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Impact of Oxygen Vacancies on the Structural, Electronic, and Optical Properties of Cu_2O and Nitrogen-Doped Cu_2O for Optoelectronic Applications: A First-Principles Study

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Abstract

This study utilizes Density Functional Theory (DFT) within the Quantum ESPRESSO framework to explore the effects of oxygen vacancies and nitrogen doping on the electronic structure and optical properties of cuprous oxide (Cu2O). Pristine Cu2O, an intrinsic p-type semiconductor, typically exhibits a direct band gap. Introducing an oxygen vacancy in the absence of a dopant broadens the band structure, leading to both direct and indirect band gap characteristics. In contrast, nitrogen doping transforms the band gap into a direct one, significantly reducing it from 1.97 eV to 1.09 eV, which deviates from previous findings due to potential variations in the initial state of the Cu_2O *host crystal. Furthermore, spin-polarization effects indicate spin-dependent behaviour within the material. The study also examines the absorption properties of pristine, defective, and nitrogen-doped* Cu_2O *systems using the complex dielectric function. The results show distinct absorption peaks and transitions, with nitrogen-doped* Cu_2O *exhibiting strong absorption in the visible light range, underscoring its potential for solar cell applications.*

Keywords: Defected system; Oxygen vacancy; Quantum ESPRESSO; band gap; DFT+U

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INTRODUCTION

Copper oxide (Cu_2O) has attracted significant interest in the field of photovoltaics due to its potential as a cost-effective and abundant material for solar energy conversion. With its favourable bandgap and optical properties, Cu_2O shows promise for efficient and sustainable solar cell applications. Despite its theoretical efficiency of approximately 20%,(Minami et al., 2016) one of the significant drawbacks of Cu_2O as a material for photovoltaics is its low practical efficiency. This discrepancy between theoretical and practical efficiency challenges the widespread adoption of Cu_2O-based solar cells. Numerous studies have focused on addressing this issue and improving the performance of Cu_2O-based solar cells through various strategies, such as surface passivation, interface engineering, and doping techniques.(Wei et al., 2012).

However, the performance of Cu_2O-based solar cells can be influenced by defects, such as oxygen vacancies,(Nanchen Dongfang, 2023) which can impact the material's electronic properties and overall efficiency. Oxygen vacancies in Cu_2O can significantly affect the material's electronic properties and performance. These vacancies, which are defects in the crystal lattice where oxygen atoms are missing, can create localized states within the bandgap of Cu_2O, affecting its optical and electrical properties. Some effects of oxygen vacancies on Cu_2O include increased carrier concentration, enhanced recombination, altered electronic structure, and reduced stability.

Liu et al. (2011) investigated the structural, electrical, optical, and HOMO-LUMO properties of Cu_2O supercells using Generalized Gradient Approximation (GGA). Their study revealed that the removal of oxygen tends to decrease the band gap and that the absorption coefficient decreases with increasing oxygen vacancies (Wu et al., 2012). Wu et al. (2012) conducted a first-principles study of oxygen-vacancy Cu_2O (111) surfaces. They found that relaxation mainly occurs in the top three trilayers of surfaces, with two vacancies trapping electrons of 0.11e and 0.27e, respectively. The effects of oxygen vacancies on the electronic structures were found to be rather localized, enhancing the electron-donating ability of the surfaces. The formation energy of 1.75 and 1.43 eV for oxygen vacancies indicate that partially reduced surfaces are stable and easily produced (Liu & Liu, 2011). In 2021, Ricca et al. explored the importance of surface oxygen vacancies for ultrafast hot carrier relaxation and transport in Cu_2O (111) using hybrid DFT calculations. They reported that the oxygen vacancies are doubly ionized, and the associated defect states strongly suppress electron transport. Notably, the excited electronic state of a singly charged oxygen vacancy plays a crucial role in non-radiative electron capture, with a capture coefficient of about 10^{-9} cm^3/s and a lifetime of 0.04 ps. This explains the experimentally observed ultrafast carrier relaxation. They concluded that engineering surface oxygen vacancy chemistry is crucial for optimizing Cu_2O for photoelectrode applications(Ricca et al., 2021).

Understanding the impact of oxygen vacancies on Cu_2O is crucial for optimizing the material for photovoltaic applications and developing strategies to mitigate their effects on device performance. One promising approach to enhance the performance of Cu_2O in photovoltaic devices is through nitrogen doping. Nitrogen is a non-toxic, low-cost, and widely available gas that has been shown to improve the electrical conductivity, carrier concentration, and charge transport properties of Cu_2O, ultimately leading to enhanced device performance. Additionally, nitrogen doping can help passivate defects such as oxygen vacancies, reducing recombination losses and further improving the efficiency of Cu_2O-based solar cells.

