Biointerface Research in Applied Chemistry
Open-Access Journal (ISSN: 2069-5837)

Article
Volume 13, Issue 2, 2023, 196
https://doi.org/10.33263/BRIAC132.196

$(ZnO)_{60}$: a UV Active Magic Nanocluster under DFT Study

Bijal R. Mehta [1], Esha V. Shah [1], Debesh R. Roy [1,*]

[1] Materials and Biophysics Group, Department of Physics, Sardar Vallabhbhai National Institute of Technology, Surat 395007, India
* Correspondence: drr@phy.svnit.ac.in (D.R.R.);

Scopus Author ID 9275387500
Received: 13.01.2022; Accepted: 4.03.2022; Published: 7.04.2022

Abstract: The minimized energy geometries of $(ZnO)_{6n}$ (n= 8 to 11) clusters were optimized using a systematic approach using density functional theory (DFT). In addition to our previously identified magic nanocluster $(ZnO)_{42}$, the present work reports a novel ultraviolet active magic nanocluster $(ZnO)_{60}$. $(ZnO)_{60}$ is identified as an exceptionally stable 'magic' nanocluster upon investigation on its electronic properties in terms of the HOMO-LUMO energy gap (HLG), ionization potential (IP), electron affinity (EA), chemical hardness (η), electrophilicity index (ω) and energy gain of formation (ΔE). Interestingly, as the stoichiometry of (ZnO) in $(ZnO)_{6n}$ series increases in the multiple of six, the energy gain (ΔE) of ZnO clusters demonstrates a zigzag pattern, identifying 'magic' $(ZnO)_{60}$ nanocluster. Furthermore, the optical absorption spectra analysis show $(ZnO)_{60}$ is active in the UV-A region. The developed magic nanocluster in the present work is expected to find useful applications as quantum dots and cluster assembled materials in semiconductor, optoelectronics, and biomedicinal domains.

Keywords: density functional theory; ZnO nanocluster; magic cluster.

1. Introduction

The shrinkage of material dimensions to a few nanometres discloses their world of unique and exceptional properties. The structure and properties of these nano-sized materials varied extensively from their corresponding bulk materials due to the occurrence of the quantum confinement effect and increased surface-to-volume ratio at the nanoscale [1-3]. As the nano-world unveils fascinating material properties, the discipline of nanoscience and nanotechnology has become an integral part of materials research in recent decades. The remarkable progress in the theoretical and experimental techniques now aids the researchers in extending their scrutiny for the growth and characterization of materials beyond the nanoscale towards the sub-nanoscale and atomic scale. Hence the study of atomic clusters and their affinity to bond with specific atomic kinds over others to combine into nanoparticles aids in identifying the constitution and reason for their explicit properties.

Zinc oxide (ZnO) is an up-and-coming, versatile, promising material due to its direct bandgap of 3.3 eV at room temperature and large exciton binding energy of 60 meV for developing exciton-based optoelectronic devices such as light-emitting diode (LEDs) and photovoltaic cells [4,5]. In general, due to the quantum confinement effect, quantum dots have unique physical properties, which have potential in nanoscale device applications such as next-

generation electronic and optoelectronic devices (including LEDs and solar cells) [6-12]. Furthermore, the method for ZnO nanostructure synthesis has diverse methods, including low-cost and low-temperature techniques. ZnO has potential applications in ultraviolet lasers, photodetectors, dye-sensitized solar cells, and biomedical applications [13-19]. Recently, our group has developed a visibly active magic nanocluster, namely $(ZnO)_{42}$ [20].

In the present study, we have performed a detailed study on the structural, electronic, and optical properties of $(ZnO)_{6n}$ (n=8 to 11) atomic magic clusters using the density functional theory (DFT). The DFT investigation on relatively small $(ZnO)_{6n}$ (n=1 to 7) clusters have been studied by our group in the past [20]. The electronic parameters, viz. HOMO-LUMO gap (HLG), ionization potential (IP), electron affinity (EA), chemical hardness (η), electrophilicity index (ω), and energy gain (ΔE) account for the stability and reactivity of the considered $(ZnO)_{6n}$ clusters. Finally, we report optical absorption activities of the $(ZnO)_{60}$ cluster through simulation of UV-Vis spectrums.

