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Enhanced Localized surface plasmon resonance and Interfacial Charge Transfer in Cu/ZnO Nanosphere Heterostructures: Insights from Combined DFT and FDTD Simulations

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Abstract

Localized surface plasmon resonance (LSPR) enhances light absorption and quantum conversion efficiency in photocatalysts. The LSPR mechanism in Cu nanospheres loaded on ZnO nanospheres was investigated using FDTD simulations, while DFT was used to analyze interfacial charge transfer in Cu/ZnO heterostructures. Structures include A, a Cu nanosphere on ZnO; B, a partially embedded Cu nanosphere in ZnO; and C, a Cu/ZnO core-shell structure. Cu nanoparticles exhibit a response around 570nm. Increasing nanoparticle size strengthens plasmon-interband coupling, enhances extinction intensity, induces a red shift, and produces local electric field enhancement up to ~1000 times the incident field. Embedding Cu nanospheres in ZnO to form a core-shell structure improves hot-electron utilization, suppresses corrosion, and tunes the dominant plasmonic response. Structure A shows LSPR peaks at 585nm (normal incidence) and 577nm (parallel incidence), with a three fold higher electric field under normal illumination. Structure B exhibits a peak at 594nm for both directions, indicating reduced angular sensitivity. Increasing ZnO radius (30–50nm) results in red shifts of 22nm, 23nm, and 47nm for structures A, B, and C, respectively. LSPR response depends on refractive index (1.333–2.25), with all structures converging to 658nm at $n = 1.7843$. PDOS analysis indicates strong Cu/ZnO orbital hybridization, leading to charge redistribution, Schottky barrier formation, and an upward shift of the Fermi level. Interfacial coupling enhances hot-electron transfer and contributes to LSPR strengthening and red-shift behavior, particularly in core-shell structures with larger contact areas. These results inform plasmonic heterostructure design for photocatalytic and plasmon-enhanced solar energy conversion applications.

Keywords:

Cu nanosphere, ZnO nanosphere, photocatalyst, localized surface plasmon resonance (LSPR).

Statements and Declarations

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Data Availability

The datasets generated and/or analyzed during the current study are not publicly available but are available from the corresponding author upon reasonable request.

Author Contributions

Mobina Eskandari: Conceptualization, methodology, software, formal analysis, investigation, data curation, visualization, and writing – original draft also performed the FDTD simulations, conducted the main data analysis and interpretation, prepared the figures, and developed the manuscript. Mohsen Vafaei: Supervision. Mokhtar Nasrollahpour: Assistance with the DFT simulations and data analysis. All authors read and approved the final manuscript.

1. Introduction

Nowadays, pollution has penetrated all aspects of our living environment. Among the methods for removing these pollutants, Semiconductor-based photocatalytics are particularly noteworthy[1]. In a photocatalytic process, both the absorption wavelength range and quantum efficiency of the reaction must be carefully controlled[2–4]. Over the past decades, a wide variety of methods have been investigated to manage these two factors. One such approach involves the effects of localized surface plasmon resonance (LSPR)[5–7]. This physical phenomenon can expand the light absorption range of a photocatalyst within the visible and near-infrared spectrum by modifying the particle size[8], morphology[9], and dielectric environment[10]. Additionally, the separation of electron-hole pairs in a localized surface plasmon resonance effect is influenced by the enhanced field at the metal-semiconductor interface[11], and the generation of hot electrons increases the quantum efficiency of the photocatalyst[12–14]. Gold (Au), Silver (Ag), Copper (Cu), Aluminum (Al), Platinum (Pt), Palladium (Pd), Nickel (Ni), Titanium (Ti), Zinc (Zn), Iron (Fe), when structured into nanoparticles, exhibit strong LSPR effects due to their free electrons oscillating in response to light[15] which enhances the photocatalytic activity[16,17]. Among these metals, copper, being in the same group as gold and silver, shares similar properties with them. Its localized surface plasmon resonance absorption peak is around 500 nm, within the visible light range and given its cost-effectiveness, copper is a suitable candidate for further study[18–20]. Thus, Cu is recognized as a metal with suitable LSPR, and by adding an appropriate semiconductor to it, a photocatalyst can be developed to exploit the LSPR properties of Cu because LSPR in copper nanoparticles can increase the performance of photocatalysts [21]. On the other hand, based on the aforementioned points, using Cu-based hybrids, such as core-shell structures, can enhance photocatalytic activity[22–24]. Our proposed semiconductor is ZnO, as this material alone possesses photocatalytic properties in the UV range[25–27]. However, we know that only a small percentage of sunlight consists of UV light[28], which causes the low efficiency of this photocatalyst under sunlight [29]. Because ZnO has a theoretical bandgap of approximately 3.4 eV, it requires photon energies equal to or greater than this value to excite electron-hole pairs and enable charge transfer from the ground state to higher energy states in the photocatalyst [30,31]. By Puja Goel et al., Cu/Cu₂O core-shell nanoparticles were employed as an efficient photocatalyst for the degradation of endosulfan under solar light. The LSPR effect of the Cu core facilitated the generation of hot electrons, which were subsequently transferred to the Cu₂O shell, thereby improving charge separation and reducing electron-hole recombination. As a result, the overall photocatalytic efficiency was greatly enhanced compared to bare Cu₂O[32]. The study by Pan et al. (2020) showed that the localized surface plasmon resonance (LSPR) properties of copper nanoparticles in contact with TiO₂ differ significantly from the LSPR properties of isolated single particles. In this research, copper nanoparticles were brought into contact with layered structures containing TiO₂, and it was observed that the LSPR resonance peak shifted significantly from the visible region (~600 nm) to the near-infrared region (~835 nm). This shift was attributed to the interaction between the nanoparticle surfaces and their surrounding environment,

particularly due to charge transfer and variations in the dielectric environment [33]. B. Lamprecht and et al. showed that when the energy range of interband transitions overlaps with the energy of the localized surface plasmon resonance (LSPR), plasmonic absorption is significantly reduced. This overlap leads to increased losses and a decrease in near-field enhancement due to the additional non-radiative decay channels introduced by the interband transitions. These findings support the view that, in pure metal nanoparticles, the simultaneous presence of interband transitions in the spectral region of the LSPR weakens both the absorption strength and the electric field intensity associated with the resonance[34,35]. The LSPR effects on copper are influenced by the morphology and size of the copper nanoparticles, along with the dielectric properties of the surrounding medium [20,36,37]. The precise control of this morphology is highly challenging, which is why it remains a subject of advanced research. S. Sriram et al. , using simulation methods, doped ZnO with different percentages of Cu (10%, 20%, and 30%) and reported that the band gap of this structure decreased to 2.31 eV, 2.44 eV, and 2.56 eV, respectively [38]. Moreover, ZnO is non-toxic and highly stable in the environment, making it suitable for environmental and biomedical applications. Its high electron mobility allows for efficient charge transfer during photocatalysis[39]. There are many different methods for constructing photocatalysts, but considering the time-consuming nature and potential errors in experimental approaches, it was decided in this work to investigate the photocatalyst properties of Cu/ZnO using simulation methods. We used the Lumerical FDTD and DFT simulations in this study. The FDTD method models the propagation of electromagnetic waves and their interactions with materials, while DFT helps to understand the electronic structures, energy levels, and charge transfer mechanisms in photocatalysts. In this study, we present a comprehensive investigation of the localized surface plasmon resonance (LSPR) effects of copper nanospheres on ZnO nanospheres within various predefined structural configurations exhibiting distinct morphologies. This research systematically examines how variations in nanoparticle size, morphology, and dielectric environment affect the photocatalytic performance of Cu/ZnO systems. Furthermore, we introduce a specially designed Cu/ZnO heterostructure aimed at closely studying the surface phenomena induced by Cu on ZnO. This approach, combined with precise simulation and analysis methods, provides new insights into the plasmonic enhancement mechanisms and interfacial charge transfer processes that are crucial for improving the photocatalytic efficiency of these structures.

