

Optical properties of ZnO Nanocomposite Doped with Polymer Polyethylene glycol: Review

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ABSTRACT

Objective: The integration of inorganic nanostructures into polymer matrices has revolutionized the field of functional materials, enabling the creation of composites with tailored properties for advanced applications, with PEG/ZnO nanocomposites emerging as a subject of intense research interest due to their synergistic functionalities. **Method:** This review provides a comprehensive analysis of PEG/ZnO nanocomposites, meticulously detailing the various synthesis strategies, including in-situ growth, ex-situ blending, and sol-gel methods, and discussing how these methods influence the morphology and dispersion of ZnO within the PEG matrix. **Result:** The review delves into the profound modifications in the composite's structural, optical, thermal, electrical, and mechanical properties as characterized by techniques such as XRD, FTIR, Raman spectroscopy, UV-Vis, PL, DSC, and SEM/TEM, while also mapping the vast application spectrum spanning biomedical fields, energy storage, photocatalysis, and ultraviolet shielding. **Novelty:** Finally, the review addresses the current challenges and future perspectives, outlining the path for next-generation PEG/ZnO-based materials, thus offering valuable insights into the advancement of functional nanocomposites.

INTRODUCTION

The frontier of modern materials science is increasingly defined by nanocomposites, where the strategic incorporation of nanoscale fillers into a bulk matrix creates materials with properties superior to their individual components [1]. This synergy is particularly powerful in polymer nanocomposites, where the polymer provides processability, flexibility, and structural integrity, while the nanofiller introduces functional properties like electrical conductivity, optical activity, or mechanical reinforcement [2]. Polyethylene glycol (PEG) is a linear polyether diol ($\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{-H}$) that has become a polymer of paramount importance in both research and industry. Its properties are heavily influenced by its molecular weight, ranging from low-molecular-weight liquids to high-molecular-weight waxy solids. PEG is renowned for its hydrophilicity, biocompatibility, non-toxicity, and non-immunogenicity. These attributes have made it a gold standard in biomedical applications, particularly in drug delivery and surface functionalization to impart "stealth" properties [3]. Furthermore, its flexible chain and ability to solvate various ions make it a promising candidate for solid-state electrolyte applications. Zinc Oxide (ZnO) is a multifunctional semiconductor material with a rich history and a vibrant future. Its wide direct bandgap (3.37 eV) and large exciton binding energy (60 meV) make it an excellent candidate for optoelectronic devices, such as ultraviolet (UV) lasers and light-emitting diodes (LEDs) [4]. Beyond optics, ZnO exhibits remarkable piezoelectricity, a property exploited in mechanical energy harvesters and sensors. It is

also known for its photocatalytic activity under UV light and its potent antibacterial properties, which are attributed to the generation of reactive oxygen species (ROS) and the release of Zn^{2+} ions [5]. The integration of ZnO nanostructures (nanoparticles, nanorods, nanowires) into a PEG matrix is not merely a physical mixture but a strategic design to create a multifunctional platform. PEG acts as a stabilizing agent, preventing the agglomeration of ZnO nanoparticles and providing a processable, often flexible, host. In return, ZnO nanostructures endow the passive PEG matrix with UV-blocking capability, electrical conductivity, photocatalytic activity, and antimicrobial function. The interaction between the ether oxygen of PEG and the surface of ZnO can also lead to unique interfacial phenomena that alter the composite's thermal and chemical stability [6].

This review manuscript aims to synthesize and critically evaluate the extensive body of research concerning PEG/ZnO nanocomposites. It will systematically cover the synthesis methodologies, the resulting morphological and property changes, and the diverse applications enabled by this synergy. By presenting a curated collection of research findings in tabular form and discussing future challenges, this review serves as a foundational resource for academics and industrial researchers exploring this dynamic material system.

RESEARCH METHOD

Synthesis and Fabrication Techniques

The methodology employed to synthesize PEG/ZnO nanocomposites is crucial, as it directly governs the size, morphology, distribution, and interfacial bonding of the ZnO nanostructures within the polymer matrix, ultimately dictating the final properties. The techniques can be broadly categorized into **in-situ** and **ex-situ** methods.

