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Enhancement Structural Properties and Optical Energy Gap of PVA–ZrO_2–CuO Nanostructures for Optical Nanodevices

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As a promising nanostructure to use in various optoelectronic nanodevices, PVA–ZrO_2–CuO nanocomposites (NCs) are created in this study using the casting method with different ratios of ZrO_2/CuO. Compared to other nanosystems, the PVA–ZrO_2–CuO nanostructures stand out for their low cost, high corrosion resistance, good optical properties, and lightweight. The investigation is focused on examining the structural and optical characteristics of nanocomposites composed of PVA–ZrO_2–CuO. FTIR spectra indicate a physical interference between the pure polymer and nanoparticles. The optical microscope is used to describe the structural properties and the changes in the surface morphology of nanocomposite. The findings about the optical characteristics indicate an increase in absorption by approximately 283%. Additionally, the energy gap experiences a decrease by approximately 107% for allowed indirect transitions and 408% for forbidden indirect transitions. These changes are observed, when the PVA–ZrO_2–CuO content reaches a weight percentage of 6%. Consequently, these results suggest that the material may possess suitability for a range of optoelectronic devices.

Як перспективну наноструктуру для використання в різних оптоелектронних нанопристроях, у цьому дослідженні створено нанокомпозити ПВС–ZrO_2–CuO з використанням методу лиття з різними співвідношеннями ZrO_2/CuO. У порівнянні з іншими наносистемами, наноструктури ПВС–ZrO_2–CuO вирізняються низькою вартістю, високою корозійною стійкістю, хорошими оптичними властивостями та легкістю. Дослідження зосереджено на вивченні структурно-оптичних характеристик нанокомпозитів у складі ПВС–ZrO_2–CuO. Спектри інфрачервоної спектроскопії на основі перетворення Фур'є вказують на фізичну інтерференцію між чистим полімером і наночастинками. Оптичний мікроскоп використовується для опису структурних властивостей і змін морфології поверхні нанокомпозиту. Висновки про оптичні характеристики свідчать про збільшення поглинання приблизно на 283%. Крім того, енергетична щілина зменшується приблизно на 107% для дозволених непрямих переходів і на 408% для заборонених непрямих переходів. Ці зміни спостерігаються, коли вміст ПВС–ZrO_2–CuO сягає вагового відсотка у 6%. Отже, ці результати свідчать про те, що матеріял може мати придатність для цілого ряду оптико-електронних пристроїв.

Key words: polyvinyl alcohol, ZrO_2–CuO nanoparticles, optical properties.

Ключові слова: полівініловий спирт, наночастинки ZrO_2–CuO, оптичні властивості.

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1. INTRODUCTION

Authors and engineers have begun to take polymer nanocomposite more seriously as a high-performance matrix; this led to a drastic improvement in the polymer's properties and materials due to the nanoparticle's contribution to manipulating the structure and improving the materials' properties [1, 2]. Nanomaterials and nanocomposites, currently regarded as novel and captivating fields within materials science, have been observed in natural occurrences for centuries. Nevertheless, the techniques for characterizing and manipulating the structure at the nanoscale have only been developed much later. A nanocomposite is a conventional compound composed of two components: filler and matrix. In a traditional composite, a filler material such as glass fibre or carbon fibre is typically employed, whereas in a nanocomposite, the filler material consists of nanomaterials. Nanomaterials encompass a variety of substances, including carbon nanotubes, carbon fibre tubs, and nanoparticles composed of gold, diamond, silver, silicon, and copper [3, 4]. Polyvinyl alcohol (PVA) is considered one of the most important polymers. He is widely used in many important applications, such as electrochromic, fuel cells, biomedical fields, and sensors [5, 6]. Polyvinyl alcohol is a synthetic polymer that cherished widespread usage during the initial decades of the twentieth century. This substance has been utilized to produce diverse end products, including lacquers, resins, surgical threads, and food-processing materials that come into direct contact with food. These applications span diverse sectors, including manufacturing, commercial, medicinal, and food industries [7, 8]. PVA exhibits notable mechanical properties such as high tensile strength and flexibility.

Additionally, PVA demonstrates a remarkable ability to act as a barrier against oxygen and aroma. Additionally, it possesses commendable characteristics in terms of film formation, blending, and adhesion. The transmission of visible light exhibits exceptional strength. The significance of PVA polymeric composites in scientific applications has been widely acknowledged [9, 10].

Due to their diverse potential applications, the metallic ZrO_2 nanoparticles have garnered considerable attention within the wide bandgap semiconductors. Additionally, they hold a prominent position in photocatalysis research owing to their notable surface-to-volume ratio [11, 12]. Zirconium dioxide (ZrO_2) is categorized as an n-type semiconductor based on electronic characteristics. The material has bandgap energy of approximately 5 electron volts (eV) and demonstrates significantly advantageous photocatalytic efficiency when exposed to ultraviolet (UV) light irradiation. Applying ZrO_2 nanoparticles is primarily influenced by their crystalline structure and phase transitions. Furthermore, it is worth noting that ZrO_2 nanoparticles demonstrate a significantly low thermal conductivity and a high thermal expansion coefficient. This substance has been employed in manufacturing various final products, such as lacquers, resins, surgical threads, and food processing materials that have direct contact with food. Furthermore, the substance exhibits nontoxic characteristics, thereby rendering it ecologically sustainable. It also demonstrates improved thermal and chemical stability while offering cost-effectiveness [13, 14].