2. Methods

2.1 FDTD simulations.

In this work, a Cu/ZnO nanostructure was irradiated by a planar light source in the range of 300 to 1000 nm along the x-axis, with polarization along the z-axis. The structure was placed in an environment with 100 layers of PML (Perfectly Matched Layer). The PML is an artificial absorbing boundary condition widely used in electromagnetic simulations to suppress non-physical reflections from the boundaries of the computational domain. It is designed to absorb outgoing electromagnetic waves over a broad range of incident angles and wavelengths, thereby effectively mimicking an open and infinite space. mesh of the system was set to a size of 2 nm along the x, y, and z axes. This work utilized Cu nanoparticles with dielectric constants from experimental data [40]and ZnO nanoparticles with dielectric constants derived from a thin film [41]. The specified conditions were maintained across all simulation models. The simulation was conducted by positioning the structure at the center of the PML, placing absorption and scattering monitors at the interface between the PML and the structure, and positioning a field intensity monitor. The data obtained from the absorption and scattering monitors were combined to yield the extinction cross-section data.

2.2 DFT calculations.

The electronic properties of the hybrid structure were studied using Density Functional Theory (DFT). All optimization and electronic calculations for this section were performed in the CASTEP software, executed via the Materials Studio tool [42]. The hybrid structure, made from two bulk structures, was prepared using Virtual Nano Lab software. To facilitate calculations, the Cu and ZnO structures were considered as atomic bilayers and positioned adjacent to each other. The (001) surface (Miller index) was selected for both bulk structures to represent the layered configuration due to its stability and its common use in modeling Cu/ZnO interface systems in previous theoretical studies[43]. These layered structures were initially placed approximately 3 Å apart, and optimization calculations were performed. The energy and force convergence criteria were set to 10^{-6} eV and 10^{-2} eV/Å, respectively. To account for van der Waals interactions between the Cu and ZnO structures, the Grimme method [44] was employed. Exchange-correlation potential estimation was done using the PBE functional [45]. Ultrasoft pseudopotentials were used for all calculations [46]. The cutoff energy for confining the Kohn-Sham orbitals was set to 490 eV. The k-point mesh in the reciprocal lattice was set to $1 \times 6 \times 2$.

3. Results

Based on what has been discussed about the generation of LSPR (Localized Surface Plasmon Resonance) in nanoparticles, there are two methods for population decay: one is radiative damping, in which the plasmons of the particles convert into photons, and the other is non-radiative damping, which occurs through electron-hole excitations. Radiative damping itself results from two processes: intraband and interband excitations[47–49]. Electrons in Cu nanoparticles occupy energy states below the Fermi level under equilibrium conditions. Upon absorption of photon energy, some electrons are excited to higher energy states above the Fermi level, generating excited carriers. These excited electrons can collectively oscillate in response to an external electromagnetic field, leading to localized surface plasmon resonance (LSPR) in Cu nanoparticles [35,50,51]. This characteristic leads to the appearance of two resonance peaks in the extinction cross-section of Cu: one related to interband transition interactions with LSPR (i), and the other associated with LSPR (ii). It has been reported that a double resonance appears when a plasmon overlaps with the interband transition threshold [35,52,53]. Therefore, the extinction cross-section of Cu nanoparticles with different radii in an air environment (with a dielectric constant ($n = 1$)) was examined. The extinction cross-section is equal to the sum of the absorption and scattering cross-sections [54]. Additionally, the real and imaginary parts of the dielectric function for Cu were plotted using data obtained from reference materials. The plot for the real part of the dielectric function (n) shows a cutoff wavelength at 500 nm, while the imaginary part of the dielectric function (k) becomes more negative from 500 nm to 1000 nm, which is where the Cu LSPR peak is expected to appear [40,55]. Based on Figures 1 (a,b) it can be understood that intensity of peak (i) increases with increasing nanoparticle size. This indicates that as the nanoparticle size increases, the interaction of interband transitions with LSPR intensifies. Additionally, the Cu LSPR peaks are observed around 570 nm, and moreover, the (i) peaks are taller than the (ii) peaks. It can therefore be concluded that increasing the size of Cu nanoparticles can enhance the interaction of interband transitions with LSPR. On the other hand, increasing the size of Cu nanoparticles leads to a shift toward the longer wavelength in the LSPR absorption peak. Additionally, the trend in the change of the plasmon extinction cross-section peaks with increasing nanoparticle radius is seen in Figures 1(a).

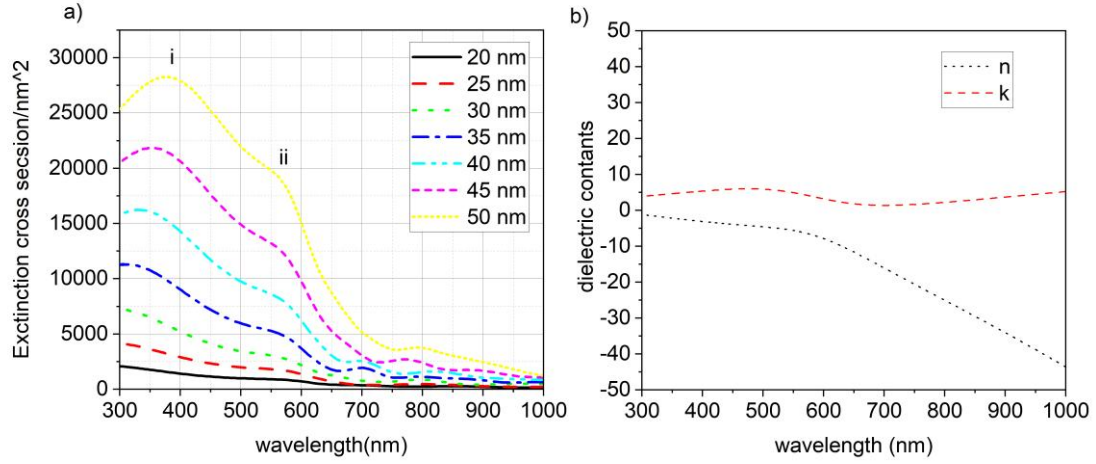


Fig. 1 a) cross-section of Cu with radii of 20, 25, 30, 35, 40, 45, and 50 (nm) according to wavelength. b) Plot of real part (n) and imaginary part (k) of Cu dielectric function