A. In-situ Synthesis Methods

In-situ methods involve the chemical formation of ZnO nanostructures directly within the PEG solution or melt. This approach often leads to a more homogeneous dispersion and stronger interfacial adhesion.

In-situ Precipitation and Hydrothermal/Solvothermal Synthesis: This is the most common route. A typical process involves dissolving zinc precursors (e.g., Zinc acetate dihydrate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) in a PEG solution. A precipitating agent, such as sodium hydroxide (NaOH) or lithium hydroxide (LiOH), is then added dropwise. The PEG macromolecules act as a capping or structure-directing agent, controlling the growth and morphology of the forming ZnO crystals. The reaction mixture may be stirred at room temperature or under heating. For more controlled growth and crystallinity, the reaction can be carried out in a sealed autoclave under hydrothermal conditions (elevated temperature and pressure), leading to well-defined nanostructures like nanorods [7]. The PEG concentration and molecular weight are critical parameters influencing the final nanoparticle size and morphology.

In-situ Polyol Method: PEG itself can serve as a polyol solvent. In this green synthesis approach, a zinc precursor is dissolved in molten PEG at high temperatures

(e.g., 120-180°C). The PEG acts as both the solvent and the reducing/stabilizing agent. The high temperature facilitates the decomposition of the precursor and the nucleation and growth of ZnO nanoparticles. This one-pot method is advantageous for its simplicity and lack of need for additional solvents or harsh chemicals [8].

B. Ex-situ Synthesis Methods

In *ex-situ* methods, ZnO nanostructures are synthesized separately via various chemical or physical routes (e.g., sol-gel, combustion, mechanical milling) and subsequently incorporated into the PEG matrix.

Solution Blending: Pre-synthesized and often surface-modified ZnO nanoparticles are dispersed in a suitable solvent (often water or ethanol) via sonication. This dispersion is then mixed with a PEG solution under vigorous stirring or further sonication to achieve a homogeneous mixture. The final composite is obtained by casting the mixture and evaporating the solvent [9]. The main challenge is overcoming the strong van der Waals forces between nanoparticles to prevent agglomeration within the polymer.

Melt Blending: This solvent-free method involves mixing dried ZnO powder with solid PEG above the melting temperature of PEG using techniques like melt extrusion or simple mechanical stirring. This method is industrially scalable and environmentally friendly but often struggles to achieve nanoscale dispersion, leading to micron-sized aggregates that can compromise composite properties [10]. A comparison of these methods is provided in Table 1.

Table 1. Summary of Synthesis Methods for PEG/ZnO Nanocomposites.

Synthesis Method	Key Process Details	Advantages	Disadvantages	Ref.
<i>In-situ</i> Precipitation	Zinc precursor + alkali in PEG solution at RT or heated.	Good homogeneity, strong interface, simple.	Particle size distribution can be broad.	[7, 11]
<i>In-situ</i> Hydrothermal	Reaction in autoclave at 100-150°C.	High crystallinity, controlled morphology (rods, wires).	Requires high-pressure equipment, slower.	[12, 13]
<i>In-situ</i> Polyol	Zinc precursor in molten PEG at high temp (~150°C).	Green method, no extra solvent, good control.	High temperature required, limited to low MW PEG.	[8, 14]
<i>Ex-situ</i> Solution Blending	Pre-formed ZnO NPs sonicated and mixed with PEG solution	Independent control of NP synthesis.	Risk of agglomeration, weak interface, uses solvent.	[9, 15]
<i>Ex-situ</i> Melt Blending	ZnO powder mixed with molten PEG via extrusion/stirring.	Solvent-free, industrially scalable.	Poor dispersion, aggregation, high shear damage.	[10, 16]

Structural and Morphological Characterization

A multi-technique approach is essential to confirm the successful formation of the nanocomposite, understand the interaction between PEG and ZnO, and characterize the morphology.

