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Electronic Structures and Optical Properties for Nano Particles: Experimental and Theoretical Calculations

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Abstract: The use of copper nanoparticles (Cu NPs) and copper oxide nanoparticles (Cu_2O NPs) has increased dramatically both in the medical and industrial fields. In the present study, we have used various techniques like, dynamic light scattering (DLS) for particle size, zeta potential determination, X-ray diffraction (XRD), transmission electron microscope (TEM) and scanning electron microscope (SEM) for development and characterization of Cu and Cu_2O NPs. We have also performed the ab-initio calculations based on the density functional theory (DFT) where the theoretical results are in well accordance with the experimental reports. The Hubbard correction is included over the generalized gradient approximation (GGA) for a better description of Cu and Cu_2O NPs. The plot of densities of states (DOS) and energy band structures of Cu and Cu_2O nanocrystals predicts the metallic and semiconducting nature of Cu and Cu_2O, respectively. The energy bands and DOS shows strong hybridization of Cu-O and predicts the metallic nature of Cu and semiconducting nature of Cu_2O. The optical absorption results show that both the Cu_2O and Cu samples are absorbing strongly at the minimum energy. The band structure of Cu Nano crystals reveals a metallic nature where the valence band crosses the Fermi energy level at W point. However, an indirect energy band gap can be seen above the EF.

Keywords: Cu Nanoparticles, Cu_2O Nanoparticles, X-ray Diffraction, Density Functional Theory

1. Introduction

Copper is an important trace element for energy production in biological systems. Cu nanocrystals are widely investigated for the preparation of metal oxide to study their forked properties (catalytic, sensing, electrical, and mechanical) making them suitable for various applications. They have been involved in several industrial, biological, and medical applications as they are cost effective and have simple accessibility [1]. They are also a synthesis necessity for various enzymes, including cytochrome c oxidase, superoxide dismutase, tyrosinase, lisyl oxidase and cupro-protein [2]. Cu based compounds like copper oxide (Cu_2O) NPs have been widely used in inks, lubricants, coatings, semiconductors, heat transfer fluids, antimicrobial preparations, and intrauterine contraceptive devices [3]. Ab-initio density functional theory (DFT) calculations are theoretically an appropriate tool to examine and analyze the electronic band structures and density of states of materials.

Hence, in this manuscript we present computational

analysis of Cu and Cu_2O nanocrystals such as electronic structure and optical properties.

2. Experimental Analysis

The Cu NPs and Cu_2O NP_S in crystalline form were analyzed by X-ray with power of 45 KV and current of 30 mA with the scan step time of 0.5 sec at 25°C. Cu and Cu_2O NP_S are used in the powder form. In the process of data collections, the samples are placed on top of an aluminum slide and are widely spread to increase the exposure of X-rays on the specified area. The Transmission electron microscopy (TEM) technique uses energetic electrons to produce crystallographic information and morphology of nanoparticles. The surface structure and chemical composition of the prepared samples are determined using Scanning electron microscopy (SEM)[4].

SEM and TEM of Cu NPs and Cu_2O NPs

The TEM reveals a cuboidal Cu NP shape with an average size of 13 ± 1 nm, as shown in (Figure 1a). The CuO_2 NPs demonstrated spherical sprinkled tiny particles with an average size of 20 ± 3 nm (Figure 1b).

