$ nanoclusters are presented. They include minimal and maximal interatomic distances between Zn and O atoms in quadrangles (d_1, Å) and hexagons (d_2, Å), respectively, diameter (distance between the edges of a cluster D, Å) of the clusters, and range of values for angles in quadrangles (α_1, °) and hexagons (α_2, °). In Table 2, we present the properties of electronic spectra of $(ZnO)_{96}$ and $(ZnO)_{120}$ nanoclusters. In the first column, we have total energy per formula unit of each isomer, second column is the difference between total energies with respect to the isomer with lowest energy separately for $(ZnO)_{96}$ and $(ZnO)_{120}$, third column is binding energy per formula unit, and band gap energy is given in the fourth column.

Table 1 Geometry parameters of $(ZnO)_{96}$ and $(ZnO)_{120}$ nanoclusters

Isomer	d_1, Å	d_2, Å	D, Å	α_1, °	α_2, °
$(ZnO)_{96}$-A	1,847-1,918	1,871-1,929	20,238	83,475-92,167	111,475-132,167
$(ZnO)_{96}$-B	1,798-1,947	1,898-1,977	19,847	86,715-91,837	118,291-127,672
$(ZnO)_{96}$-sodalite	1,817-1,983	1,892-1,961	21,075	82,462-91,834	109,394-132,503
$(ZnO)_{120}$-A	1,857-1,942	1,757-1,894	23,184	84,371-93,492	114,506-137,276
$(ZnO)_{120}$-B	1,793-1,934	1,838-1,966	22,848	85,974-94,630	107,349-128,408
$(ZnO)_{96}$-sodalite	1,954-1,982	1,852-1,978	24,342	86,741-92,273	110,415-128,374

Table 2 Electronic properties of $(ZnO)_{96}$ and $(ZnO)_{120}$ nanoclusters

Isomer	E_{total}/ZnO, eV	ΔE/ZnO, eV	E_b/ZnO, eV	E_g, eV
$(ZnO)_{96}$-A	-51074,52	0	-8,714	3,98
$(ZnO)_{96}$-B	-51074,49	0,03	-8,756	3,87
$(ZnO)_{96}$-sodalite	-51074,46	0,06	-8,738	4,06
$(ZnO)_{120}$-A	-51074,88	0	-9,103	4,12
$(ZnO)_{120}$-B	-51074,86	0,02	-9,074	3,95
$(ZnO)_{96}$-sodalite	-51074,83	0,05	-9,248	4,26

Conclusions

Density functional theory studies of the structural and electronic properties of $(ZnO)_n$ (n = 96, 120) nanoclusters were performed. Optimization of structure geometry, as well as the band structure research, was performed. It was established that for the $(ZnO)_{96}$ nanoclusters, the most stable are the fullerene-like hollow structures that satisfy the rule of six isolated quadrangles. For the $(ZnO)_{120}$ 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 fourteen $(ZnO)_{12}$ clusters with common quadrangle edges.

References

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