Several studies have demonstrated the potential of nitrogen doping to enhance the performance of Cu_2O for photovoltaic applications. For example, a study by (Ishizuka et al.,

2001) explored the effects of nitrogen doping on the optical and electronic properties of Cu_2O thin films, showing improvements in carrier concentration and photoresponse. Yan et al. (2014), using first-principles calculations, found that nitrogen atoms doped into Cu_2O widen the band gap, with an increase of 0.22 eV over the undoped oxide, consistent with experimental results. They also found that nitrogen is an effective p-type dopant for Cu_2O, increasing carrier concentration with higher nitrogen levels, and significantly reducing the effective mass of carriers, leading to very low resistivity (1.14 Ω cm) in experiments(Yan et al., 2014).

Zhao et al. (2013) investigated the effects of nitrogen doping on the crystal structure, electronic structure, and optical properties of Cu_2O using an ultrasoft pseudopotential plane wave method based on first-principles calculations. Their results showed that nitrogen doping slightly widens the band gap and forms an intermediate band within the gap, primarily due to hybridization between N-2p and Cu-3d states. N-doped Cu_2O can absorb across the solar spectrum, from near-infrared to ultraviolet, making it a suitable intermediate band material for novel solar cells.(Zhao et al., 2013). Li et al. (2012) studied the effect of nitrogen doping on the electronic properties of Cu_2O crystals using density functional theory. They reported that nitrogen-doped Cu_2O, with or without oxygen vacancies, shows different modifications to the electronic band structure. In N anion-doped Cu_2O, some N 2p states overlap and mix with the O 2p valence band, slightly narrowing the band gap compared to undoped Cu_2O. The coexistence of nitrogen impurities and oxygen vacancies contributes to band gap widening, explaining the experimentally observed optical band gap widening due to nitrogen doping.(Li Min1, 2012).

Zhang Ping et al. (2014) systematically investigated the effect of nitrogen doping on the crystal structure, electronic structure, and optical properties of Cu_2O using first-principles calculations. Their results revealed an intermediate energy band in the forbidden gap of highly nitrogen-doped Cu_2O, consistent with experimental absorption peaks. They concluded that nitrogen-doped Cu_2O could be a suitable absorbing material for wide-spectrum detectors or intermediate-band solar cells.

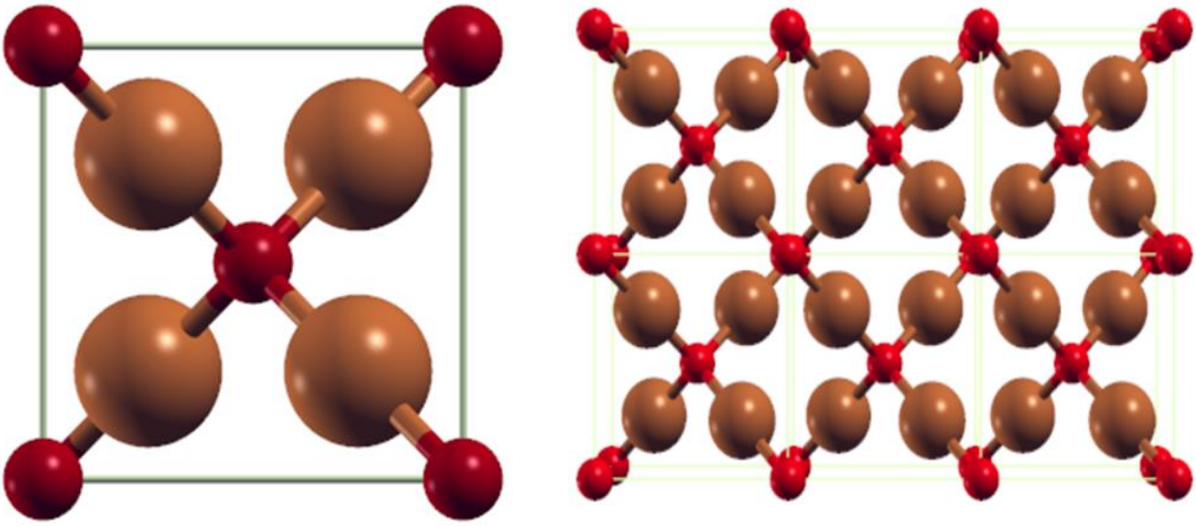


Figure 1: Shows the (a) unit cell of pristine Cu_2O and (b) Optimized 3x2x1 Supercell of pristine Cu_2O. The brown and red spheres represent Cupper and Oxygen atoms respectively.

COMPUTATIONAL METHOD

In this study, simulations were conducted using density functional theory (DFT) with first-principle calculations implemented in the QUANTUM ESPRESSO code (Giannozzi et al., 2009). The electronic structure calculations were performed within the framework of the Generalized Gradient Approximation (GGA) employing the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. The PBE+U functional was chosen for its effectiveness in core electron corrections and the U value used for this calculation is 8.5eV for both Cu and O atoms. For describing the electronic wave functions, the projected augmented wave (PAW) method was employed to accurately represent the interactions between electrons and atomic cores. To ensure precision in the calculations, a self-consistent convergence criterion was applied.