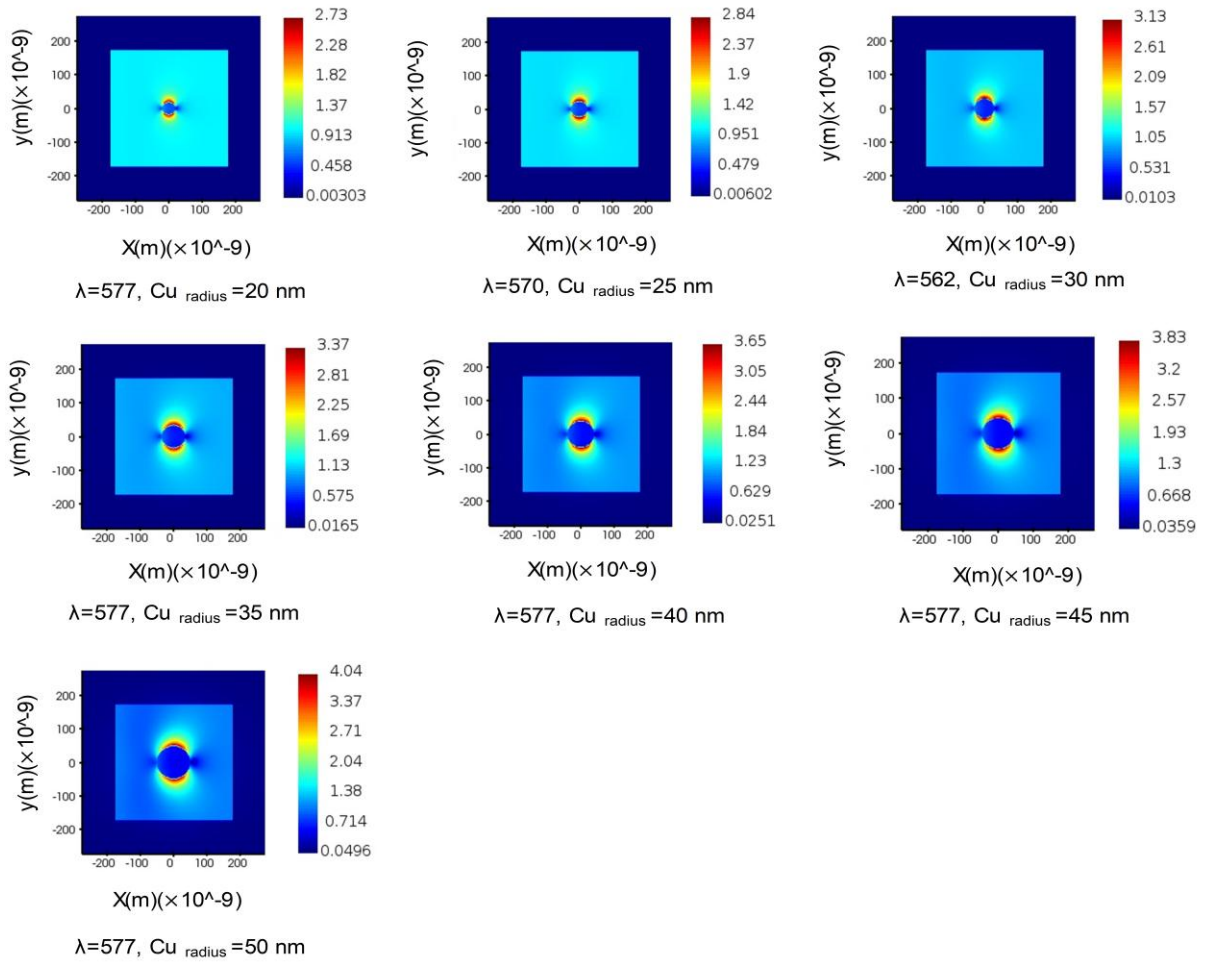


Fig. 2 Electric field profiles of Cu nanoparticles with different dimensions at LSPR wavelength

By examining the field profile of Cu nanoparticles in Figure 2 it can be concluded that as the radius increases, the electric field intensity $|E|^2/|E_0|^2$ also increases. This is because, in plasmon resonance, the scattered field intensity can significantly increase due to the strong interaction between the incident light and the collective electron oscillations. An increase in the radius of a sphere reduces its surface curvature [56], which leads to stronger confinement and enhancement of the electric field near the nanoparticle surface, suggesting increased localization of the plasmonic response for larger nanoparticles. The collective oscillation of free electrons on the surface of Cu under the influence of the electromagnetic field of the incident light, which then generates energetic hot electrons, creates a local electric field on the surface of Cu nanoparticles [57]. This local field promotes the separation of photogenerated electron-hole pairs [58]. The local plasmonic electric field intensity at hot spots is approximately 1000 times larger than the incident electric field [59]. Photogenerated hot electrons lose some of their energy due to collisions with lattice phonons, which shortens their lifetime [50]. Guo-Ying Yao et al. stated that controlling the size of Cu nanoparticles is effective for tuning LSPR excitation above the Fermi level [18]. In another work, Zhou-jun Wang et al. reported that photo-generated hot electrons on the Cu surface and electron transfer to the ZnO surface can contribute to photocatalytic reactions such as methanol synthesis [60]. Therefore, we introduced a ZnO semiconductor shell for Cu, which not only has the photocatalytic ability to use hot electrons, but also can prevent the corrosion of Cu metal in the environment. It can also be effective for modulating the LSPR peak of Cu nanoparticles.

3.1 Introducing the proposed structures for Cu/ZnO.

In this work, we propose three structures for Cu/ZnO, which are named structures A, B, and C. Figure 3 Structures A and B have a symmetry axis passing through the centers of the two nanospheres, so their optical response depends on the direction of the incoming light.

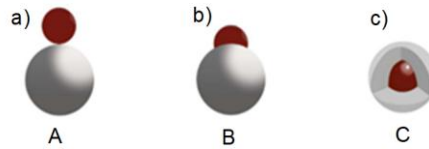


Fig. 3 A view of the proposed structures A (a), B (b), C (c), (red Cu nanospheres and gray ones are ZnO)

3.2 Simulation of structure A, B with two normal and parallel directions of incident light.

As illustrated in Figure 4, structures A and B were illuminated once parallel and once perpendicular to the symmetry axis to study the effect of light direction on the LSPR behavior. In structure A, the peak intensity of LSPR with normal incident light (at a wavelength of 585 nm) is significantly higher than that in the parallel incident light state (at a wavelength of 577 nm). Additionally, the electric field intensity in the normal state is three times stronger than in the parallel state. On the other hand, based on the electric field intensity profile, it can be observed that LSPR in the normal state interacts well with ZnO. Considering the field profile, it can be seen that the field generated by LSPR in the normal state is only distributed at the contact point of the two nanospheres, and a very small intensity has been able to propagate through the structure from Cu to ZnO, with most of the intensity being observed at the surface of the Cu nanoparticles. In the parallel state, the increased electric field intensity resulting from light is observed at both sides of the contact surface and mostly at the surface of the Cu nanospheres. In structure B, the peak intensity of LSPR in the normal state (at a wavelength of 594 nm) is significantly higher than that in the parallel state (at a wavelength of 594 nm). However, there is no significant difference in electric field intensity between the normal and parallel states. Nonetheless, the field intensity in the normal state is still slightly higher than

that in the parallel state. Based on the field profile, it can be observed that the field generated by LSPR in the parallel state propagates on both sides of the contact point between the nanoparticles. In contrast, in the normal state, it not only spreads at the contact point but also extends from one end of the Cu nanosphere to the other end of the ZnO nanosphere. In this case, model A shows a greater dependence on the direction of the incident light compared to model B. This indicates that in the context of photocatalysis, the direction of the incident light should be considered when utilizing LSPR effects to enhance the performance of photocatalysts[61,8].