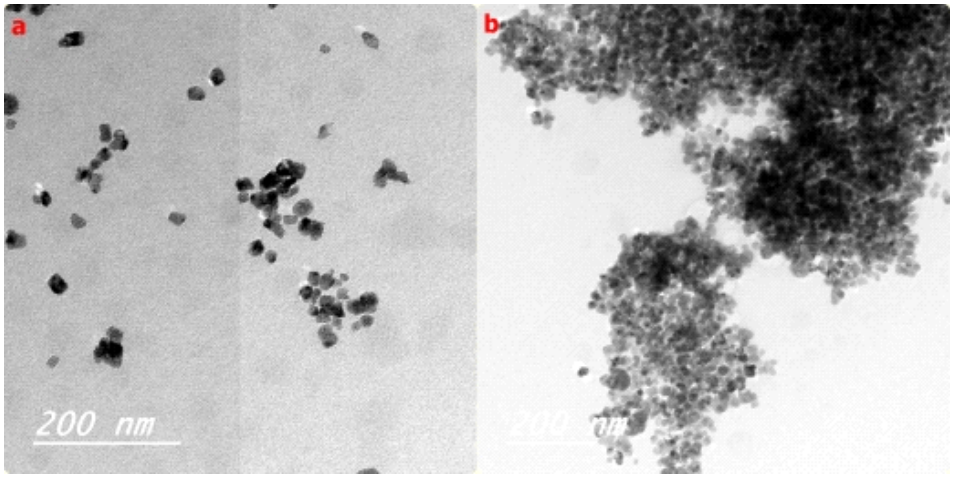

Figure 1. *TEM micrographs of a) Cu NPs and b) Cu_2O NPs.*

SEM also proved that Cu NPs are cuboidal and are shown as tiny clusters (Figure 2a). The SEM image of the prepared Cu NPs is illustrated in Figure 2b, which underlines the spherical form of particle's surface.

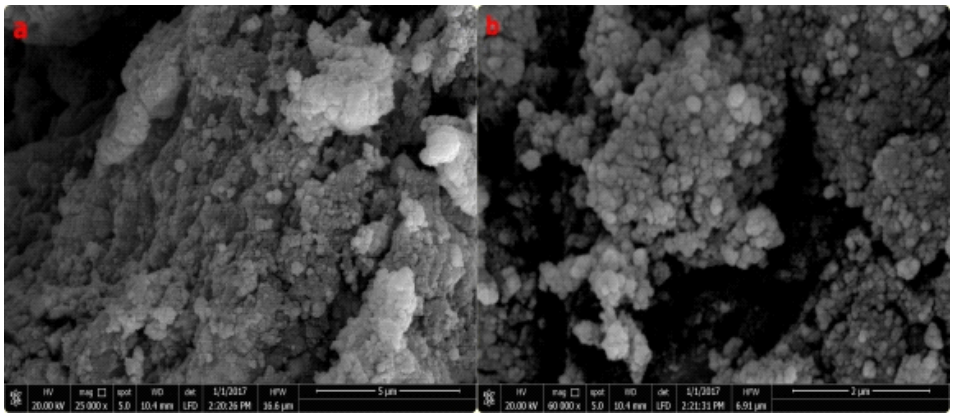

Figure 2. *SEM micrographs of a) Cu NPs and b) Cu_2O NPs.*

3. Computational Details

Ab-initio calculation is also performed within the framework of density functional theory (DFT) [5] based on the pseudopotential and plane-wave method as implemented in the Quantum-Espresso code [6]. The projector augmented-wave (PAW) formalism is used to describe the electron-ion interactions. In contrast, the exchange-correlation terms is described using the Generalized Gradient Approximation (GGA) proposed by Perdew-Burke-Ernzerhof (PBE) [7], for a better description of the electronic band structure of the Cu_2O. GGA plus Hubbard term (U) in the self-interaction correction scheme is also applied, where the U value (U=7.0 eV) is determined using the density functional perturbed theory (DFPT). The plane-wave energy cutoff and the charge density cutoff are set to 100 Ry and 900 Ry, respectively. A 15 X 15 X 15 k-points mesh in the Monkhorst-Pack description is used to integrate the Brillouin zone (BZ), and spin polarization calculation is also considered. Optical properties are calculated using a high density of 58 X 58 X 58 k-points grid, where intra-transitions are considered [8, 9].