The computational parameters included a plane wave cut-off energy of 35 Rydberg (Ry) for the optimized structure, which dictates the maximum kinetic energy of plane waves used in the basis set. Brillouin zone sampling was achieved using a Monkhorst-Pack scheme (Zheng & Zheng, 2023) with a 3 × 3 × 1 grid, ensuring comprehensive coverage of reciprocal space. Specifically, the study focused on investigating defects in Cu_2O by removing one oxygen atom from an optimized 3x2x1 supercell as shown in Figure1b, leading to the formation of a defective Cu_2O crystal, as depicted in Figure 2(a). The 3x2x1 Cu_2O crystal consists of 36 atoms, and by removing one oxygen atom without replacement, we determined that the oxygen atom contributes 31.43% to the Cu_2O layer, while the copper atoms contribute 68.57%. After optimizing the defective Cu_2O crystal, we doped it with a nitrogen atom. We then substituted the vacant site with a nitrogen atom to alter the electronic configuration of the Cu_2O crystal at various doping percentages. In the revised supercell containing 36 atoms (11 oxygen, 1 nitrogen, and 24 copper atoms), the contributions to the total composition are approximately 30.56% from oxygen, 2.78% from nitrogen, and 66.67% from copper. The structural models of both the defective and doped Cu_2O crystals were visualized using XCRYSDEN software(Kokalj, 1999). These computational details highlight a rigorous approach aimed at accurately modelling and analyzing the electronic and structural characteristics of Cu_2O and its modified forms using advanced DFT techniques.

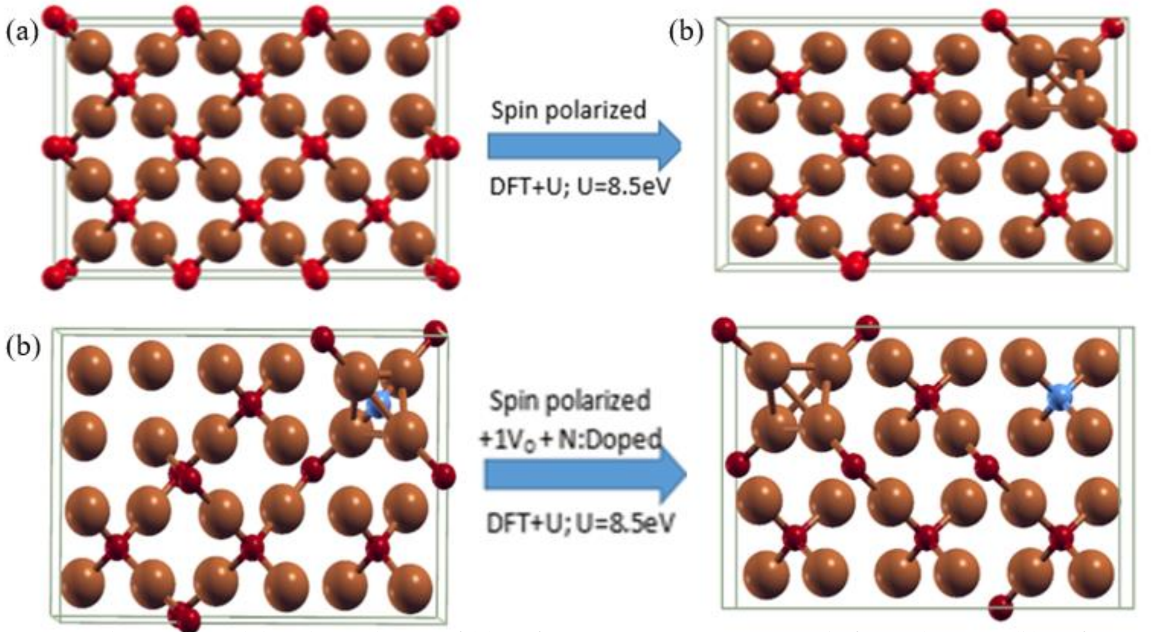


Figure2: Schematic model and simulation of (a) Defective 1V$_O$ Cu_2O structure before relaxation (b) Defective 1V$_O$ Cu_2O structure after relaxation and (c) Defective 1Vo N: Cu_2O Structure before relaxation (d) Defective 1Vo N: Cu_2O Structure after relaxation. The red, brown, and blue spheres represent Cu, O and N respectively.

RESULTS AND DISCUSSION

Optimized Structure of Cu_2O and N-Doped Cu_2O

The optimized crystal structures for the 3x2x1 supercell of defective Cu_2O before and after relaxation are shown in Fig. 2(a) and 2(b). These structures were analyzed using the XCrySDen software package (Kokalj, 1999). The optimized lattice parameter for the Cu_2O unit cell is 4.2706 Å, which closely matches the experimental findings reported by (Meyer et al., 2012). The bond lengths for Cu–O, O–O, and Cu–Cu were found to be 1.8505 Å, 3.6985 Å, and 3.0785 Å, respectively, aligning well with the values reported by (Meyer et al., 2012).

