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A Comprehensive Overview of the Diverse Properties of Zinc Oxide (ZnO)

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Abstract

ZnO is a wide band gap semiconductor with excellent electrical, optical, and thermal properties, making it useful in solid-state electronics, solar cells, and photocatalysis. It also has antimicrobial and UV-absorbing characteristics, that is why it is found in products like sunscreens, cosmetics, and paints. Additionally, ZnO has applications in rubber manufacturing, as a catalyst in chemical processes, and in the production of varistors and sensors. Its important properties make it a fascinating material and is widely studied in the field of research. Tuning of band gap, synthesis of nanoscale thin films, nano composites with different type of nano structures all explain the intensive interest and broad applications. This review aims to understand the important properties of ZnO that make it one of the most versatile materials of the II-VI group oxide materials and invites consistent attention of the researchers worldwide.

Key words: Zinc Oxide, Compound Semiconductor, Direct Band gap, Zinc Blende, Wurtzite Structures, Photoluminscene.

1. Introduction

Due to its diversified applications in electronics, optics and photonics and in several novel devices, ZnO compound semiconductors evolved as potential materials[1-4]. ZnO is an *n*-type semiconductor with direct band gap value of 3.37 eV at room temperature and optical transmittance in the visible range[5]. It is a proven substance for the development of transparent optoelectronic devices, sensors etc. in comparison to other large band gap semiconductors like gallium nitride (GaN) and zinc selenide (ZnSe). ZnO is highly resistant to damage from radiation, so it finds its use in satellites. It has an added advantage as a transparent electrode material in photovoltaic cells because of good material properties as compared to indium tin oxide (ITO)[6,7]. Band gap in semiconducting materials may be either direct or indirect. Direct band gap semiconductors are preferred over indirect band gap semiconductors because phonons are required to satisfy wave vector conservation in the latter case. Most of the group II-VI elements exist as direct band gap semiconductors and dominate the optical and electronics domain for short wavelength applications. With the development of nanotechnology, it is now universally established fact that when particle size of an inorganic crystalline solid is of the order of nanometers, interesting optical effects are obtained e.g. a decrease in the absorption wavelength occurs due to the increase in optical band gap as the size of nanoparticles decrease[8,9]. The band gaps of semiconductors have significant impact on their optical and electrical properties. Therefore, importance of ZnO is further enhanced as its band gap can be tuned to desired value by reducing its particle size to nano scale[10]. Due to its *n*-type semiconducting characteristics and excellent thermal stability, ZnO is an active channel for thin film transistors and can be well developed in crystalline form on various substrates[11,12]. Large bond strength and its ability to grow single crystal substrate, low power threshold for optical pumping, radiation hardness, high exciton binding energy, broad chemistry leading to wet chemical etching and biocompatibility makes ZnO an ideal candidate for future applications in electronic devices. Besides, economical and its non-toxic nature, it is environment friendly also. Since 1990, GaN has been a dominant source for blue lasers and also being extensively used in fabricating devices like photo-detectors, light emitting diodes, piezoelectrics and waveguide devices. Zinc oxide has emerged as a potential alternate to GaN for optoelectronic applications owing to its structure and direct wide band gap[13]. Table 1 illustrates the characteristics of ZnO and GaN[14].

Table 1. Comparison between Zinc Oxide and Gallium Nitride[14].

Property	**ZnO**	**GaN**
Energy Band Gap(eV)	3.37	3.39
Room Temp Exciton Binding Energy (meV)	60	25
Room Temp Stable Phase	Wurtzite	Wurtzite
Lattice Constant a_o(Å)	3.25	3.12
Lattice Constant c_o(Å)	5.21	5.19
Bulk Growth	Yes	Difficult
Epitaxial Growth	Yes	Yes