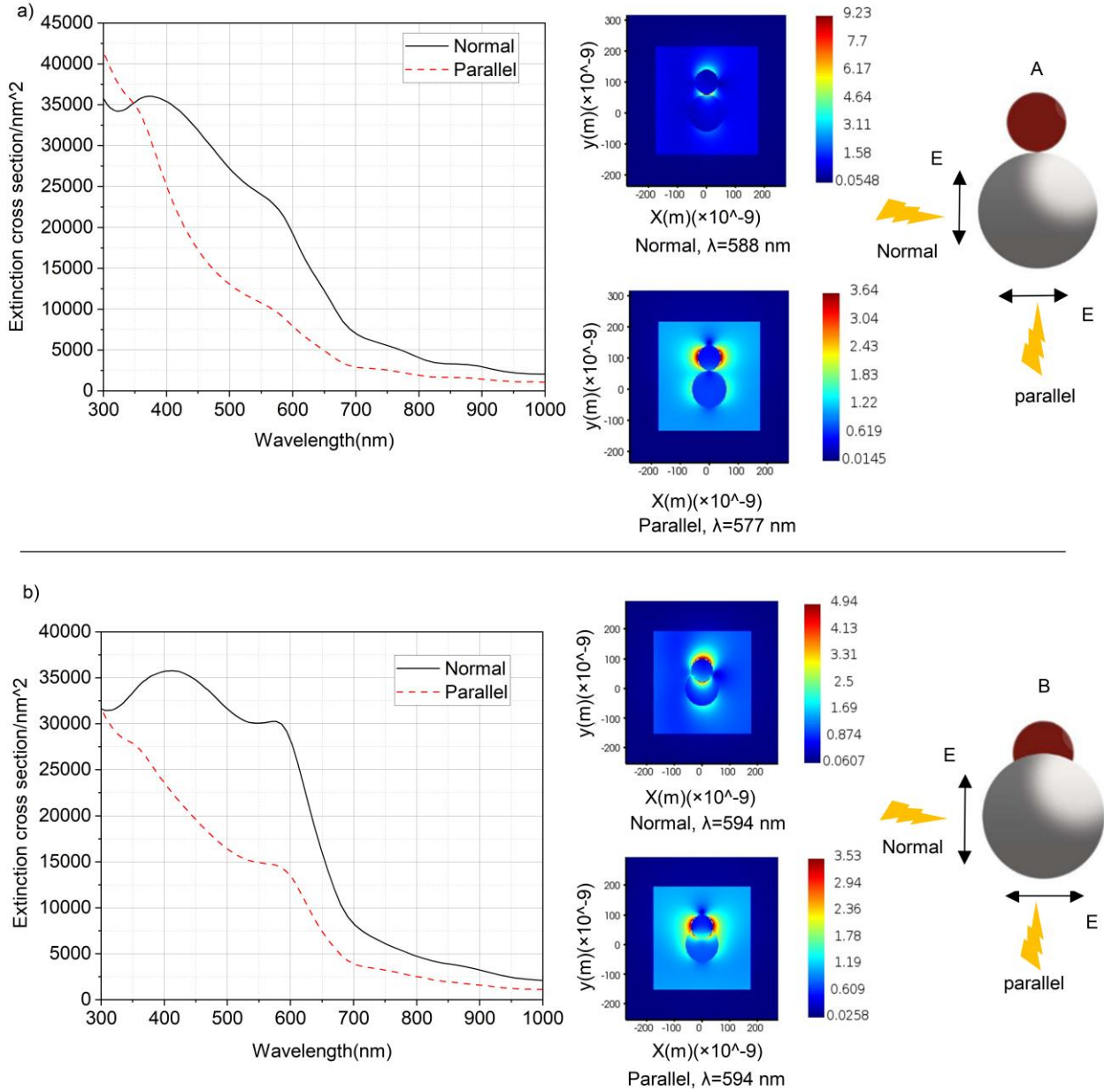


Fig. 4 Structures A (a) and B (b) were shown to be illuminated once parallel and once perpendicular to the symmetry axis of the structure, structures A and B are composed of Cu nanospheres with a 40nm radius and ZnO nanospheres with a 60nm radius

3.3 Investigating the effect of the size of ZnO nanospheres on the structure of A, B, C.

This section examines how the dimensions of ZnO nanospheres influence the plasmonic behavior of Cu/ZnO nanostructures. In all configurations, the Cu nanosphere has a fixed radius of 25 nm. For structures A and B, the ZnO nanosphere radius varies between 30 and 50 nm, with structure B featuring partial embedding of the Cu nanoparticle to a depth equal to its radius. In structure C, the Cu nanoparticle is fully centered within a ZnO shell, whose thickness ranges from 5 to 25 nm. Figures 5-7 display the extinction cross-section as a function of wavelength, along with corresponding local electric field distributions. Structure A shows two prominent peaks: a shorter-wavelength peak at 300–400 nm corresponding to ZnO absorption [62] and a longer-wavelength peak between 500–1000 nm originating from Cu's LSPR. The LSPR peak is centered around 577 nm, while a broad feature at 400–500 nm reflects interaction between Cu's interband transitions and LSPR [7]. With an increase in the radius of the ZnO nanosphere, the intensity of these peaks increases, and the peak positions experience a red shift. [63]. Around 450 nm, as the structure transitions from B to C with the Cu nanosphere moving deeper into ZnO and becoming fully encapsulated, the peak intensity decreases. This occurs because, as the LSPR peak of the Cu nanoparticles passes through the interband transition region, the interaction between the LSPR and the interband transition weakens [52]. However, from structure A to B, this trend is reversed; that is, as the Cu nanosphere is embedded into the ZnO nanosphere, the peak intensity increases. This is due to a stronger interaction between the LSPR peak and the interband transition as it passes through the interband transition region. Also the red shift of the LSPR wavelength becomes more pronounced with increasing the degree of immersion of the Cu nanosphere in the ZnO nanosphere. The refractive index of ZnO ($n = 1.7843$) is higher than that of air ($n = 1$). Thus, the refractive index of the surrounding dielectric medium increases as Cu is further immersed in ZnO, leading to a red shift of the LSPR peak. Also the ZnO coating acts as a protective factor against environmental influences. In Figure 5,6 for structure A and B, with an increase in the radius of the ZnO nanosphere, the intensity of the local field generated by the Cu LSPR, as well as the intensity of the extinction cross-section peaks, increases. Additionally, a red shift of 22 nm occurs in structure A and a red shift of 23 nm occurs in structure B. Therefore, it can be concluded that in structure A, B increasing the size of the semiconductor nanosphere may enhance its photocatalytic efficiency. In Figure 7 for structure C, as the radius of the ZnO nanosphere increases, the intensity of the local field generated by the Cu LSPR decreases, but the extinction cross-section peaks increase. Additionally, the LSPR wavelength shifts out of the Cu interband transition region, with a red shift of 47 nm occurring in this structure. It can be stated that semiconductors with a higher refractive index as the shell are an effective way to control the LSPR peaks. Structures A and B exhibit a smaller red shift compared to structure C. Although the present results show that increasing the ZnO dimension enhances the extinction intensity and local electric field distribution within the investigated size range, this behavior is not expected to continue indefinitely for arbitrarily larger structures. In plasmonic nanoparticles, increasing particle size beyond a critical regime can enhance radiative damping, plasmon dephasing, and retardation effects, which reduce field confinement and consequently weaken the localized surface plasmon resonance (LSPR) enhancement[64].