The relaxed supercell structures for N-doped Cu_2O (N: Cu_2O) systems are shown in Fig.2. The Cu–N bond length is 1.84 Å, which is slightly longer than the Cu–O bond length. This result is consistent with the findings of (Li, 2012), indicating that nitrogen doping causes a slight local expansion of the Cu_2O lattice. Additionally, the configuration between Cu and O atoms maintains the defective angle when an oxygen vacancy is created; specifically, the O–Cu–O bond angle remains at 109.9610°. This angle does not change in the nitrogen-doped model, as the bond angles O–Cu–N and O–Cu–O remain at 109.9610°, while the pristine bond angle is 109.4710°.

Typically, lattice distortions occur when point defects are introduced into the host lattice due to differences in ion radius and valence electron configuration. However, in this study, we found that lattice distortions are not significant for the nitrogen-doped model. This minimal distortion suggests that the N-doped Cu_2O exhibits exceptional photoelectric performance.

Electronic properties of Cu_2O and N Doped Cu_2O

We employed Hubbard parameters of 8.5 eV for both the Cu-3d and O-2p orbitals to derive the electronic band structure of Cu_2O. The semiconducting nature of Cu_2O is well explained by DFT + U calculations. The direct band gap at the Γ-point is estimated to be 1.67 eV, which closely aligns with experimental values reported by (Meyer et al., 2012). For the Cu_2O unit cell, the valence band maximum (VBM) at the Γ-point consists of three highly dispersive degenerate bands, as shown in Fig. 3(a). These highly dispersive bands suggest covalent bonding in Cu_2O. The VBM is due to the strong overlap of Cu-d orbitals with Cu-s and O-p orbitals. The nearly flat bands from -5.1 to -6.4 eV near the Γ-point in the valence band are attributed to the non-bonding Cu-d orbitals with minimal overlapping. The conduction band minimum (CBM) at the Γ-point consists of a single highly dispersive band with a width of approximately 2 eV. The strong overlapping between the O-s orbitals and Cu-s and Cu-d orbitals gives rise to the CBM, which plays a crucial role in determining the conductivity and optical properties of the semiconductor. The doubly degenerate dispersive bands at ~2.0 eV at the Γ-point in the conduction band originate from the overlapping Cu-p orbitals.

To study the effect of N dopants on the defective Cu_2O crystal (optimized structure shown in Fig. 2(b)), we calculated the band structure corresponding to the 3x2x1 defective Cu_2O supercell, as shown in Fig. 3(b). We found that the defective Cu_2O exhibits both direct and indirect band gap semiconductor characteristics, with the VBM and CBM located at the Γ and X points, respectively, with band gaps of 1.91 eV and 1.97 eV. The number of up-spin electrons is equal to the number of down-spin electrons, indicating the absence of spin polarization in the band structure and density of states. The upper valence band (VB) is dominated by Cu-3d states, while the VB in the region from -17.5 to 15 eV mainly consists of O-2p states, which aligns with the work of Zhao et al. The lower conduction band (CB) does not exhibit the electronic states of single atoms but rather the hybridized states between them, with Cu-3d states contributing more significantly due to the induced defect, as shown in Fig. 3(f).

