Comparative Study of ZnO Nanoparticles: Experimental Evaluation and Density Functional Theory Predictions of Electronic and Optical Properties

Md. Didarul Islam[1], Md. Jahidul Islam[1], and M.E. Hoque[1]

[1]Department of Physics, Shahjalal University of Science and Technology, Sylhet 3114, Bangladesh

Email: didarul59@student.sust.edu

Abstract

Preparation of ZnO nanoparticles has been carried out in recent years with the help of the laser ablation process. According to literature reports, the band gap was found to be in the range of 3.3–3.6 eV, and an ultraviolet-visible (UV-Vis) absorption peak was observed between 320–380 nm. We conducted density functional theory (DFT) calculations on ZnO utilizing Perdew-Burke-Ernzerhof (PBE) pseudopotentials with Hubbard corrections in the Quantum Espresso package to compare these experimental results with theoretical predictions. In our computational results, we found that the calculated band gap of ZnO is within the range of 3 eV - 3.3 eV, and a UV-Vis absorption peaks from 330 nm to 374 nm, which is well matched with the experimental values. The slight variations in the observed data and theoretical data are comparatively small and this difference could be due to measurement conditions and approximations used in the computation. Nevertheless, the overall agreement between the experimental and theoretical findings highlights the reliability of density functional theory with Hubbard corrections in accurately predicting the electronic and optical properties of metal oxide nanoparticles.

Introduction

Nanoparticles are small materials with dimensions in the range from 1 nm to 100 nm. They have unique properties, which are not observable in strongly bulk materials. Due to the significant improvement in nanomaterial science, research on nanoparticle increased a lot. ZnO nanoparticles among them have gained much focus due to their distinctive electric and optical properties. They are transition metal semiconductors with a big direct band gap and they absorb light in the UV region making them a good candidate for application in drug delivery, gene delivery, biological sensing, biological labeling, and nanomedicine[1].

However, producing nanoparticles is very challenging due to the need for specialized equipment and precise knowledge of various parameters. In recent years, laser ablation has become popular as it requires zero toxic chemicals for the synthesis of nanoparticles. Laser ablation is the process of the removal of surface atoms by an excitation process where a laser beam is used as the main tool for the ablation of the target material.[2].

In this study, we focused on theoretically investigating the electronic and optical properties of ZnO nanoparticles using Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT) and compared these outcomes with experimental results from different literature reports. We first build nanoparticles from a unit cell using Vesta software. We then perform DFT simulations on nanoparticles of different sizes. However, we faced some difficulties in the DFT calculations. Initially, DFT failed to accurately predict the electric properties of ZnO. Though it has fully occupied the d orbital, the standard DFT exchange-correlation functional does not properly account for the strong correlations in the ZnO d-bands, leading to inaccurate electronic structure predictions[3]. So we include the Hubbard U correction term to improve the description of the strongly correlated ZnO d-orbitals. After the DFT+U correction, the calculated band gap and other electronic properties are in much better agreement with experimental data.

Literature Review

Laser ablation involves the use of a high-energy laser to irradiate a target material i.e., zinc metal submerged in a liquid typically water or alcohol. The laser causes the target material to vaporize and subsequently condense into nanoparticles as the vapor cools down. This method is known for its simplicity and control over particle size, distribution, and morphology. The optical band gap calculated by the absorption spectra is found to be size-dependent showing an increase for a decreasing particle size[4].