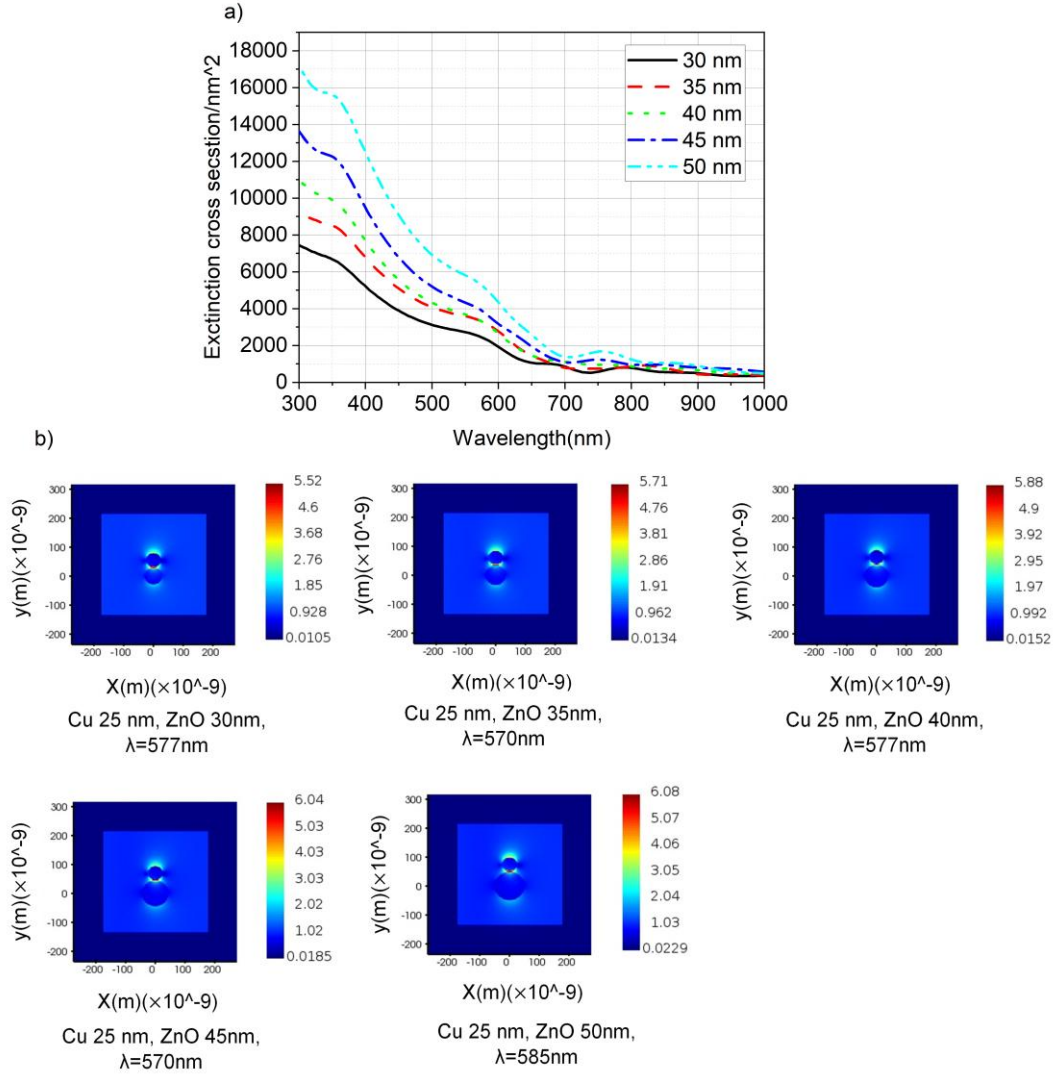


Fig. 5 A view of the extinction cross-sections in terms of wavelength (a) and the shape of the field profiles (b) for the LSPR wavelength of structure A

Therefore, an optimal particle-size regime is expected for maximizing plasmonic performance. In the present study, the investigated dimensions remain within a regime where increasing the semiconductor size still strengthens the plasmonic response, particularly in structures B and C due to their larger interfacial coupling and dielectric confinement. Among the studied configurations, structure C exhibits the strongest redshift behavior owing to the complete encapsulation of the Cu nanoparticle by ZnO, whereas structure B provides strong local electric field enhancement with efficient interfacial interaction. These findings suggest that the plasmonic response depends on a balance between particle size, morphology, dielectric environment, and interfacial coupling. Further investigation of larger particle dimensions may reveal the transition regime where the enhancement reaches its maximum and subsequently decreases.

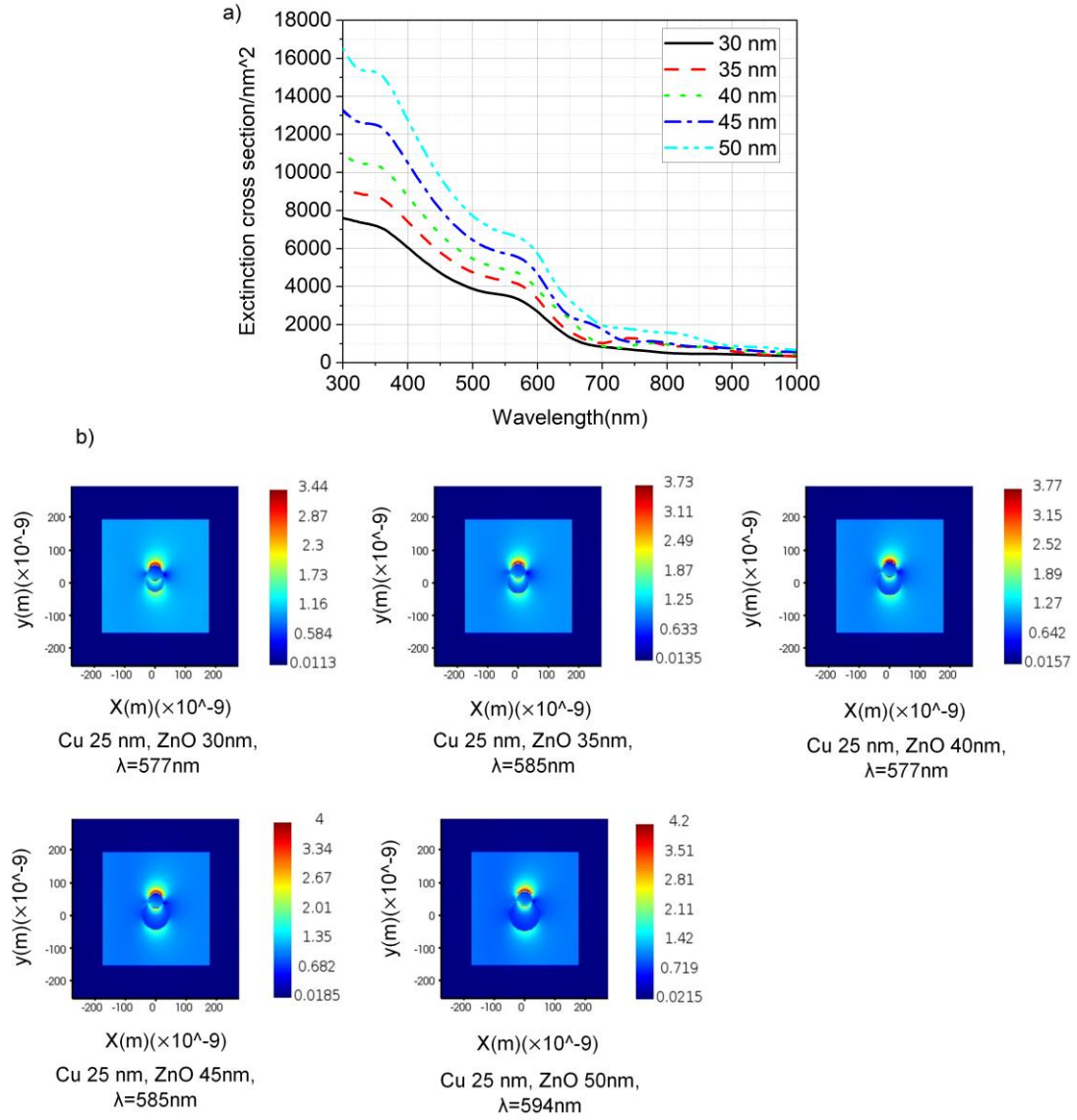


Fig. 6 A view of the extinction cross-sections in terms of wavelength (a) and the shape of the field profiles (b) for the LSPR wavelength of structure B