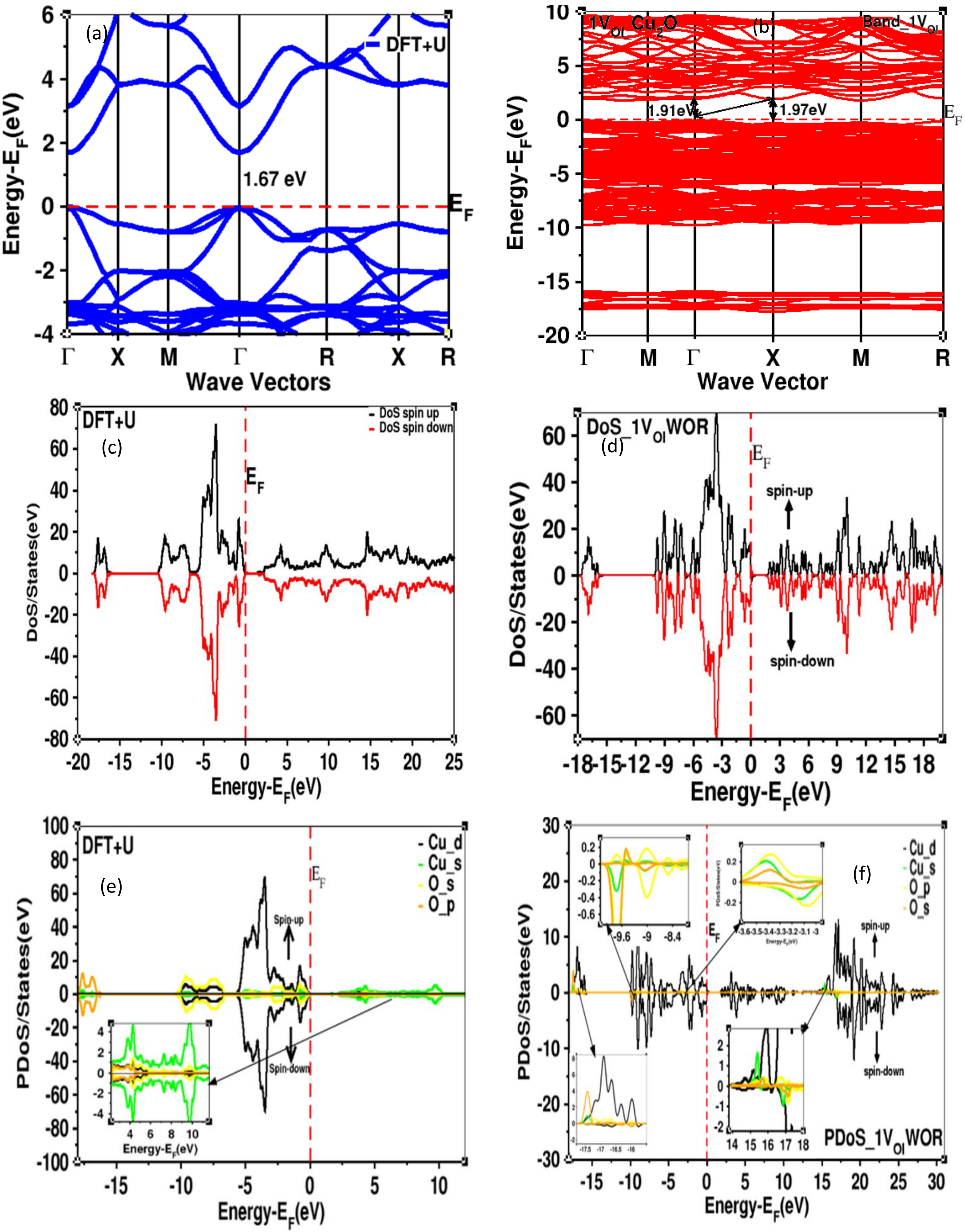
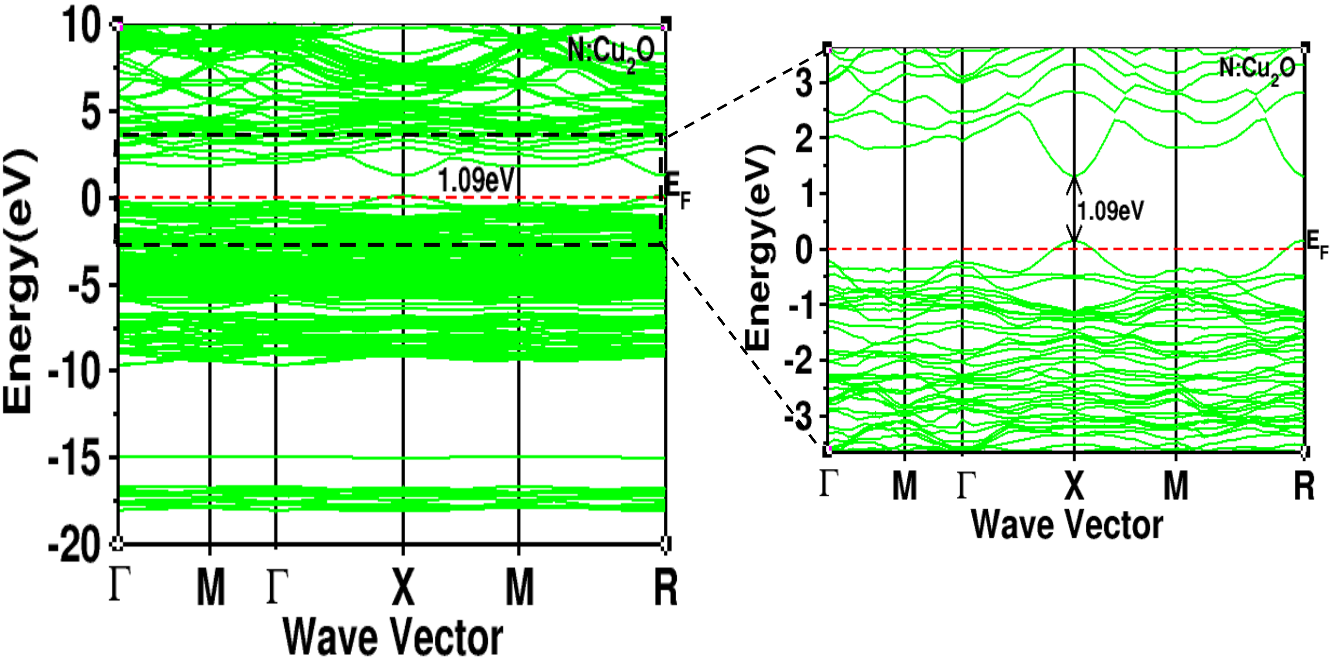


Fig. 3 depicts the band structure (a,b), Density of state (DoS).(c,d), and Partial Density of State (PDoS).(e,f) of pristine Cu_2O, and defected Cu_2O under DFT+U calculation with spin polarization and Hubbard value of 8.5eV.