2. Theory and Computation

The density functional theory computations [21-23] of $(ZnO)_{6n}$ (n=8 to 11) nanoclusters were conducted employing the GAUSSIAN 09 program package [24]. The geometry optimization and various physicochemical properties of $(ZnO)_{6n}$ (n=8 to 11) nanoclusters considered were carried out using hybrid B3LYP functional with LANL2DZ basis set [25,26]. A molecular orbital method is adapted using a linear combination of atomic orbitals (LCAO) to examine the electronic structure.

The energy gap between the ground state and the first excited state resembles the HOMO-LUMO gap (*HLG*) and is represented by

$$HLG = \epsilon_{LUMO} - \epsilon_{HOMO} \quad \text{a)}$$

According to Koopmans' theorem [21], ionization potential (I.P.) and electron affinity (E.A.) are defined as:

$$IP \approx -\epsilon_{HOMO} \quad ; \quad EA \approx -\epsilon_{LUMO} \quad \text{b)}$$

R.G. Peasrson [27, 28] proposed chemical hardness (η) as a parameter of chemical stability for an chemical molecule as:

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} \quad \text{c)}$$

The electrophilicity index (ω) [29] is proposed to assess the global reactivity of a molecule and is defined as:

$$\omega = \mu^2/2\eta \quad \text{d)}$$

The energy gain (ΔE) in assembling ZnO clusters to $(ZnO)_{6(n-1)}$ (n = 8, 9, 10, 11) cluster in forming $(ZnO)_{6n}$ cluster is calculated as:

$$\Delta E = \left[E\{(Zno)_{6(n-1)}\} + 6 \times E\{(Zno)_1\} - E\{(Zno)_{6n}\}\right] \quad \text{e)}$$

3. Results and Discussion

Figure 1, represented below, shows the optimized structures for the developed zinc oxide nanocluster in the present work, viz., $(ZnO)_{60}$. It may be noted that $(ZnO)_{60}$ nanocluster shows unique closed triangular fullerene-like structures composed of hexagons in the body and distinguished tetragons at the three vertices.

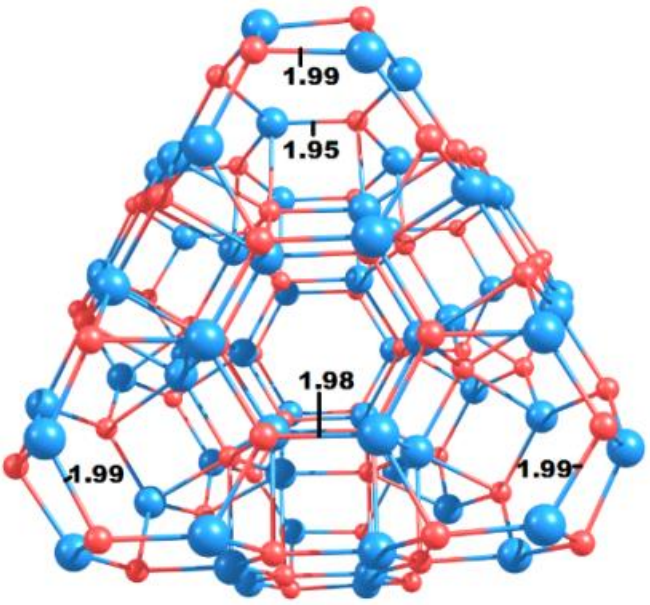

Figure 1. Optimized structure of $(ZnO)_{60}$ nanocluster.

Table 1. Electronic parameters, viz. HOMO-LUMO gap (HLG), Ionization potential (IP), Electron Affinity (EA), Chemical Hardness (η), Electrophilicity Index (ω), and Energy Gain (ΔE) of the zinc oxide $(ZnO)_n$ nanoclusters.