The binding energy of an exciton is an important parameter for optical devices such as LEDs and lasers. Since the separated electrons and holes are more vulnerable to be trapped by the various defects in the crystal, it is very likely to have a material with a large exciton binding energy for optoelectronic applications[15]. Exciton binding energy of ZnO is much larger than that of GaN (Table 1) and also much greater than the room temperature thermal energy (25 meV), so that excitonic recombination process is possible even at room temperature. Whereas, in GaN, the electron hole plasma transition is the dominant recombination process[16].In addition, ZnO is an important material to be used in optoelectronic devices. ZnO has a high melting point around 2000°C that makes it stable at high temperatures during doping and formation of ohmic contacts. As it is quite hard and can tolerate mechanical stresses along with high melting point, so the lifetime of LEDs and blue laser diodes made up of ZnO is increased[13]. Therefore, ZnO has become a potential wide band gap material that can be used in high frequency light emitting devices such as solar cells,electroluminescence devices, light emitting diodes, photo-detectors and the next generation of UV semiconducting lasers[5],chemical sensor for some gases[12,17],biosensors for detection of bio-molecular interactions[18],luminescent and electrical devices, vacuum fluorescent displays (VFDS), solid state white light source[19], sun screen due to UV absorption property, piezoelectric devices[20], electro-acoustic transducer[21], UV light emitting diodes, laser diodes[22].

2. PROPERTIES OF ZnO

2.1 Physical Properties

Table 2 illustrates the physical properties of ZnO at room temperature. Zinc oxide is an amphoteric oxide and quite stable at room temperature. At about 1975°C, it decomposes into zinc vapor and oxygen[23]. Crystalline zinc oxide is thermo-chromic. Apart from the ability to react with acids, ZnO also reacts with bases and produces soluble zincates[24]. Naturally zinc oxide (zincite) is found in the earth crust. It is the synthetic ZnO that exists in the form of white powder, produced in laboratories at a large scale and is widely used in research and industries[25].

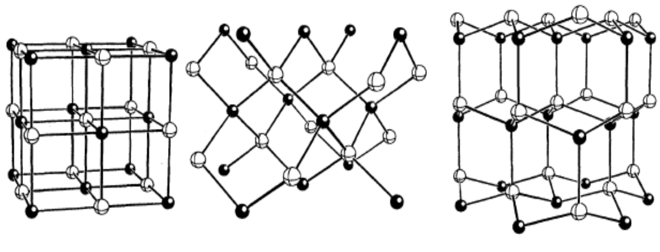
Table 2. Physical properties of wurtzite ZnO at room temperature[26].

Properties	**Values**
Lattice Constant (*a*)	0.32469 nm
Lattice Constant (*c*)	0.52069 nm
Density	5.606 g/cm^3
Melting Point	2248 K
Relative Dielectric Constant	8.66
Band Gap Energy	3.4 eV
Intrinsic Carrier Conc.	$< 10^6$ cm^{-3}
Exciton Binding Energy	60 meV
Electron Effective Mass	0.24
Electron Mobility	200 cm^2 /VS
Hole Effective Mass	0.59
Hole Mobility	5-50 cm^2 /VS
Refractive Index	2.01
Static Dielectric Constant	8.656

2.2 Crystal structure of Zinc Oxide

Figure 1 shows the rocksalt, zinc blende, and wurtzite structures of crystalline ZnO[27]. ZnO exhibits primarily covalent bonding but with a significant contribution from ionic bonding. The thermodynamically stable phase of ZnO exhibits wurtzite symmetry at room temperature. The zinc blende structure of ZnO can be stabilized only by growing on cubic substrates, while the rocksalt (NaCl) structure may be obtained under relatively high pressures. The reduction of the lattice parameters results in an increase in the inter-ionic coulomb interaction that favours more ionic character and thus stabilizes rock salt phase. On the contrary, the wurtzite structure of ZnO has four-fold coordination with a hexagonal unit cell with two lattice parameters: a = 0.3297 nm and c = 0.52065 nm. The c/a ratio is around 1.60 which is slightly different from the ideal value of c/a=1.633 for wurtzite structure, owing to the high polarity of ZnO. The wurtzite structure of ZnO can be described as a number of alternating tetrahedrons composed of coordinated $O^{2-}$and Zn^{2+} ions, stacked alternately along the c axis (Figure 2). One Zn^{2+} ion is surrounded by four O^{2-} ions in a tetrahedral unit cell and vice versa. The ionicity of ZnO is 0.616 on the Philips iconicity scale, which is exactly at the borderline of covalent and ionic semiconductors[28].

ZnO is an anisotropic material and thus exhibits different values of surface energies for different faces. This anisotropy is vital to the growth of nanostructure as it results in the preferential growth of ZnO along the c-axis. Atom or molecule will preferably to be incorporated on the polar faces(c-plane) rather than on the side non-polar faces (a and m planes) during the growth process (Figure 3).This non-centro symmetric structure results in piezoelectric and pyroelectric characteristics and finds its use in a large number of technical devices including a variety of electromechanical coupled sensors and transducers[25].