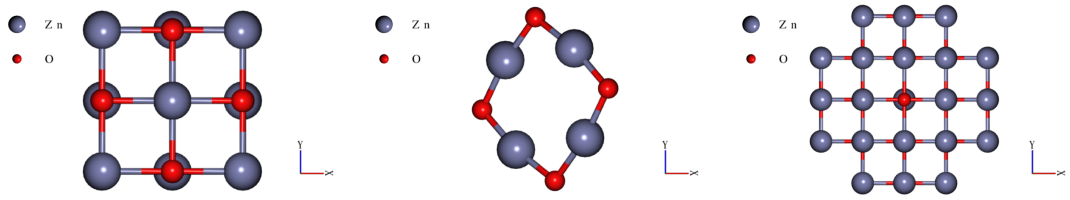
The studies by Haibo Zeng [5], Gondal[6], and Adawiya J Haider[7] all utilized the laser ablation method but under different conditions to synthesize ZnO nanoparticles. Despite the common technique, their results highlight how variations in parameters such as laser wavelength, energy, and ambient conditions can influence the nanoparticle properties.
Haibo Zeng synthesized ZnO nanoparticles using pulsed laser ablation (PLA) of a Zn metal in aqueous media. He monitored the output of the 1064-nm laser with the output of 70 mJ/pulse using a Scientech power meter. He adjusted the laser beam to point directly at the metal plate whose spot size was approximately 2mm in diameter with the help of a distance of 150 mm lenses. After that, characterization was carried out using X-ray diffraction (XRD) and UV-Vis absorption spectroscopy revealing a band gap of 3.54 eV and UV-vis absorption peak at 350 nm. The study emphasized the high purity of the nanoparticles due to the absence of chemical precursors.
In contrast, Gondal used the same Nd laser but at a wavelength of d-YAG laser (Spectra physics Model GCR 100) operating at 355 nm wavelength using a third harmonic generator. This laser can deliver a maximum pulse energy of 300 mJ with a pulse width of 8 ns and operates at a 10 Hz pulse repetition rate. The peak UV vis absorption occurred at 348nm and the band gap found was approximately 3.38 eV.
Adawiya J Haider varied the laser pulse duration, using a femtosecond laser in a vacuum chamber. At different temperatures 473k and 673k with the same energy 400mJ they get different bandgap of pure ZnO like 3.33eV and 3.32eV respectively . so, the energy bandgap slightly reduces with increasing temperature.

Computational Details

DFT calculations were performed using the Quantum espresso packages. Structural optimizations, electronic properties, and optical properties were investigated using PBE(Perdew Burke Ernzerhof) pseudopotential. Electronic characteristics were addressed using the projected augmented wave approach, whereas optical properties were done using the norm-conserving Troullier Martins method. The optimizations of crystal structure were performed using the BFGS quasi-Newton algorithm. A 4 4 4 K-point grid sampled by the Monkhorst-Pack was used for unit cell structure. Hubbard corrections were used in self-consistent field calculations to precisely predict electronic characteristics. For the DFT calculation, a kinetic energy cutoff of 50 Ry was used for the unit cell, and for nanoparticles, 70 Ry was used.

Results

Structural Properties



(a) Unit Cell **(b)** Zn_4O_4 **(c)** $Zn_{28}O_{28}$

Figure 1. Structural representations of ZnO (a) The unit cell of ZnO in a wurtzite structure, (b) A Zn $_4O_4$ cluster illustrating a nanoscale subunit. (c) A $Zn_{28}O_{28}$ nanoparticle displaying the alternating arrangement of Zn (purple) and O (red) atoms.

Figure 1 shows the structures of the unit cell and the nanoparticles after geometric optimizations. The unit cell is simple cubic in nature and has a cell parameter of A = 5.3 Angstroms. The crystal structure was obtained from the material project database[8]. The nanoparticles were formed using Vesta software. Figures 1(a) and (b) show nanoparticles with 8 and 56 atoms, respectively. The cell parameter for Zn_4O_4 is 2 nm and 3 nm for $Zn_{28}O_{28}$. A sufficient amount of vacuum was added in the cells of nanoparticles to avoid the effect of periodic repetitions of plane wave DFT simulations.