No.	$(ZnO)_n$	HLG	IP	EA	η	ω	ΔE
1	$(ZnO)_{48}$	3.89	6.64	2.75	1.95	5.67	1.18
2	$(ZnO)_{54}$	3.86	6.61	2.76	1.93	5.69	1.19
3	$(ZnO)_{60}$	3.78	6.75	2.98	1.89	6.27	1.50
4	$(ZnO)_{66}$	3.88	6.60	2.72	1.94	5.60	0.93

It is very interesting to note a zigzag behavior in all the considered electronic parameters (HLG, IP, EA, η, and ω) along with the growth of $(ZnO)_6$ unit in the $(ZnO)_{6n}$ series from Table 1, and better visualization is presented in Figure 2.

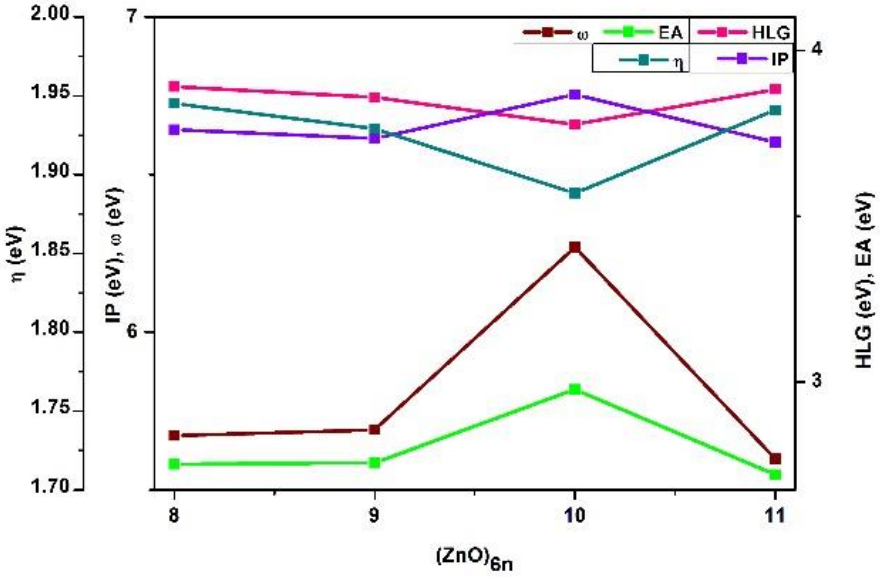

Figure 2. Electronic properties of the zinc oxide nanoclusters, viz. $(ZnO)_{6n}$ (n = 8 to 11).

Although $(ZnO)_{48}$ exhibits the highest HLG and chemical hardness values, the ability of $(ZnO)_{60}$ to attract electrons is high compared to all other considered zinc oxide atomic clusters as it shows maximum electron affinity value in the series. The maximum electrophilicity index of $(ZnO)_{60}$ indicates its good reactivity and ability to bind with similar

atomic clusters or molecules. The energy gain (ΔE) of $(ZnO)_{60}$ is found to be 1.50 eV, as highest among all considered zinc oxide atomic clusters, identifying it as an unusually stable 'magic cluster' in the series. The conceptual DFT-based electronic properties are also very reliable on many occasions in the past [30-32].