(a) **(b)** **(c)**

Figure 1. ZnO crystal structures: (a) Rocksalt, (b) Zinc Blende (c) Wurtzite[27].

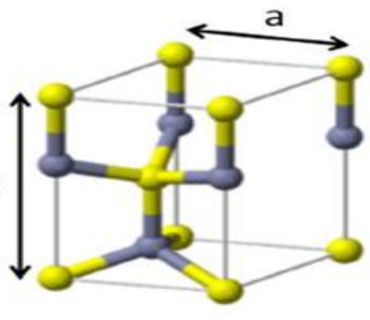


Figure 2. Unit cell of hexagonal wurtzite structure of ZnO. The grey balls represent zinc atoms and the yellow balls represent oxygen atoms.

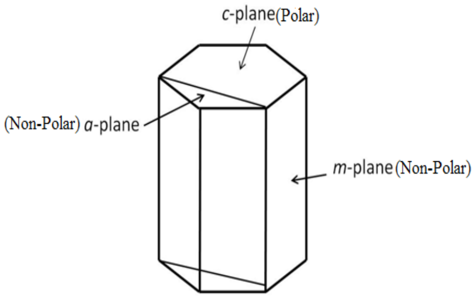


Figure 3. Polar and non-polar faces of ZnO.

2.3 Band Structure of ZnO

It is well established that the band structure of semiconductors plays a vital role in deciding their potential applications. Thus, an exact knowledge of the band structure of a semiconductor is vital for exploiting its applications and also for the improved efficiencies of the devices based on it. Determination of the electronic band structures in semiconductors through optical measurements and theoretical band-structure calculations indeed complement each other. Photo Luminescence (PL), X-ray Diffraction (XRD), UV emission, reflection/transmittance, X-ray photoelectron spectroscopy (XPS) and angle resolved photoelectron spectroscopy (ARPES) are a few conventional techniques which are used to determine the electronic core levels in solids[29-32]. The energy difference is measured by inducing transitions between electronic levels in solids. Zhao *et al.,*[33] reported the band structure, density of states (DOS) and partial DOS (PDOS) near the Fermi level of pure ZnO and observed that valence band maximum and conduction band minimum are both in the G-point, indicating that pure ZnO is a semiconductor with wide band gap. They further reported that the band width of ZnO is mainly decided by 2*p* states of oxygen and the 4s states of zinc. Their studies strongly established that the band structure determination in combination with X-ray and UV photoemission spectra provide an effective approach to establish the complete valence band structure of semiconductors. The comparison between experimental and the theoretical values leads to the result that ZnO has a direct band gap with the conduction band minimum and the valence band maximum located at K=0 in the brillouin zone. The conduction band of ZnO is primarily *s*-like, while the valence band is *p*-like. Spin-orbit splitting results in partial lifting of the valence band degeneracy. The splitting of six-fold degenerate valence band occurs as a four-fold (j=3/2) and a two-fold band (j=1/2). The poor symmetry of the wurtzite structure raises valence band degeneracy. Thus crystal field splitting and spin-orbit coupling result in three two-fold degenerate valence bands: A(Γ_9), B(Γ_7), and C (Γ_7) or the heavy-hole, light-hole, and crystal field split-off bands, respectively near the zone center (G point)[34,35].The lattice parameters change with temperature and pressure, thereby changing the electronic band structure. However, at G point the band gap shrinks with increasing temperature.

Following equation gives the temperature dependence of the band gap:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T+\beta} \qquad \textbf{(1)}$$

Where α = - 5.5 $\text{x}10^{-4}$ eV K^{-1} and β= - 900K exhibit the temperature coefficients for temperatures up to 300 K. The excitonic transition energies associated with the A, B, and C valence bands follow the same dependence with temperature coefficients having the values: α= -7.2$\text{x}10^{-¼}$ eV K^{-1} and β= -1077K[36].