Electronic Properties

Figure 2 illustrates the differences in density of state(DOS) between ZnO nanoparticles of different sizes and the bulk ZnO unit cell. The Fermi energy is plotted at zero so that the dos of all three structures can be visualized properly. From the graph, it is clearly visible that the electrons are more localized in the valance band in the

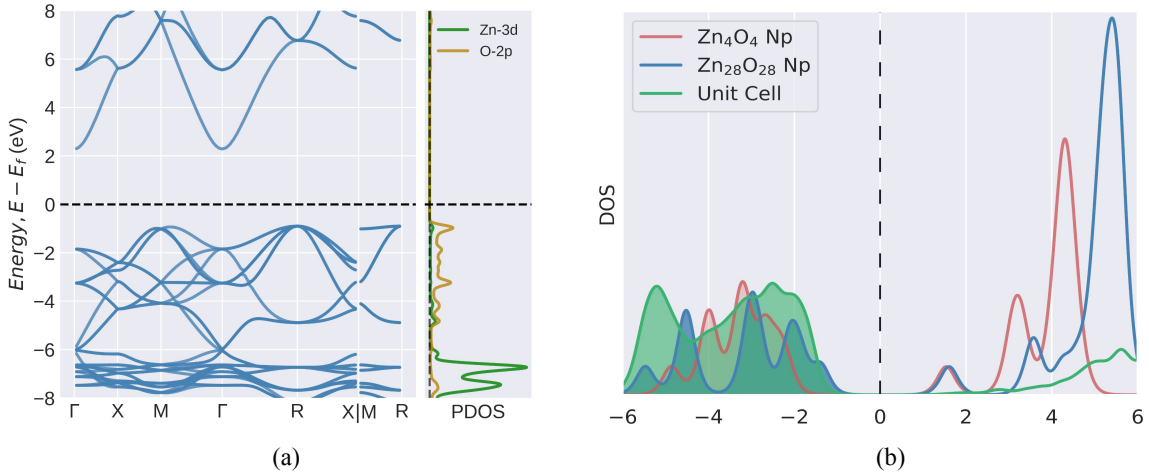


Figure 2. (a) Band Structure Of ZnO Unit Cell (b) Density Of State of Unit Cell, Zn_4O_4 and $Zn_{28}O_{28}$ Np

unit cell structure while the nanoparticles show a higher peak in the conduction band. This suggests that bulk ZnO has more evenly distributed electronic states compared to the nanoparticles. Around the Fermi energy, there are no significant states available for all the structures which indicates a clear band gap for these structures. The band gap obtained for the ZnO unit cell is 3.01 eV, for Zn_4O_4 nanoparticle the band gap is 3.31 eV and for $Zn_{28}O_{28}$ nanoparticle it is 3.25 eV. The comparison of the band gap between these structures obtained from DFT calculations and the experimental result is shown in table 1.

Type	Pseudopotential	Hubbard	Band Gap (eV)	Fermi Energy (eV)
ZnO unit cell	PBE+U	6	3.01	9.25
Zn_4O_4 Np	PBE+U	6.7	3.31	-6.10
$Zn_{28}O_{28}$ Np	PBE+U	6.1	3.25	-6.80
Experimental	–	–	3.3 - 3.6	

Table 1. Band gaps (eV), Fermi Energy of bulk, nanoparticles of ZnO from PBE+U calculations.