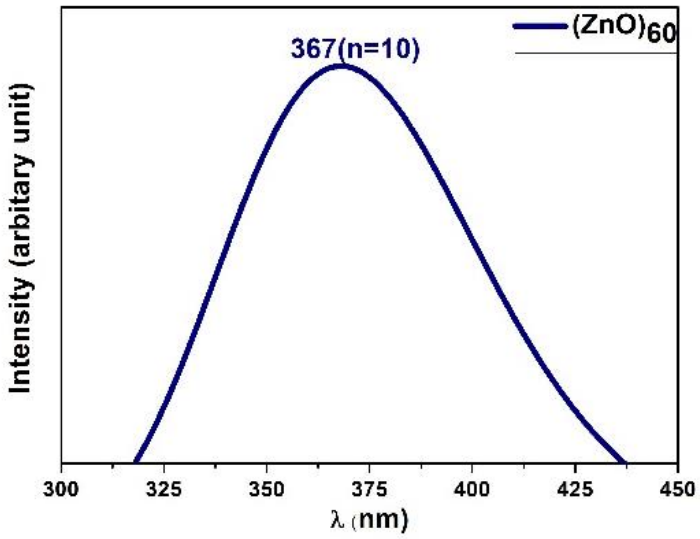

Figure 3. Optical absorption spectra of $(ZnO)_{60}$ nanocluster.

The simulated optical absorption spectra (UV-Vis) of $(ZnO)_{60}$ nanocluster are provided in Figure 3. Interestingly, the magic $(ZnO)_{60}$ nanocluster reveals to be a UV-A active (λ=367 nm) compound in the series, which might find possible future applications in optoelectronics in air/water purification systems as intense disinfectants, etc. The magic stability and active optical nature also may find the useful antibacterial activity of $(ZnO)_{60}$ nanocluster against various bacterial strains and also as a possible drug carrier.

4. Conclusions

In summary, the present work reports a novel 'magic' $(ZnO)_{60}$ nanocluster with exceptional stability and affinity and its UV active nature, under density functional investigation. The electronic properties of the series of $(ZnO)_{6n}$ (n=8 to 11) nanoclusters are assessed with various quantum chemical parameters of DFT. The developed 'magic' $(ZnO)_{60}$ nanocluster may certainly find novel semiconductor and optoelectronic and biomedicinal applications in the future in its quantum dots and assembled materials.

Funding

DRR is thankful for a research grant from SERB, New Delhi (Grant No. CRG/2020/002634).

Acknowledgments

DRR is thankful for the research grant, and BRM is thankful for the fellowship from SERB, New Delhi (Grant No. CRG/2020/002634).