2.4 Optical Absorption and Band Gap

Absorption coefficient α is generally a measure of optical absorption and can be derived from transmittance or absorbance measurements. If I_0 is the intensity of incident light, I is the intensity of transmitted light and R is the reflected light, then the transmittance

$T=I/ I_0$ can be expressed as[37]

$$T = \frac{(1-R)^2\exp(-\alpha t)}{1-R^2\exp(-2\alpha t)} \qquad \textbf{(2)}$$

Where t is the material thickness in the limit of large αt, this equation reduces to

$$T = (1-R)^2\exp(-\alpha t) \qquad \textbf{(3)}$$

in case reflectance is very small so that it can be ignored, the equation (3) is further simplified to

$$I = I_o exp(-\alpha t) \qquad \textbf{(4)}$$

In terms of absorbance A,

$$\alpha = \frac{1}{t}(2.303A) \qquad \textbf{(5)}$$

The relation between the incident photon energy, band gap energy and the absorption coefficient in a direct transition is given by

$$\alpha h\nu = A(h\nu - Eg)^n \qquad \textbf{(6)}$$

Where A is a constant, E_g is the optical energy gap. The value of n is 1/2, 3/ 2 for direct allowed and direct forbidden transitions respectively. Thus, a plot of $(\alpha h\nu)^2$ versus $h\nu$ allows one to determine the energy gap[38].

2.5 Mechanical Properties

ZnO is known as one of the hardest materials in the II–VI group compound semiconductors because it possesses high melting point and large cohesive energy. Hence, degradation of the material because of the introduction of dislocations while fabricating the device or during its operation is less. ZnO has smaller elastic constants than III-IV group semiconductors. It finds its application in ceramics due to high heat capacity and high melting point, low thermal expansion and low heat conductivity. The piezoelectric character of ZnO has been extensively examined for various applications like acoustic wave resonators, force sensing, acousto-optic modulator and piezo transducers that require a large electro-mechanical coupling[39-41]. The origin of piezoelectricity in ZnO is due to the tetrahedral bonding of zinc and oxygen atoms. The center of positive charge and negative charge in a non-centrosymmetric structure can be displaced by the lattice distortion produced by external stresses. This leads to the development of local dipole moments and consequently a macroscopic dipole moment is developed over the crystal[41]. ZnO has the highest piezoelectric tensor among the various tetrahedrally bonded semiconductors, thereby providing a large electromechanical coupling. Polar face dominated nanostructures of ZnO are due to the spontaneous polarization in the ZnO crystal structure[39]. The tetrahedron of zinc and oxygen atoms stack along [001] direction and the position of the positive charge is displaced due to the spontaneous polarization from the negative charge along [001] direction. As a consequence, [001] surface gets charged and in order to acquire minimum energy, this charged surface modifies itself to make a nano ring[42].

2.6 Electrical properties

ZnO is known to be an intrinsic *n*-type wide band gap semiconductor with band gap value of 3.2 eV[43]. This *n*-type semi-conductivity is a consequence of crystal lattice imperfections, interstitial zinc atoms and oxygen vacancies whose quantity depends primarily upon the method of preparation. Chopra *et al.*[44]prepared thin films by physical methods and reported conduction properties of ZnO thin films (thickness~0.1-0.7µm) having a carrier concentration of 4×10^{19}- $2\times10^{20}cm^{-3}$, mobility of 15-30$cm^2V^{-1}s^{-1}$, a resistivity of 8×10^{-4}-7×10^{-3}ohm cm and an average transmittance of 0.8-0.9. Meulenkamp[45] reported spin coating of ZnO thin films having thickness~0.05-0.1µm on ITO glass with mobility10^{-3}-$10^{-1}cm^2V^{-1}s^{-1}$, carrier concentration 5×10^{18}-$10^{20}cm^{-3}$.The low mobility value was attributed to an excessive scattering of electrons at the boundary of tiny particles. He concluded that effective electronic properties of the semiconductor films depend mainly upon nature and microstructure of the material which in turn is a function of deposition parameters. Therefore, mobility value measured for the above film is a characteristic of ZnO film deposited by wet spin-coating films composed of tiny nanoparticles. Lin *et al.*[46] reported nanorods having diameter 60-70 nm with 500-520nm height, grown on Si substrates using CBD with a carrier concentration of 3×10^{17} cm^{-3} and mobility of 36 $cm^2V^{-1}s^{-1}$. In general, re-crystallization with appropriate heat treatment at 500-600^{0}C reduced the particle–particle interfaces and increased the mobility up to 200 $cm^2V^{-1}s^{-1}$and resistivity of the order of 0.1 ohm cm could be achieved. Varistors were fabricated by sintering ZnO powder in a mixture of other oxides making use of conducting properties of ZnO[47-49]. However, the carrier mobility has been found to decrease after doping as compared to the undoped ZnO because of the carrier scattering mechanism due to ionized and non-ionized impurities, polar optical phonon and acoustic phonon scatterings. The electron mobility was observed to be 200 $cm^2V^{-1}s^{-1}$ as compared to the hole mobility which was in the range of 5-50 $cm^2V^{-1}s^{-1}$ at room temperature[40]. This difference in the mobility was attributed to the difference in their respective masses, 0.24m_o and 0.59m_o for electron and hole respectively[50]. Alvi *et al.*[51] fabricated *p-n* hetero junction LEDs based on ZnO nanostructures. Threshold voltages of these LEDs were around 4V. They further reported that nanotubes based LEDs exhibited higher current as compared to the other nanostructures based LEDs with same set of operating conditions and attributed the performance of nanotubes based LEDs due to the existence of more oxygen sub vacancies and the larger surface area of the nanotubes as compared to other nanostructures.