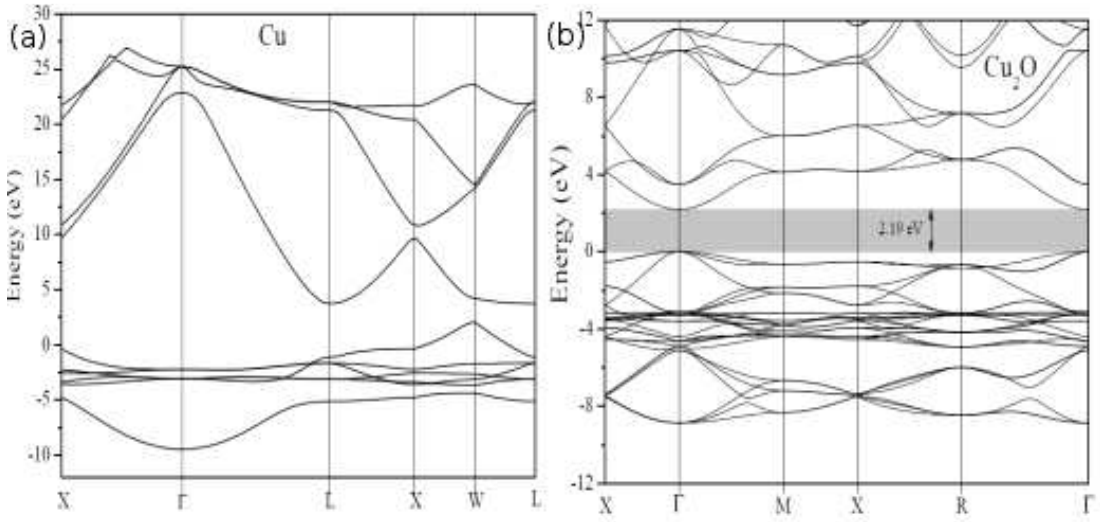

Figure 3. *Energy band structure for (a) Cu and (b) Cu_2O.*

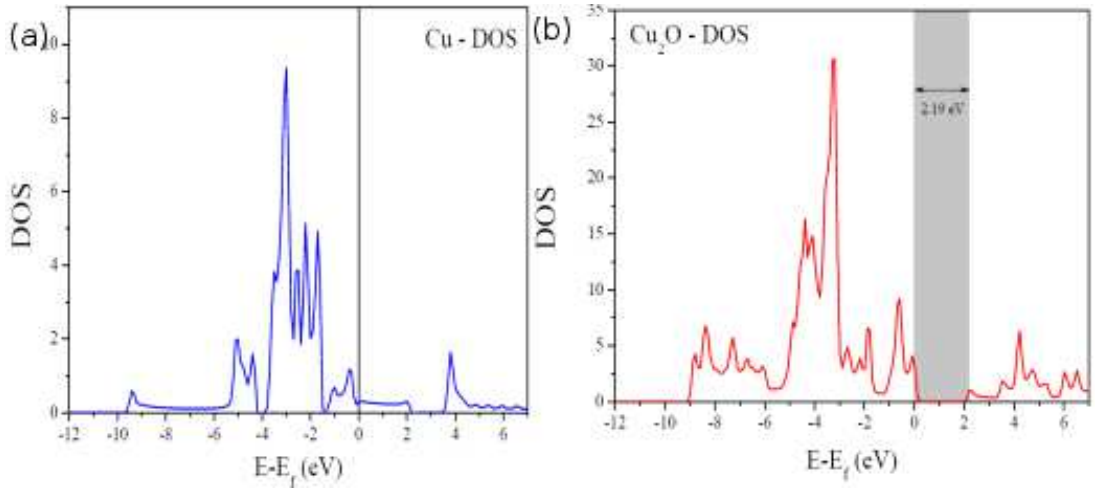

Figure 4. *Total density of states (DOS) of (a) Cu and (b) Cu_2O.*

3.1. Electronic Band Structure

In order to understand the nature of Cu and Cu_2O nanocrystals, their electronic band structure is analysed from ab initio calculations within the density functional theory, using the GGA functional. The band structure of Cu and Cu_2O nanocrystals along high symmetry directions of the brillouin zone (BZ) are calculated and shown in Figure 3(a, b). Cu_2O is a semiconductor with a direct band gap of 2.19 eV in accordance with the experimental reports with the valence band maximum (VBM) and the conduction band minimum (CBM) lying at the Γ point. There exists large number of bands in the energy range of -5 eV – 0 eV indicating the hybridisation between the Cu-d and O-p states [10]. Many literature reviews reports a deviation from the experimental band gap of 2.172 eV for Cu_2O [11]. Ruiz et al. [12] obtained an Eg of 9.7 eV using a posteriori density-functional correction to the self-consistent solution to the Hartee-Fock-Roothan equation. Sieberer and collaborators [13] have reported an Eg of 0.48 eV using GGA+U, whereas French and coworkers [14] revealed an Eg of 0.45 eV by incorporating spin-orbit coupling. However, Heinemann et al. [15] estimated an energy band gap of 2.02 eV using the hybrid functional which is in agreement with the reported value of Bruneval et al. [16]. The band structure of Cu nanocrystals reveals a metallic nature where the valence band crosses the Fermi energy level at W point. However, an indirect energy band gap can be seen above the EF.

To further elucidate the electronic band structure we have analyzed the density of states (DOS) for both Cu and Cu_2O NPs which have been displayed in Figure 4(a, b). The DOS plot of Cu revealed its metallic nature with sharps peaks arising in the energy range of -2 to -4 eV. The DOS plot of Cu_2O reflects its semiconducting nature and the Fermi energy region mostly consists of states arising from the Cu-d and O-p states [17]. At the energy range of -6 eV to -9 eV, we find states mainly composed of O-p states. Tahir et al. [18] have reported the electronic structure of bulk Cu and Cu_2O using the X ray photo electron spectroscopy method and have demonstrated a similar DOS behavior as our results for both the nanocrystals.

3.2. Optical Properties