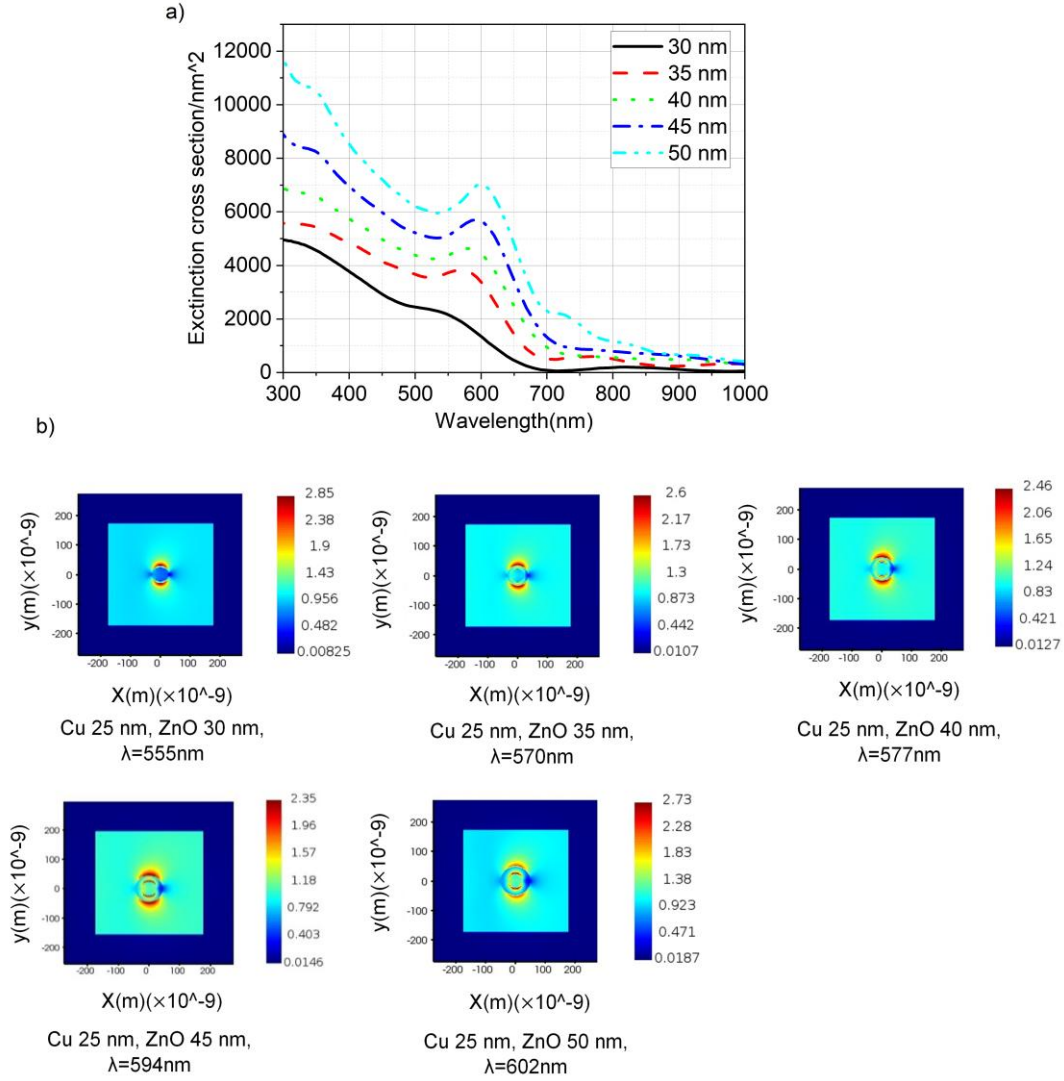


Fig. 7 A view of the extinction cross-sections in terms of wavelength (a) and the shape of the field profiles(b) for the LSPR wavelength of structure C

3.4 Investigating the influence of the refractive index of the medium.

The localized surface plasmon resonance (LSPR) of metal nanoparticles is strongly influenced by both their intrinsic properties and the dielectric characteristics of the surrounding environment[65,66]. To investigate this effect, Cu/ZnO nanostructures with various morphologies were studied in media with different refractive indices, such as water ($n = 1.333$), ethanol ($n = 1.36$), methanol ($n = 1.44$), and concentrated NaCl solution ($n = 1.54$) Figure 8 and Tables 1,2. When the refractive index of the medium is lower than that of ZnO ($n = 1.7843$) all three nanostructures display a red shift in their LSPR wavelength. Among them, structure B shows the largest red shift, whereas pure Cu exhibits the smallest. The local electric field intensity also varies with the refractive index. In structures B and C, as well as in pure Cu, the field generally increases with increasing refractive index, whereas in structure A, the field intensity decreases, contrary to the trend in the other two structures. Across all tested indices below 1.7843, structures A and B show stronger electric fields than pure Cu, suggesting enhanced interactions between Cu and ZnO. At a refractive index equal to that of ZnO (1.7843), all structures exhibit the same LSPR wavelength of 658

nm, indicating that under this condition, structural differences have minimal influence on the plasmon resonance. For refractive indices higher than ZnO, the LSPR behavior diverges: pure Cu experiences the largest red shift, followed by structure A, while structure B shifts less, and structure C shows no clear trend. The corresponding electric field intensity does not follow a uniform pattern, demonstrating that LSPR behavior depends strongly on the surrounding medium. At a refractive index of 2.25, the field intensities of most structures become comparable, suggesting that at high refractive indices, the morphology of the nanostructure has limited influence on local LSPR intensity, even though LSPR peaks remain distinct. These findings underscore the importance of considering both the refractive index of the photocatalyst and that of the surrounding medium when evaluating plasmonic photocatalytic performance.

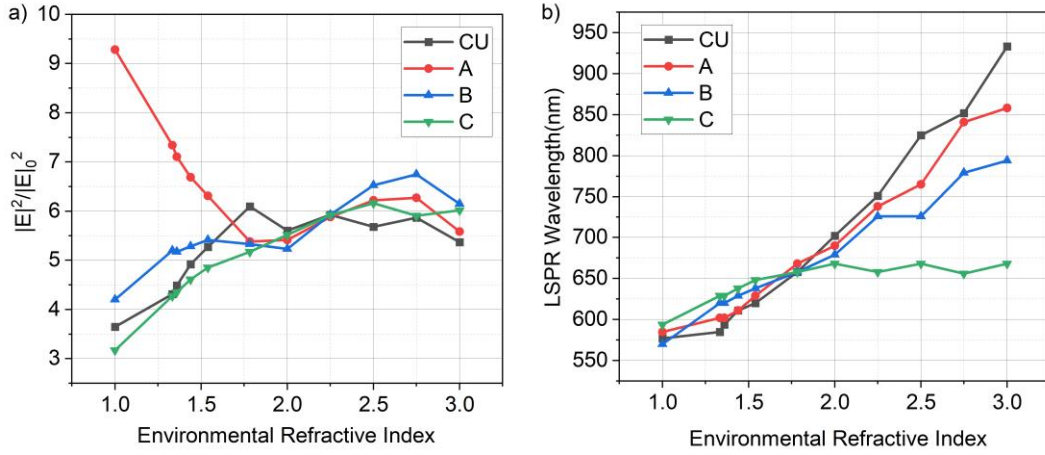


Fig. 8 LSPR wavelength(a) and electric fields (b) for structures A, B, C in environments with different refractive index

Refractive Index	$\lambda_{Cu}(nm)$	$\lambda_A(nm)$	$\lambda_B(nm)$	$\lambda_C(nm)$
1.0	577	585	570	594
1.333	585	602	620	629
1.36	594	602	620	629
1.44	611	611	629	638
1.54	620	629	638	648
1.7843	658	668	658	658
2	702	690	679	668
2.25	751	738	726	658
2.5	825	765	726	668
2.75	852	841	779	656
3	933	858	794	668

Table 1 LSPR wavelength for different refractive indices.