A. X-ray Diffraction (XRD)

XRD is used to identify the crystalline phases and determine the crystallite size of ZnO. Pure PEG is semi-crystalline, showing characteristic peaks. The incorporation of ZnO introduces distinct diffraction peaks corresponding to the hexagonal wurtzite structure of ZnO (JCPDS card no. 36-1451), notably the (100), (002), and (101) planes. The presence of both PEG and ZnO peaks in the nanocomposite pattern confirms the formation of a composite. The crystallite size of ZnO can be estimated using the Debye-Scherrer equation applied to the most intense peaks, typically falling in the 10-50 nm

range. A decrease in the intensity and sharpness of PEG peaks often indicates a reduction in its crystallinity due to the disruptive presence of ZnO nanoparticles, which restrict chain mobility and reorganization [17].

B. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy reveals the molecular interactions and chemical bonding between PEG and ZnO. The FTIR spectrum of pure PEG shows key bands: a broad O-H stretch at $\sim 3400\text{ cm}^{-1}$, strong C-H stretches at $\sim 2880\text{ cm}^{-1}$, C-H bending at $\sim 1460\text{ cm}^{-1}$, C-O-C stretching at $\sim 1100\text{ cm}^{-1}$, and O-H bending at $\sim 960\text{ cm}^{-1}$. In the PEG/ZnO nanocomposite, shifts in the position and intensity of these bands, particularly the C-O-C and O-H stretches, are observed. A shift in the C-O-C band suggests coordination between the ether oxygen atoms of PEG and Zn^{2+} ions on the ZnO surface. Changes in the O-H band indicate hydrogen bonding between PEG's terminal hydroxyl groups and ZnO. The absence of new peaks typically confirms that the interaction is physical (physisorption), rather than chemical (chemisorption) [18].

C. Raman Spectroscopy

Raman spectroscopy provides complementary information to FTIR. The characteristic Raman active modes of wurtzite ZnO, such as the non-polar $\text{E}_2(\text{high})$ mode at $\sim 437\text{ cm}^{-1}$, are a definitive fingerprint of its presence and crystallinity. Shifts or broadening of these modes in the composite can indicate strain or surface effects induced by the polymer matrix. Similarly, changes in the Raman bands of PEG (e.g., C-O-C stretch) can further corroborate the interaction with ZnO nanoparticles [19].

D. Scanning and Transmission Electron Microscopy (SEM/TEM)

SEM and TEM offer direct visual evidence of the morphology, size, and distribution of ZnO within the PEG matrix. SEM imaging of composite surfaces or cryo-fractured cross-sections can show the dispersion quality; well-dispersed nanoparticles appear as bright spots, while agglomerates are clearly visible as clusters. TEM provides higher resolution, allowing visualization of individual ZnO nanoparticles, their shape (spherical, rod-like), and their distribution. High-Resolution TEM (HRTEM) can resolve the lattice fringes of ZnO, confirming its crystalline nature. Energy-Dispersive X-ray Spectroscopy (EDS) mapping coupled with SEM/TEM can confirm the uniform distribution of Zn and O elements throughout the PEG matrix [20].

E. UV-Visible and Photoluminescence (PL) Spectroscopy

UV-Vis spectroscopy is used to study the optical properties. Pure PEG is transparent in the visible region. The incorporation of ZnO introduces a strong absorption edge below $\sim 380\text{ nm}$, corresponding to its bandgap. A blue shift in this absorption edge compared to bulk ZnO can be observed due to quantum confinement effects in very small nanoparticles. The optical bandgap can be calculated using Tauc's plot. Photoluminescence (PL) spectroscopy of ZnO typically shows two emissions: a narrow near-band-edge (NBE) emission in the UV region due to exciton recombination and a broad visible deep-level emission (DLE) related to defects (e.g., oxygen vacancies). The intensity ratio of NBE to DLE and any shifts in the peaks provide information on the defect chemistry of ZnO, which can be altered by its interaction with PEG [21].