To determinate optical properties, we have calculated the dielectric function $\varepsilon(\omega)$:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\,\varepsilon_2(\omega)$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and complex parts of the dielectric function, respectively. The complex part is related to the momentum matrix (p) element between occupied (vk, valence bands) and unoccupied (ck, conduction bands) electronic bands state α and β with crystal momentum k,

$$\varepsilon_2(\omega) = \left(\frac{\hbar e^2}{\pi m^2 \omega^2}\right) \sum_{c,v} \int d^3k \left\langle c_k \left| p^\alpha \right| v_k \right\rangle \left\langle v_k \left| p^\beta \right| c_k \right\rangle \delta\left(E_{c_k} - E_{v_k} - \omega\right)$$

The real part can be extracted from the imaginary part using the Kramers-Kroning relationship:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{(\omega')^2 - \omega^2} d\omega'$$

where P is the principal value of the integral. Knowing the real $\Re(\varepsilon)$ and complex $\Im(\varepsilon)$ part of the dielectric functional, we can determine other properties, such as refractive index, reflectivity, and optical absorption.

In Figure 5a, we show the real and complex part of the dielectric function of the Cu and Cu_2O compounds. For the Cu, there are two peaks at 2.1 and 4.9 eV for the imaginary part, $\Im(\varepsilon)$, which could be related to 3d-Cu transitions at k-points W and L, respectively. Whereas for the real part, $\Re(\varepsilon)$, there are two peaks at 1.7 and 4.6 eV and at zero frequency limits the value of $\Re(\varepsilon)$ is 7.5. For the case of the Cu_2O, the imaginary part, $\Im(\varepsilon)$, show two peaks at the lowest energies with respect to the Cu compound at 0.2 and 0.6 eV, related with transitions from 3d-Cu to 2p-O states, and from 4s-Cu to 2p-O states at Γ k-point. The real part, $\Re(\varepsilon)$, show a negative value for a range of lowest frequencies energies, related to a metallic behavior in this frequency region. The band gap for Cu is 0 eV (metallic) and 2.1 eV for Cu_2O.

In figure 5b, we show the optical absorption for the Cu and Cu_2O compounds, where the optical transition for the Cu is in the visible region with a wavelength of 518 nm, corresponding to the cyan color. Whereas Cu_2O is optical transitions are not located in the visible region. The optical absorption results (figure 5b) show that both the Cu_2O and Cu samples are still absorbing strongly at the minimum energy shown (800 nm, or 1.55 eV).