2.7 Luminescence

Semiconducting zinc oxide is a well established luminescent material and several reports are available in the literature about its luminescent properties[52]. Increased demands of optoelectronic devices with enhanced properties have further encouraged the fundamental research interests in optical properties of ZnO. Typically, photoluminescence (PL) spectra of ZnO nanostructures exhibit one peak in UV region just before the onset of absorption and a broad band in the visible region at room-temperature. Generally, the peak in UV region is due to the radiative annihilation of excitons with a very short lifetime in the range of several tens to hundreds of picoseconds. Although, other emission peaks such as red and yellow have also been reported in the range from 450 to 730nm, the visible photoluminescence (PL) is commonly green. On the contrary, the lifetime of the PL emission in the visible range, is much higher (~microseconds). This increase in life time may be assigned to the presence of crystal defects and non-stoichiometry. The most reported defects in ZnO are Zn interstitial (Zn_i), oxygen vacancies (V_O), Zn vacancies (V_{Zn}), Zn anti-sites (O_{Zn}), etc (Figure 4). The V_O and Zn_i defects act as shallow donor states whereas V_{Zn}, O_i and O_{Zn} are considered deep level acceptor states in the band gap[53]. The yellow emission is generally assigned to oxygen interstitial defects, along with some impurities such as lithium[54]. In addition, the possible presence of $Zn(OH)_2$ at the surface was identified as another possible cause for the weak UV and the strong visible (broad yellow and green) emission. The existence of orange-red emission around 640-650 nm was attributed to the presence of excess oxygen interstitials in the specimens. The origin of green defect emission has been a subject of many speculations. The electronic, structural, atomic geometrical, and formation energy of native point defects in ZnO were determined using first principles methods[55]. Under *n*-type conditions, zinc vacancies are deep acceptors and exhibit low formation energies, therefore may exist as compensating defects[56]. It was also proposed that green luminescence in ZnO was due to the zinc vacancies. Oxygen interstitials due to their high formation energies are not expected to exist in large numbers but can exist as deep acceptors at the octahedral site in *n*-type samples[57]. Roy *et al.*[58] reported the effect of the fabrication environment and annealing conditions on the PL spectra. The PL spectra appeared was more consistent with an intrinsic defect than an extrinsic impurity. Vanheusden *et al.*[59] proposed that green PL originated from a transition between singly charged oxygen vacancy and photo excited hole. Wang *et al.*[60] examined the PL spectra of ZnO nanoparticles (20nm) annealed in air, argon (Ar) and oxygen (O_2) atmosphere. The green emissions were observed to be centred at 490 nm in Ar, at 515 nm in O_2 and 520 nm in air respectively, after annealing in air atmosphere at 900°C for 1h, respectively, as shown in Figure 5. The corresponding XPS analysis revealed the presence of oxygen vacancies on the surface of ZnO annealed in Ar, whereas little oxygen vacancies on the surface of the ZnO annealed in O_2. Therefore, the existence of green emission at about 490nm was attributed to the formation of oxygen vacancy defects. In turn, the emission at 520 nm could be the consequence of the anti-site defects (O_{Zn}). Other proposed mechanisms that would be involved with the PL behaviour of ZnO included transition between the deeply trapped hole at oxygen vacancy containing no electrons (V_0^{++}) centre and electron near the conduction band, shallow donor–deep level transitions donor–acceptor, zinc interstitials and oxygen ant site[61-64].