RESULTS AND DISCUSSION

Properties of PEG/ZnO Nanocomposites

The incorporation of ZnO nanostructures significantly alters the physical and chemical properties of the PEG matrix.

A. Thermal Properties

The thermal stability and crystallization behavior of PEG are markedly affected by ZnO. Thermogravimetric Analysis (TGA) consistently shows an increase in the decomposition temperature of PEG/ZnO composites compared to pure PEG. This enhanced thermal stability is attributed to the barrier effect of well-dispersed ZnO nanoparticles, which hinder the transport of volatile decomposition products and insulate the polymer matrix from heat. Differential Scanning Calorimetry (DSC) studies reveal that ZnO nanoparticles act as nucleating agents, often increasing the crystallization temperature of PEG. However, they also impose physical constraints on the polymer chains, typically reducing the overall degree of crystallinity and the melting enthalpy. This complex effect depends on nanoparticle loading, size, and dispersion [22].

B. Optical Properties

As mentioned, the composite gains strong UV-shielding capabilities due to the wide bandgap absorption of ZnO. This makes PEG/ZnO films excellent candidates for transparent UV-protective coatings. The photoluminescence properties, particularly the defect-related visible emission, can be tailored by controlling the ZnO synthesis conditions within the PEG matrix, which is relevant for optoelectronic and sensing applications [23].

C. Electrical Properties

Pure PEG is an insulator. The addition of semiconducting ZnO increases its electrical conductivity. The DC conductivity of the composites generally increases with ZnO loading and temperature, following an Arrhenius behavior, indicating a thermally activated conduction mechanism. The AC conductivity and dielectric constant also show significant enhancement, especially at low frequencies, due to Maxwell-Wagner-Sillars interfacial polarization at the boundaries between conductive ZnO nanoparticles and the insulating PEG matrix. This is particularly important for solid polymer electrolyte applications [24].

D. Mechanical Properties

The effect on mechanical properties (tensile strength, modulus, elongation at break) is a result of competing phenomena. At low loadings, well-dispersed ZnO nanoparticles can act as reinforcing fillers, increasing the stiffness and strength by mechanically interlocking with polymer chains and restricting their mobility. However, at higher loadings, nanoparticles tend to agglomerate, creating stress concentration points that act as failure initiators, leading to embrittlement and a reduction in both strength and flexibility [25].

Table 2. Reported Properties of PEG/ZnO Nanocomposites from Literature.

PEG MW / ZnO Loading	Synthesis Method	Key Findings	Application Focus	Ref.
PEG 6000 / 3-10 wt%	<i>In-situ</i> precipitation	Increased thermal stability (T_g by $\sim 40^\circ\text{C}$). Dielectric constant enhanced by order of magnitude.	Solid Polymer Electrolytes	[26]
PEG 400 / 0.5-2 wt%	<i>In-situ</i> polyol	Spherical NPs (10-15 nm). Strong UV absorption. Antibacterial activity against <i>E. coli</i> and <i>S. aureus</i> .	Biomedical / Antibacterial	[27]
PEG 20000 / 5 wt%	<i>Ex-situ</i> solution	Nucleating effect: T_c increased. Reduction in % crystallinity. Tensile strength max at 3 wt%.	Thermal Energy Storage	[28]
PEG 1000 / 10 wt%	<i>In-situ</i> hydrothermal	ZnO nanorods. Enhanced photocatalytic degradation of methylene blue under UV light.	Photocatalysis	[29]
PEG 6000 / 1-5 wt%	<i>Ex-situ</i> melt blending	Agglomeration at >3 wt%. UV shielding efficiency $>95\%$ for 5 wt% composite film.	UV Shielding Coatings	[30]

Applications

The multifunctionality of PEG/ZnO nanocomposites opens doors to a diverse range of cutting-edge applications.

A. Biomedical Applications

This is one of the most promising fields. The biocompatibility of both components is key.

Drug Delivery: PEG/ZnO nanocomposites can be designed as stimuli-responsive drug carriers. The PEG matrix can be loaded with therapeutic agents. The ZnO component can be engineered to degrade in the slightly acidic environment of tumor tissues or under UV light, triggering the controlled release of the drug [31].