Refractive Index	I_{Cu}	I_A	I_B	I_C
1.0	3.65	9.28	4.2	3.17
1.333	4.31	7.34	5.2	4.27
1.36	4.49	7.11	5.17	4.35
1.44	4.92	6.69	5.28	4.61
1.54	5.27	6.31	5.41	4.85
1.7843	6.1	5.38	5.33	5.17
2	5.6	5.41	5.23	5.52
2.25	5.93	5.88	5.93	5.92
2.5	5.68	6.22	6.53	6.16
2.75	5.87	6.27	6.75	5.91
3	5.37	5.58	6.15	6.02

Table 2 electric field intensity for different refractive indices.

3.5 Density of states and Surface properties of the heterogeneous Cu/ZnO structure.

Figure 9 (a,b) presents the electronic structure and density of states (DOS) of bulk Cu obtained from DFT calculations. The results confirm the metallic nature of Cu, where localized 3d states are mainly distributed below the Fermi level, while an s-p hybridized band crosses the Fermi level. Under light excitation, electrons near the Fermi level participate in collective oscillations with the external electromagnetic field, leading to localized surface plasmon resonance (LSPR). The decay of these plasmons may occur through radiative (between the d band and conduction band (CB)) and nonradiative (in the conduction band) processes [67]. Although the majority of the d-band states are distributed below approximately -1.75 eV, a small portion extends toward the Fermi level due to d-sp hybridization. Constructing semiconductor-metal heterostructures is a well-known strategy for improving photocatalytic efficiency through enhanced charge separation and light absorption. In this work, PDOS calculations were performed to investigate the electronic interactions between Cu and ZnO at the interface. Figure 10 schematically illustrates the Cu/ZnO heterostructure model used in the DFT calculations. The structure consists of Cu and ZnO (001) bilayers with an initial interlayer separation of approximately 3 Å, followed by full structural relaxation. The schematic represents the initial configuration, while all electronic properties are calculated based on the optimized geometry obtained after relaxation. Projected density of states (PDOS) calculations were performed to analyze the orbital interactions between ZnO and Cu atoms. As shown in Figure 11, the strongest orbital contributions arise from Zn(p)-Cu(d) and Zn(p)-Cu(p) interactions, while the Zn(d)-Cu(d) contribution is comparatively weak. In addition, O(p) orbitals in ZnO overlap with Cu d and p orbitals, indicating significant electronic interaction at the interface between the two materials. Also in Figure 9 (b-e), the comparison of PDOS of ZnO and Cu layers in the heterostructure and bulk state reveals a pronounced downward shift of the electronic bands in both materials, indicative of an upward displacement of the Fermi level. This shift indicates a redistribution of electronic states near the Fermi level. At the Cu/ZnO interface, ZnO exhibits an increase in density of states near the Fermi level compared with its bulk form. This indicates an enhanced density of electronic states near the Fermi level, originating from strong electronic coupling between the two materials. Conversely, for Cu, the density of states decreases near the Fermi level in comparison with bulk Cu, when it is in contact with ZnO. Such interfacial electronic modifications have been reported in previous studies to be associated with Schottky-type behavior at Cu/ZnO interfaces [57,58,68]. In the present work, no direct band alignment calculations

are performed; therefore, this interpretation is qualitative and based on previous literature. Accordingly, the presence of interfacial states may facilitate charge-transfer processes across the Cu/ZnO interface and could contribute to the simulated optical response (FDTD), including changes in the LSPR intensity and resonance position. Therefore, the greater the contact area, the more interfacial electronic states are formed [68], leading to a stronger redshift and increased intensity of the peaks. In this regard, the core-shell structure (C) of Cu/ZnO provides the largest contact area and therefore exhibits the strongest LSPR effects. On the other hand, Figure 9 (b-e) shows that a comparison of the total DOS plots for the individual and hybrid structures indicates that the density of states at the Fermi level mainly originates from the copper structure. This suggests that the conductivity of the hybrid structure is primarily due to the contribution of copper.