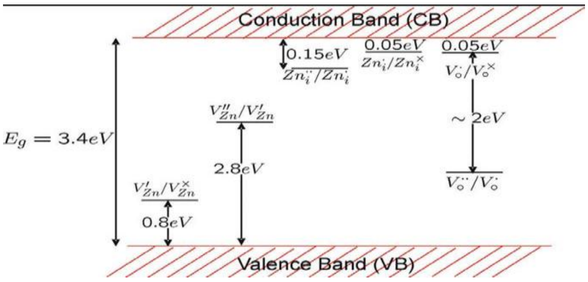


Figure 4. Energy levels of native defects in ZnO. $Zn_i^{\cdot\cdot}$, $Zn_i^{\cdot}$, Zn_i^{x}, $V_o^{\cdot\cdot}$, $V_o^{\cdot}$, V_o are the donor defects and $V_{Zn}^{''}$, V'_{Zn} are the acceptor defects[53].

It is very likely that the origin of visible luminescence in ZnO may be specific to the individual samples. For example, impurity related emission may be represented by single crystals and phosphor powders, while intrinsic defects may be responsible in thin films and nanostructures. While studying the relationship between the luminescent properties of the ZnO nano crystallites, their synthesis method and post annealing conditions, Li *et al.*[54] noticed that the PL peak in the visible region appeared at different wavelengths in samples fabricated by chemical and evaporation techniques. A yellow luminescence was observed in the samples prepared by chemical methods and was not found to be sensitive to the surface modifications, hence appear to be originating from the defects present in the bulk, not from the surface.

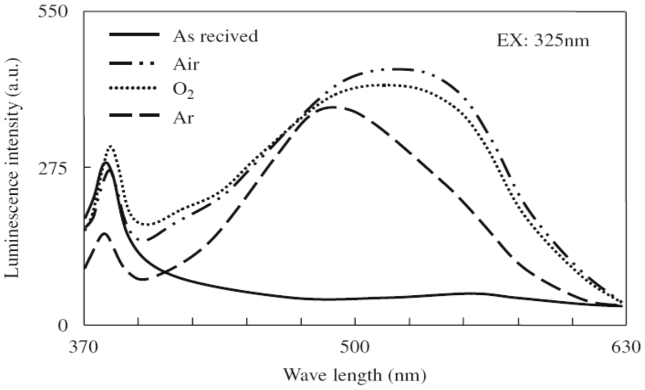


Figure 5. PL spectra of ZnO nanoparticles annealed in air, O_2 and Ar for 1 hour at $900^{o}C$ [60].

Despite the fact that no specific reason can be attributed to the presence of the broad visible emission band in ZnO, the above results indicate that it may have multiple sources; also the centers of the broad defect band are not same in all the samples. Willander[65] reported that owing to the different growth conditions, every sample will contain different numbers of deep level defects and as a result the centers of the broad defect band are different in different samples. Samples grown in zinc-rich or oxygen-rich environments exhibited broad bands, but they were centered at different wavelength positions. He further attributed the existence of the visible colored emissions in ZnO to deep level centers. By optimizing the growth parameters, ZnO nanostructures may be reproduced having the same luminescent characteristics.

3. Conclusion

In conclusion, zinc oxide (ZnO) is a remarkable material that exhibits a diverse array of properties, making it highly valuable for a wide range of applications. Its unique characteristics, such as wide bandgap, high exciton binding energy, excellent optoelectronic behavior, and high chemical stability, have garnered significant attention across fields like electronics, photonics, and environmental science. Its semiconducting properties, coupled with its piezoelectric, mechanical, electrical, photo-catalytic, provide ample opportunities for the development of advanced devices and technologies. Despite its promising potential, challenges related to the synthesis, stability, and scalability of ZnO-based materials need to be taken care of. Future research focusing on optimizing these properties and exploring novel forms of ZnO will further enhance its role in both existing and emerging applications, driving innovation in various industrial and technological sectors.

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