When the defective Cu_2O structure is doped with nitrogen, the band gap retains its direct nature at the X point but decreases from 1.97 eV to 1.09 eV, as shown in Fig. 4(a). This result contrasts with the findings of Zhao et al., who reported a slight widening of the band gap upon doping. The discrepancy in these results may be attributed to the initial conditions of the host Cu_2O. Specifically, Zhao and co-workers doped pure Cu_2O without defect engineering, whereas our study involves doping a Cu_2O crystal with an oxygen vacancy, referred to as a defective Cu_2O crystal.

A closer examination of the defect-induced changes in the host Cu_2O reveals spin-up and spin-down impurity energy levels in the defected system, as seen in the inset of Fig. 3(f). The defect modifies the electronic state of the system, as illustrated in Fig. 3(b). Figure 4(c) clearly demonstrates the effects of the defect on Cu_2O, showing spin polarization above the valence band (VB) in the energy range of -15 to -14 eV and below the conduction band minimum at 0.8 eV. This indicates the presence of electrons with opposite spin orientations (spin-up and spin-down) occupying energy levels within the VB in the specified energy range, suggesting spin-dependent behaviour.

Within this energy range, there is spin polarization below the VB, where spin-down and spin-up impurity levels form an intermediate bandgap (IB) at -15 eV, as shown in Fig. 4(a), compared to the defective Cu_2O in Fig. 3(b). Additionally, there is spin polarization in the conduction band slightly above the VB, with spin-down impurity energy levels ranging from 0.4 eV to 0.8 eV, as depicted in Fig. 5(a). The impurity energy levels mainly originate from N-2p states, with contributions from O-2p, Cu-3d, and Cu-4s states, forming the IB. Figure 4(a) shows the N-doped Cu_2O and the IB due to impurity formation. Comparing our work with that of Zhao et al., we observe that their N-doped Cu_2O exhibits only one impurity level, which is also present in our studies. The inset in Fig. 4(a) provides an enlarged view of the band structure of the N-doped Cu_2O crystal.



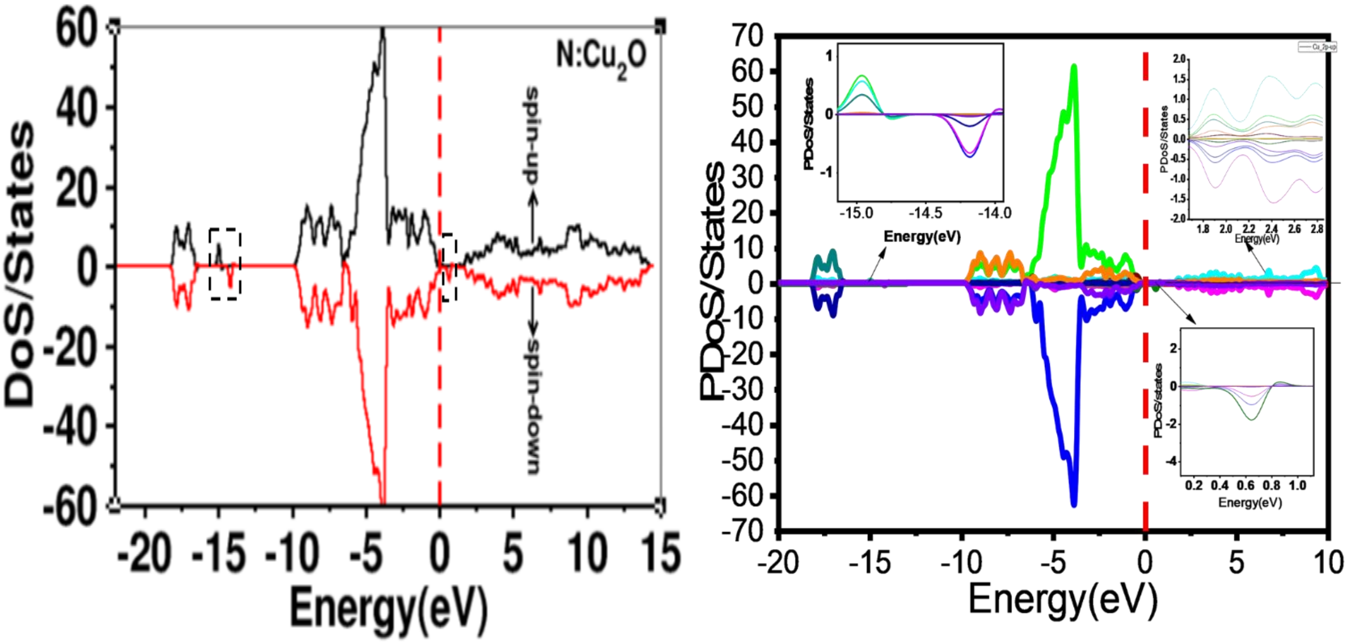


Fig. 4 depicts the band structure (a), Density of state (DoS).(b), and Partial Density of State (PDoS).(c) of doped N: Cu₂O under DFT+U calculation with spin polarization and Hubbard value of 8.5eV.