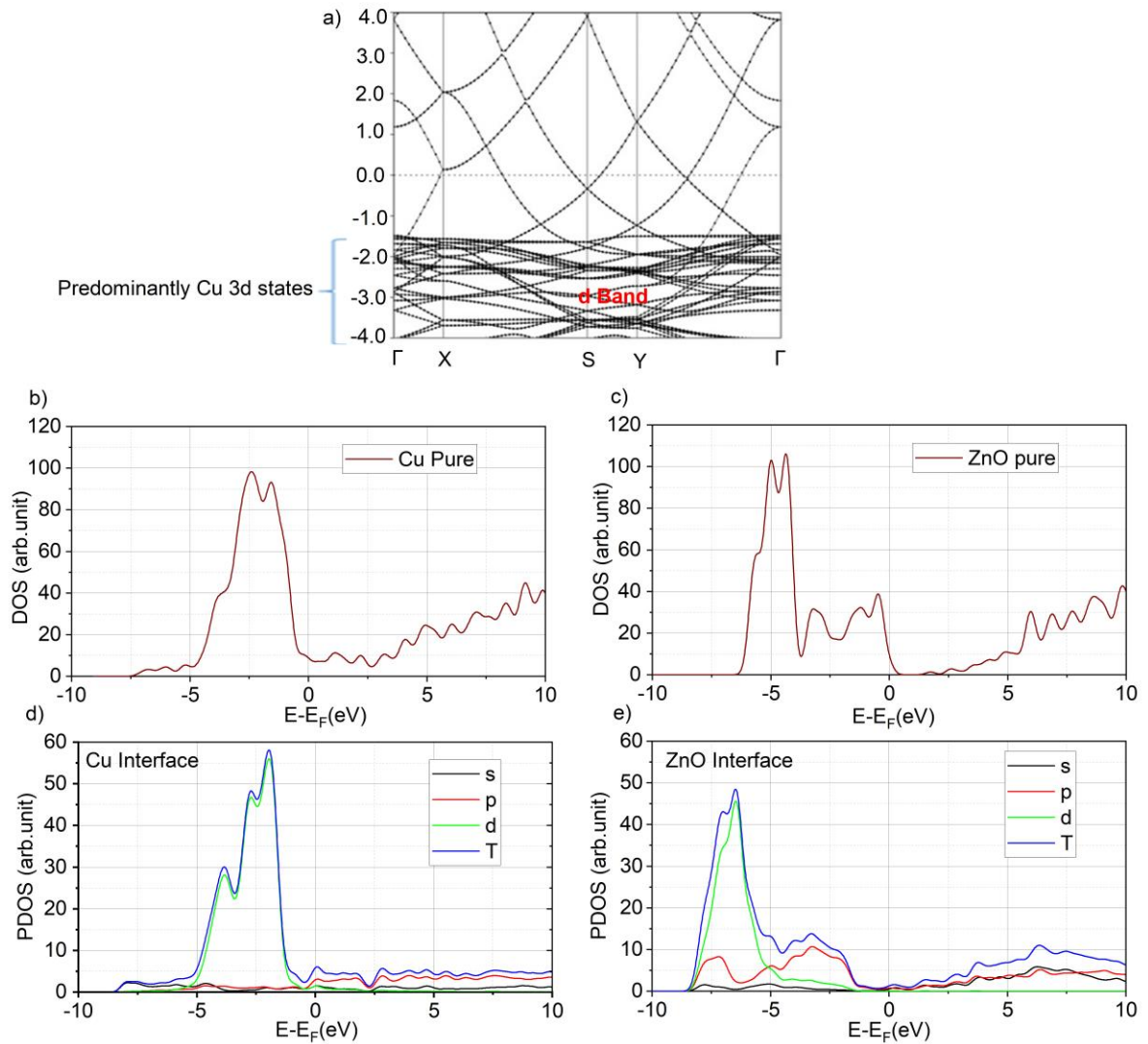


Fig. 9 (a) Electronic band structure of bulk Cu calculated using DFT. (b,c) Density of states (DOS) of pure Cu and pure ZnO. (d,e) PDOS of the Cu and ZnO interface layers in the Cu/ZnO heterostructure

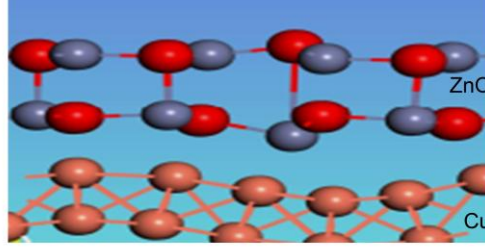


Fig. 10 Schematic side view of the Cu/ZnO heterostructure model

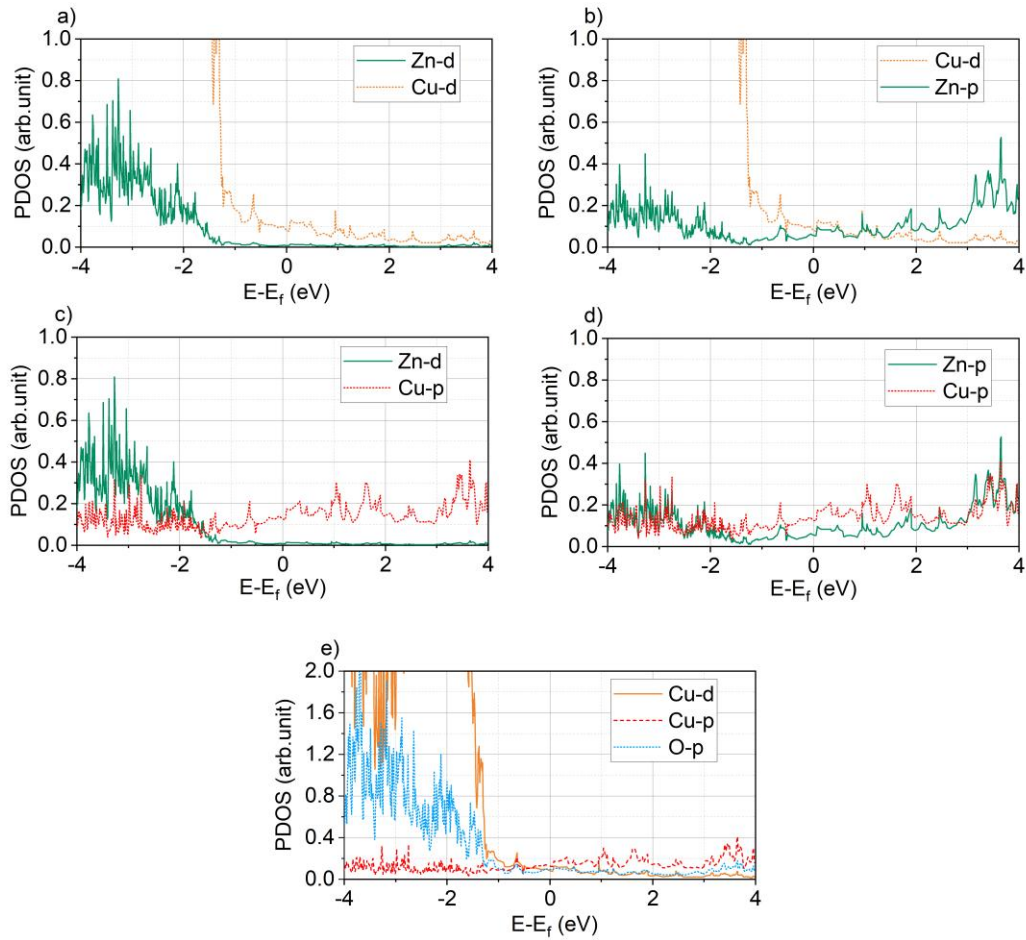


Fig. 11 The projected density of states (PDOS) for a heterostructure of Cu/ZnO

4. Photocatalytic Enhancement through Plasmonic Effects

Cu nanospheres are capable of generating the localized surface plasmon resonance (LSPR) effect, a tunable phenomenon that is exploited to enhance the photocatalytic efficiency of ZnO nanospheres. In this study, the possible mechanisms associated with the photocatalytic performance of Cu/ZnO hybrid nanostructures are investigated. When these nanostructures are exposed to full-spectrum light, electrons in the valence band of ZnO are excited to the conduction band, leaving behind holes in the valence band (the photocatalytic process). Simultaneously, hot electrons with high energy are generated due to LSPR in the Cu nanospheres, and under the influence of internal electric fields and localized electromagnetic field

enhancement caused by LSPR, they are rapidly injected into the conduction band of ZnO. The Schottky barrier at the Cu/ZnO interface prevents these electrons from returning to the Cu nanospheres. This phenomenon is known as hot electron transfer from the metal to the semiconductor. Therefore, based on previous studies, the improvement in photocatalytic performance in such nanostructures is attributed to two key factors: photoexcitation of electrons and LSPR-related interactions in the metal. For this reason, the spatial configuration between the Cu nanoparticles and the ZnO structure plays a crucial role in the intensity of the LSPR effect and the efficiency of charge transfer reactions. In other words, different nanostructure configurations can significantly influence the location of redox reactions and the pathways of charge carrier movement.

5. Conclusions

In this work, the optical and electronic responses of Cu and Cu/ZnO nanostructures were systematically investigated using FDTD and DFT calculations. The results demonstrate that Cu nanoparticles support localized surface plasmon resonance (LSPR) in the visible range. The strength and spectral position of the plasmonic response depend on particle size, structural configuration, incident light direction, and the refractive index of the surrounding medium. Increasing the size of Cu nanospheres results in stronger local electric field enhancement and a red shift of the LSPR peak, indicating enhanced light–matter interaction. The electronic structure analysis shows that occupied electronic states below the Fermi level in Cu contribute to sustaining plasmonic excitation. The surrounding dielectric environment also plays an important role in tuning the plasmonic response, where higher refractive index media lead to a systematic red shift of the resonance wavelength. Among the investigated configurations, structure B exhibits a more pronounced plasmonic sensitivity in environments with refractive indices lower than that of ZnO. In addition, although the core–shell configuration (C) exhibits the strongest field enhancement, the complete encapsulation of Cu by ZnO may influence the accessibility of interfacial regions where plasmon-induced fields are localized. However, this effect is not directly evaluated within the present computational framework and requires further investigation.

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