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Bhusan, B. 'Introduction to Nanotechnology' in Handbook of Nanotechnology (3rd Ed.), Bhushan, B. (Ed.), Springer-Verlag, NY, **2010**, pp. 1-13.
2. Jena, P.; Castleman, A.W. 'Introduction to Atomic Clusters' in Nanoclusters: A Bridge Across Disciplines, Jena, P.; Castleman, Jr., A.W. (Eds.), Elsevier, Amsterdam, **2010,** pp. 1-36.
3. Berry, R. S. 'Quantum and Classical Size Effects in Thermodynamic Properties' in Quantum Phenomena in Clusters and Nanostructures, Khanna, S. N.; Castleman, Jr., A. W. (Eds.)New York, USA: Springer, **2003**, pp. 7-28.
4. Sun, X.W.; Huang, J. Z.; Wang, J. X.; Xu, Z. A ZnO Nanorod Inorganic/Organic Heterostructure Light-Emitting Diode Emitting at 342 nm. *Nano Lett.* **2008**, *8*, 1219–1223.
5. Cole, Jesse J.; Wang, Xinyu; Knuesel, Robert J.; Jacobs, Heiko O. Integration of ZnO Microcrystals with Tailored Dimensions Forming Light Emitting Diodes and UV Photovoltaic Cells. *Nano Letters Volume* **2008**, *8*, 1477–1481, https://doi.org/10.1021/nl0804809.
6. Mishra, G.K.; Kant, R. Theory for Potential of Zero Charge and Capacitance on Metals with Nanocorrugated Steps. *The Journal of Physical Chemistry C* **2021**, *125*, 25774-25783, http://doi.org/10.1021/acs.jpcc.1c05941.
7. Jiao, L.; Zhu, J.; Zhang, Y.; Yang, W.; Zhou, S.; Li, A.; Xie, C.; Zheng, X.; Zhou, W.; Yu, S.H.; et al. Non-Bonding Interaction of Neighboring Fe and Ni Single-Atom Pairs on MOF-Derived N-Doped Carbon for Enhanced CO(2) Electroreduction. *Journal of the American Chemical Society* **2021**, *143*, 19417-19424, http://doi.org/10.1021/jacs.1c08050.
8. Xu, H.; Zhou, X.; Lin, X.; Wu, Y.; Lin, X.; Qiu, H.-J. Electronic Interaction between In Situ Formed RuO2 Clusters and a Nanoporous Zn3V3O8 Support and Its Use in the Oxygen Evolution Reaction. *ACS Applied Materials & Interfaces* **2021**, *13*, 54951-54958, http://doi.org/10.1021/acsami.1c15119.
9. Septiani, N.L.W.; Saputro, A.G.; Kaneti, Y.V.; Maulana, A.L.; Fathurrahman, F.; Lim, H.; Yuliarto, B.; Nugraha; Dipojono, H.K.; Golberg, D.; et al. Hollow Zinc Oxide Microsphere–Multiwalled Carbon Nanotube Composites for Selective Detection of Sulfur Dioxide. *ACS Applied Nano Materials* **2020**, *3*, 8982-8996, http://doi.org/10.1021/acsanm.0c01707.
10. Wang, X.; Yao, F.; Xu, P.; Li, M.; Yu, H.; Li, X. Quantitative Structure–Activity Relationship of Nanowire Adsorption to SO2 Revealed by In Situ TEM Technique. *Nano Letters* **2021**, *21*, 1679-1687, http://doi.org/10.1021/acs.nanolett.0c04481.
11. Hussain, S.; Chatha, S.A.S.; Hussain, A.I.; Hussain, R.; Yasir Mehboob, M.; Mansha, A.; Shahzad, N.; Ayub, K. A Theoretical Framework of Zinc-Decorated Inorganic $Mg_{12}O_{12}$ Nanoclusters for Efficient $COCl_2$ Adsorption: A Step Forward toward the Development of $COCl_2$ Sensing Materials. *ACS Omega* **2021**, *6*, 19435-19444, http://doi.org/10.1021/acsomega.1c01473.
12. Hussain, S.; Chatha, S.A.S.; Hussain, A.I.; Hussain, R.; Yasir Mehboob, M.; Mansha, A.; Shahzad, N.; Ayub, K. In Silico Designing of $Mg_{12}O_{12}$ Nanoclusters with a Late Transition Metal for NO2 Adsorption: An Efficient Approach toward the Development of NO_2 Sensing Materials. *ACS Omega* **2021**, *6*, 14191-14199, http://doi.org/10.1021/acsomega.1c00850.
13. Rasouli, Z.; Irani, M.; Jafari, S.; Ghavami, R. Study of interaction of metal ions with methylthymol blue by chemometrics and quantum chemical calculations. *Scientific Reports* **2021**, *11*, 6465, http://doi.org/10.1038/s41598-021-85940-w.
14. Vrankić, M.; Šarić, A.; Nakagawa, T.; Ding, Y.; Despotović, I.; Kanižaj, L.; Ishii, H.; Hiraoka, N.; Dražić, G.; Lützenkirchen-Hecht, D.; et al. Pressure-induced and flaring photocatalytic diversity of ZnO particles hallmarked by finely tuned pathways. *Journal of Alloys and Compounds* **2022**, *894*, 162444, https://doi.org/10.1016/j.jallcom.2021.162444.
15. Yadav, P.V.K.; Ajitha, B.; Kumar Reddy, Y.A.; Sreedhar, A. Recent advances in development of nanostructured photodetectors from ultraviolet to infrared region: A review. *Chemosphere* **2021**, *279*, 130473, http://doi.org/10.1016/j.chemosphere.2021.130473.
16. Verma, S.; Younis, S.A.; Kim, K.-H.; Dong, F. Anisotropic ZnO nanostructures and their nanocomposites as an advanced platform for photocatalytic remediation. *Journal of Hazardous Materials* **2021**, *415*, 125651, https://doi.org/10.1016/j.jhazmat.2021.125651.
17. Sahoo, L.; Dhindsa, P.K.; P, N.C.; Gautam, U.K. 'Pre-optimization' of the solvent of nanoparticle synthesis for superior catalytic efficiency: a case study with Pd nanocrystals. *Nanoscale Advances* **2021**, *3*, 2366-2376, http://doi.org/10.1039/D0NA01006E.