Optical Properties of Cu₂O, Defective Cu₂O, and Nitrogen-Doped Defective Cu₂O

The optical properties of Cu₂O are significantly influenced by modifications in its electronic properties, such as the creation of oxygen vacancies and subsequent nitrogen doping. To precisely understand the effect of these changes, we computed the optical properties of pristine Cu₂O and defective Cu₂O, comparing them with those of nitrogen-doped defective Cu₂O. The dielectric constant, including the real ε_1 and imaginary ε_2 components, and the electron energy loss function were investigated using the random phase approximation (RPA) and the Perdew-Burke-Ernzerhof (DFT + RPA) method, as implemented in the YAMBO code. Additionally, we calculated other optical properties such as reflectivity, refractive index, and extinction coefficient using the real and imaginary parts of the dielectric function, as detailed below.

$$\eta(\omega) = \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \frac{\varepsilon_{2(\omega)}}{2}\right]^{1/2} \qquad 1$$

$$K(\omega) = \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \frac{\varepsilon_{2(\omega)}}{2}\right]^{1/2} \qquad 2$$

$$R = \frac{(\eta-1)^2+K^2}{(\eta+1)^2+K^2} \qquad 3$$

$\eta(\omega)$ is the refractive index, $K(\omega)$ is the extinction coefficient, R is the reflectivity, $\varepsilon_1(\omega)$ is the real part of the dielectric function, $\varepsilon_2(\omega)$ is the imaginary part of the dielectric function.

Dielectric function and the electron energy loss spectroscopy (EELS)

The dielectric function for pristine Cu₂O and Defective Cu₂O-doped Nitrogen are shown in Fig. 5. The imaginary part of the dielectric function corresponds to the absorption effect, the real part corresponds to that of the dispersive effect and the electron energy loss function describes the interaction of electrons and solids which is essential for the evaluation of inelastic scattering of electron transport in solids. The absorption effect for pristine Cu_2O peaked at 3.75 eV, its dispersive effect peaked at 3.77 eV, while the EELS is observed at 22.2 eV. Also for the defective Cu_2O, the absorption effect is 3.96eV, its dispersive is 3.79eV and its EELS is 18.50. As for the Cu_2O-doped nitrogen, the absorption effect peaked at 0.24 eV, while the dispersive effect was observed at 1.3 eV. The EELS were observed to peak at 16.5 eV. Table 1 below shows the differences between pure Cu_2O, defective Cu_2O, and defective nitrogen-doped Cu_2O in terms of their absorption effect, dispersion effect, and Electron Energy Loss Spectroscopy (EELS).