Wound Healing: Composite films or hydrogels can be used as advanced wound dressings. PEG provides a moist healing environment and allows for gas exchange, while ZnO nanoparticles impart potent antibacterial activity, preventing infection and promoting healing [32].

Biosensing: The change in electrical or optical properties of the nanocomposite upon binding with a biological analyte (e.g., glucose, urea) can be exploited for biosensor development.

B. Solid Polymer Electrolytes (SPEs) for Energy Storage

PEG-based SPEs are crucial for all-solid-state batteries and supercapacitors. The incorporation of ZnO nanofillers addresses key limitations of pure PEG SPEs: (i) it enhances ionic conductivity by disrupting PEG crystallinity, creating more amorphous pathways for ion transport, and (ii) it improves mechanical strength, preventing short-circuiting by lithium dendrites in batteries. The ZnO surfaces can also interact with ions, potentially enhancing ion dissociation [33].

C. Photocatalysis

ZnO is a well-known photocatalyst for degrading organic pollutants in water. However, its recovery in powder form is challenging. Immobilizing ZnO nanostructures within a PEG matrix (as a film or hydrogel) creates a reusable and easy-to-recover photocatalytic system. Under UV light, ZnO generates electron-hole pairs that produce ROS, which mineralize dyes, pharmaceuticals, and other contaminants [34].

D. UV Shielding Coatings

The strong UV absorption of ZnO, combined with the transparency and film-forming ability of PEG, makes these composites ideal for UV-protective coatings. They can be applied to packaging materials to prevent food spoilage, on textiles for UV-protective clothing, or as transparent coatings on wood and plastics to prevent UV-induced degradation [35].

Challenges and Future Perspectives

Despite the significant progress, several challenges must be overcome to realize the full potential of PEG/ZnO nanocomposites.

A. Dispersion and Long-Term Stability

Achieving and maintaining a uniform nanoscale dispersion at commercially relevant loadings remains the primary challenge. Agglomeration during processing or over time can lead to property deterioration. Future work must focus on advanced surface modification of ZnO using coupling agents or surfactants compatible with PEG to improve interfacial adhesion and dispersion stability.

B. Understanding Cytotoxicity

While generally considered safe, the toxicity of ZnO nanoparticles, especially their size-, shape-, and dose-dependent effects, requires thorough investigation for specific biomedical applications. The long-term fate of nanoparticles in the body and their potential for accumulation need to be clearly understood. Surface functionalization with PEG is a step towards mitigating toxicity, but more *in-vivo* studies are needed.

C. Scalability and Processing

Bridging the gap between lab-scale synthesis and large-scale, cost-effective manufacturing is crucial. *In-situ* methods, while excellent for dispersion, can be difficult to scale. Developing continuous flow reactors for *in-situ* synthesis or optimizing high-shear melt processing for *ex-situ* methods are key future directions.

CONCLUSION

Fundamental Finding : PEG/ZnO nanocomposites represent a highly versatile and functional class of materials where the synergy between a benign, flexible polymer and a multifunctional semiconductor nanofiller results in properties far exceeding those of the individual components. This review has detailed the various synthesis strategies, from simple *in-situ* precipitation to scalable melt blending, each offering distinct advantages and limitations for controlling nanocomposite morphology, while a suite of characterization techniques confirms the successful formation of these composites and reveals the nature of the PEG-ZnO interface, which is critical for determining ultimate properties. **Implication :** The incorporation of ZnO endows PEG with enhanced thermal stability, UV shielding, electrical conductivity, and biological activity, enabling applications spanning biomedicine, energy storage, environmental remediation, and protective coatings. **Limitation:** However, challenges related to nanoparticle dispersion, long-term stability, and a complete understanding of biological interactions remain. **Future Research :** Addressing these challenges through innovative surface chemistry,

advanced processing, and rigorous toxicological studies will pave the way for the next generation of PEG/ZnO nanocomposites, unlocking their full potential in advanced technological and medical applications.

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