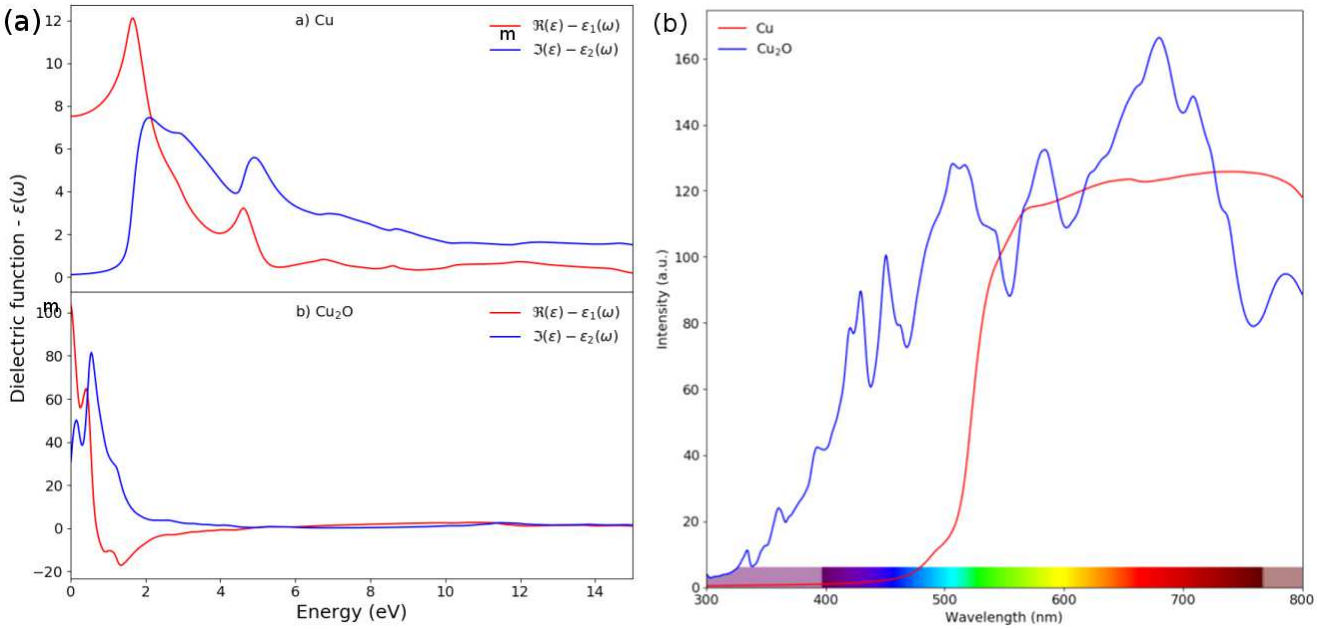

Figure 5. *(a) Dielectric function for Cu and Cu_2O compounds, (b) Optical absorption function for Cu and Cu_2O compounds.*

4. Conclusions

In this present study, Cu and Cu_2O nanoparticles have been prepared, and using the first principles method, their density of states and electronic band structures have also been investigated. The energy bands and DOS shows strong hybridization of Cu-O and predicts the metallic nature of Cu and semiconducting nature of Cu_2O. The theoretically calculated E_g of 2.19 eV for the Cu_2O nanocrystal is in well agreement with the experimental reports. Furthermore, the optical properties of Cu and Cu_2O compounds have also been

investigated which shows an optical transitions in the visible region for Cu but reflects no optical transitions for the Cu_2O compound. The optical absorption results show that both the Cu_2O and Cu samples are absorbing strongly at the minimum energy.

Author's Contributions

Heba M. Fahmy and Abeer E. Aly performed the experimental calculations, Arles V. Gil Rebaza and Dr. Abeer Esmat Aly performed the theoretical investigations, B. Thapa contributed to revise the manuscript and A. Shankar was there for evaluation of the results and is the corresponding author of the manuscript.

No Conflict of Interest

The authors declare no conflicts of interest reported in this manuscript.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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