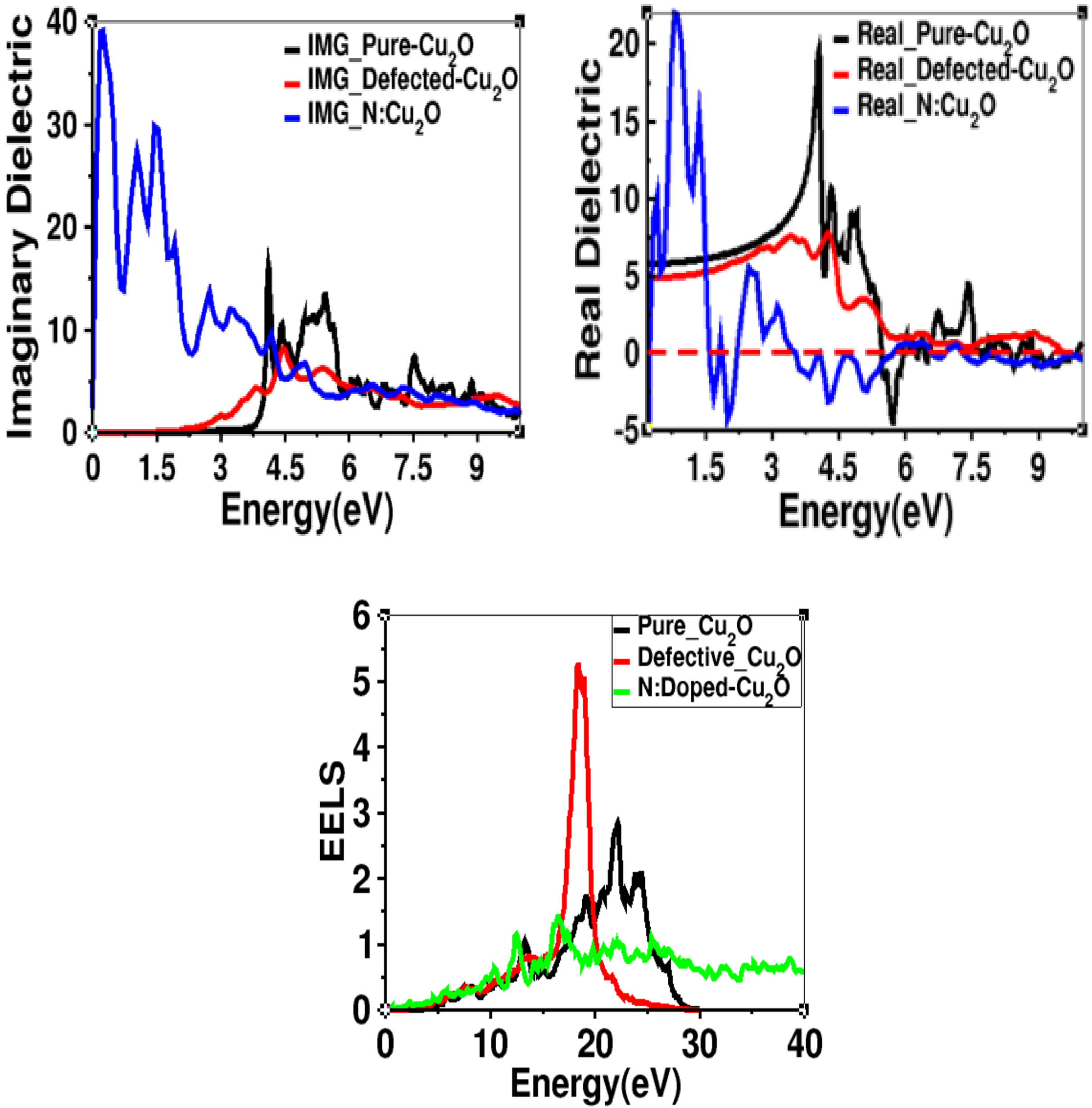


Fig. 5 depicts the imaginary (a), Real .(b), Electron Energy Loss Spectroscopy (EELS) .(c) of Pure, defective and doped N: Cu_2O under DFT+U calculation with spin polarization and Hubbard value of 8.5eV.

Table 1: Shows the pure Cu_2O, defective Cu_2O, and defective nitrogen-doped Cu_2O in terms of their absorption effect, dispersion effect, and Electron Energy Loss Spectroscopy (EELS)

Condition	Absorption Effect (eV)	Dispersion Effect (eV)	EELS (eV)
Pure Cu_2O	3.75	3.77	22.3
Defective Cu_2O	3.96	3.79	18.5
Defective Nitrogen-doped Cu_2O	0.8	1.3	16.5

In the result above its seen that the absorption energy for defective Cu_2O increases slightly compared to pure Cu_2O, suggesting that defects may create states that require more energy for electron transitions. Nitrogen doping, however, drastically reduces the absorption energy, indicating a significant alteration of the electronic structure and band gap reduction.

Similar to the absorption effect, the dispersion energy for defective Cu_2O is only slightly higher than that for pure Cu_2O. Nitrogen doping results in a much lower dispersion energy, which again points to significant changes in the material's electronic properties due to doping.

The EELS data indicate how much energy is lost by electrons traveling through the material. The decrease in EELS energy from pure to defective Cu_2O and further to nitrogen-doped Cu_2O suggests an increasing presence of defect states and/or changes in electronic structure, making it easier for electrons to lose energy.

Therefore, for optoelectronic applications, materials with lower absorption and dispersion energies are often advantageous because they can be more easily excited by lower energy (longer wavelength) light, which is beneficial for devices like photodetectors, solar cells, and LEDs. The significantly lower absorption and dispersion energies for defective nitrogen-doped Cu_2O (0.8 eV and 1.3 eV, respectively) indicate that this material is more responsive to visible or even infrared light, making it more suitable for a wider range of optoelectronic applications compared to pure and defective Cu_2O. Additionally, the reduced EELS value for defective nitrogen-doped Cu_2O suggests fewer energy losses in the material, which is advantageous for efficient energy transfer in devices.

CONCLUSION

In this study, we employed first-principles calculations to investigate the linear optical and electronic properties, such as band gap, dielectric function, electron energy loss spectroscopy (EELS), and absorption coefficient, of pristine Cu_2O, defective Cu_2O with an oxygen vacancy, and nitrogen-doped defective Cu_2O. The introduction of nitrogen dopants and defects such as oxygen vacancies can improve the separation of photogenerated electron-hole pairs. This is critical in photocatalysis, as it reduces recombination rates and enhances the efficiency of processes like water splitting and pollutant degradation. It also can narrow the band gap of Cu_2O, allowing the material to absorb a broader range of visible light. This makes the material more effective under sunlight, enhancing its performance in solar energy applications. To effectively analyze their optical behaviour, we plotted various optical properties against their corresponding energies.

The pristine Cu_2O exhibits a low band gap of approximately 0.5 eV. However, when including the effects of spin polarization and Hubbard U correction, the band gap increases to about 1.67 eV. Creating an oxygen vacancy further widens the band gap to 1.97 eV and shifts the direct band gap from the Gamma point to the X point. Nitrogen doping of the defective Cu_2O transforms the system into a direct band gap semiconductor with a reduced band gap of 1.09 eV.

The nitrogen-doped defective Cu_2O shows the most promise for optoelectronic applications due to its significantly lower absorption and dispersion energies and reduced electron energy loss. These properties align well with the requirements for efficient and responsive optoelectronic devices, making nitrogen-doped defective Cu_2O an advantageous material for such applications.

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