18. Müller, F.; Sauer, J.; Song, X.; Asmis, K.R. The Chemical Nature of $Ti_4O_{10}^-$: Vibrational Predissociation Spectroscopy Combined with Global Structure Optimization. *The Journal of Physical Chemistry A* **2021**, *125*, 9571-9577, http://doi.org/10.1021/acs.jpca.1c05552.
19. Weal, G.R.; McIntyre, S.M.; Garden, A.L. Development of a Structural Comparison Method to Promote Exploration of the Potential Energy Surface in the Global Optimization of Nanoclusters. *Journal of Chemical Information and Modeling* **2021**, *61*, 1732-1744, http://doi.org/10.1021/acs.jcim.0c01128.
20. Mehta, B. R. *et al.*, unpublished work **2022.**
21. Calais, J.-L. Density-functional theory of atoms and molecules. R.G. Parr and W. Yang. Oxford University Press, New York, Oxford, **1989**, *47*, 101, https://doi.org/10.1002/qua.560470107.
22. Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Physical Review* **1964**, *136*, B864-B871, http://doi.org/10.1103/PhysRev.136.B864.
23. Kohn, W.; Sham, L.J. Self-Consistent Equations Including Exchange and Correlation Effects. *Physical Review* **1965**, *140*, A1133-A1138, http://doi.org/10.1103/PhysRev.140.A1133.
24. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B. Gaussian 09 Revision A.1. Gaussian Inc. **2009**.
25. T. H. Dunning; P. J. Hay. Gaussian Basis Sets for Molecular Calculations. In: H. F. Schaefer, Ed., Methods in Electronic Structure Theory (Modern Theoretical Chemistry), Plenum Press, New York, **1977**.
26. Hay, P.J.; Wadt, W.R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. **1985**, *82*, 270-283, http://doi.org/10.1063/1.448799.
27. Pearson, R.G. Hard and Soft Acids and Bases. *Survey of Progress in Chemistry*, Scott, A.F., Ed.; Elsevier: **1969**; Volume 5, pp. 1-52, https://doi.org/10.1016/B978-0-12-395706-1.50007-8.
28. Parr, R.G.; Pearson, R.G. Absolute Hardness: Companion Parameter to Absolute Electronegativity. *Journal of the American Chemical Society* **1983**, *105*, 7512-7516, https://doi.org/10.1021/ja00364a005.
29. Parr, R.G.; Szentpaly, L.V.; Liu, S. Electrophilicity Index. *Journal of the American Chemical Society* **1999**, *121*, 1922-1924, http://dx.doi.org/10.1021/ja983494x.
30. Roy, D. R.; Chattaraj, P. K. 'Conceptual DFT and Aromaticity' in Aromaticity: Modern Computational Methods and Applications, Fernández, I (Ed.), Elsevier: Amsterdam, 2021, Chapter 9, pp. 285-318.
31. Chattaraj, P. K.; Sarkar, U.; Roy, D. R. Electronic Structure Principles and Aromaticity. *Journal of Chemical Education* **2007**, *84*, 354-348, https://doi.org/10.1021/ed084p354.
32. Khatua, S.; Roy, D. R.; Chattaraj, P. K.; Bhattacharjee, M. Synthesis and Structure of 1 D Na_6 Cluster Chain with Unusual short Na-Na distance: Organic like Aromaticity in Inorganic Metal Cluster. *Chemical Communications* **2007**, *(2)*, 135-137, https://doi.org/10.1039/B611693K.