Optical Properties

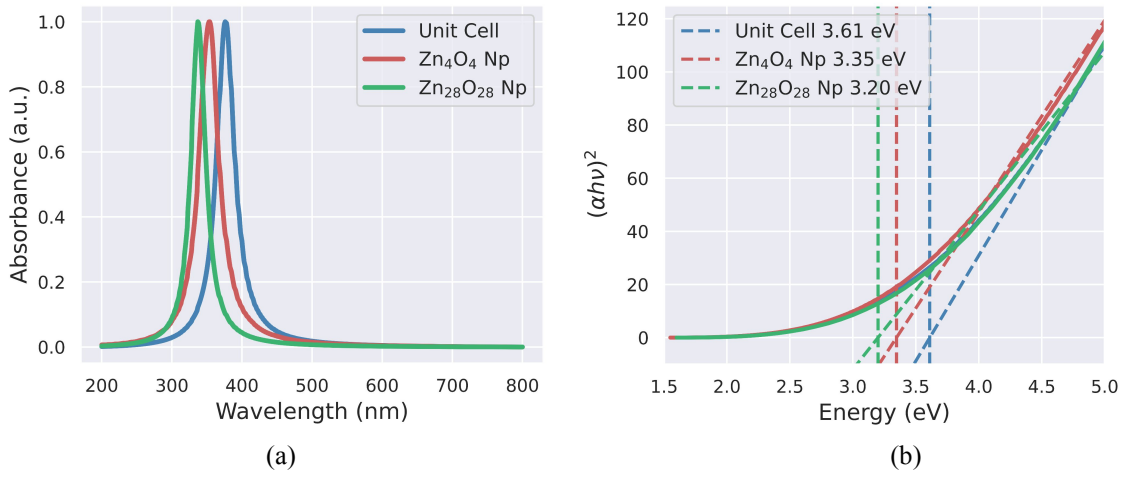


Figure 3. (a) Absorbance spectra comparison of Unit Cell, Zn_4O_4 and $Zn_{28}O_{28}$ Np covered a wavelength range of 200–800 nm, (b) Band gap determination using the Tauc method for Unit Cell, Zn_4O_4, and $Zn_{28}O_{28}$.

The Uv vis absorption is obtained using time-dependent density fucntional theory(TDDFT). Turbo Lanczos and Turbo Spectrum algorithms were used for this. Figure 3(a) shows the uv vis absorption of ZnO unit cell and ZnO nanoparticles. Peak absorption for the ZnO unit cell was measured to be 374 nm, whereas Zn_4O_4 Np and $Zn_{28}O_{28}$ Np showed peak absorption at 348 nm and 330 nm, respectively. This redshift in absorption with increasing nanoparticle size indicates a clear quantum confinement effect.
Figure 3(b) shows the Tauc plots used to determine the optical band gaps of three systems, based on data from TDDFT calculations. The optical band gap for unit cell, Zn_4O_4, $Zn_{28}O_{28}$ are found to be 3.61 eV, 3.35 eV, and 3.20 eV respectively. This gradual decrease in band gap with increasing nanoparticle size is consistent with the quantum size effect typically observed in semiconductor nanostructures. Such trends are important for tuning the optical and electronic properties of ZnO nanoparticles in applications like photocatalysis, sensors, and optoelectronic devices.

Conclusions

This study began by discussing the electronic and optical characteristics of the synthesized zinc oxide nanoparticles by the laser ablation method. Our goal was to predict the electronic and optical properties by the Density Functional Theory and compared them with the experimental results. For this, we at first performed the geometric optimizations which arranged the atoms in the most stable arrangement by minimizing the total energy of the system. From the simulations, we found that the electric band gap for nanoparticles of two different sizes was 3.31 eV and 3.25 eV. The experimental band gap range is 3.3 eV to 3.6 eV. So our DFT calculations predict very close results compared with experimental band gaps. we explained how the size of nanoparticles influenced the density of states. This consistency highlights the reliability of DFT in predicting the electronic properties of ZnO at the nanoscale.
Similarly to predict the optical properties we also performed TDDFT calculations. We obtained UV Vis absorption range from 330 nm to 374nm, with optical band gaps ranging from 3.20 eV to 3.61 eV. From the experimental result, we found that the peak absorption occurred at a range of 320nm to 380 nm, and the optical band gap ranged from 3.2 eV to 3.5 eV. This suggests that DFT not only predicts the electronic properties of nanoparticles accurately but can also precisely estimate the optical properties like absorption spectra and optical band gap.
However, we faced some difficulties during the DFT calculations. As nanoparticles are much bigger than the conventional unit cell, they require a significant amount of computational resources. Besides calculation without Hubbard potential leads to an inaccurate result in the electronic properties. Later we included the Hubbard potential to accurately capture the properties.

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