Copper oxide is classified as a semiconductor metal due to its unique optical, electrical, and magnetic properties. This material has identified diverse applications, including the development of supercapacitors, near-infrared filters, catalytic systems, sensors, magnetic storage media, and semiconductors [15, 16]. The utilization of CuO nanoparticles (NPs) has been observed in improving polymer films, regardless of whether they are derived from petroleum-based or biobased polymers; this can be attributed to the remarkable characteristics exhibited by CuO NPs, such as their significant surface-to-volume ratio, thermal stability, relatively low toxicity, and capacity to enhance the mechanical properties of polymers [17, 18]. The potential applications of CuO nanoparticles span various fields, including electronic and optoelectronic devices. These applications encompass microelectromechanical systems, gas sensors, magnetic storage media, solar cells, field effect transistors, electrochemical cells, field emitters, and nanodevices for catalysis. Consequently, CuO nanoparticles have garnered significant interest in the academic community [19, 20].

This work used graphene oxide to improve the nanocomposites' structural, optical, and electrical properties PVA–ZrO_2–CuO. This study showed a significant improvement in these characteristics mentioned above.

2. MATERIALS AND METHODS

The fabrication of nanocomposite films was carried out through the utilization of the casting technique, wherein polyvinyl alcohol (PVA), zirconium oxide (ZrO_2), and copper oxide (CuO) nanoparticles were incorporated. The procedure entailed dissolving pure polyvinyl alcohol in 45 ml of distilled water over 35 minutes; this was accomplished by employing a magnetic stirrer at a temperature of 60°C to facilitate a more uniform solution.

The polymer underwent the incorporation of zirconium oxide (ZrO_2) and copper oxide (CuO) nanoparticles at different weight percentages: 0%, 2%, 4%, and 6%. Following three days of air-drying the solution at room temperature, the observed outcome entailed the development of polymer nanocomposites. The nanocomposites consisting of PVA, ZrO_2, and CuO were obtained from the Petri dish and employed for measurement purposes. The nanocomposite samples consisting of PVA, ZrO_2, and CuO were subjected to Fourier transform infrared spectroscopy analysis within the wave number range of 1000 to 4000 cm^{-1}. The specimens were subjected to analysis at different levels of concentration. A Nikon-73346 optical microscope, specifically of the Olympus type, was employed for this purpose. The microscope had a magnification capability of ×10 and was equipped with a camera designed to capture microscopic images. The optical properties of nanocomposites comprising PVA–ZrO_2–CuO were examined in the 200–800 nm wavelength range utilizing a U.V./1800/Shimadzu spectrophotometer.

Absorbance is calculated by using relation [21]:

$$A = I_A / I_0, \tag{1}$$

where I_A is the absorbed light intensity and I_0 is the incident intensity of light (A is the absorption of the material).

Transmittance is calculated by using relation [22]

$$T_r = I_{Tr} / I_0, \tag{2}$$

where I_{Tr} is the intensity of transmitted light and I_0 is the incident intensity of light.

The indirect transition is calculated by using relation [23, 24]

$$\alpha h\nu = B\left(h\nu - E_g\right)^r, \tag{3}$$

where B is constant, $h\nu$ is the incident photon energy, E_g is the optical band gap, and the value of r is 2 for allowed indirect transitions and 3 for forbidden indirect transitions. (Let us d is the sample thickness.)

3. RESULTS AND DISCUSSION

3.1. Fourier Transform Infrared Ray Analysis of PVA–ZrO_2–CuO NCs

Fourier transform infrared (FTIR) spectroscopy has been employed to examine the interactions occurring between atoms or ions within nanocomposites consisting of polyvinyl alcohol (PVA), zirconium dioxide (ZrO_2), and copper oxide (CuO). The interactions above may encompass alterations in the vibrational modes exhibited by the nanocomposites. The transmittance spectra of nanocomposite films containing PVA–ZrO_2–CuO, as measured by FTIR, are presented in Fig. 1, *a*, *b*, *c*, and *d*). These spectra were obtained at room temperature and covered 600–4500 cm^{-1}. The figure illustrates the presence of broad bands at 3264 cm^{-1}, which can be attributed to the presence of hydroxyl (–OH) groups. The vibrational mode associated with the CH_2 asymmetric stretching is observed at approximately 2920 cm^{-1} [25, 26]. The observed peaks at a wavenumber of 1600 cm^{-1} have been ascribed to the stretching mode of the C=C bond. The peak observed at approximately 1416 cm^{-1} is attributed to the symmetric bending motion of CH_2. The spectral peak at approximately 1085 cm^{-1} indicates the C–O bond. When examining PVA–ZrO_2–CuO samples with varying ratios of ZrO_2/CuO, the FTIR spectra exhibit shifts in peak position and alterations in shape and intensity compared to pure PVA.

This observation suggests dissociation between the respective vibrational modes of two polymers and nanoparticles composed of ZrO_2 and CuO [27, 28].

3.2. The Optical Microscopy of PVA–ZrO_2–CuO Nanocomposites

Figure 2 depicts the optical microscope images of PVA–ZrO_2–CuO nanocomposites at various ratios, observed under a magnification power of ×10. The graphical illustration of the polymer blend film depicted in the image (*a*) demonstrates a uniform phase without any discernible phase separation. This observation suggests that the PVA exhibits exceptional miscibility at this blend ratio. When the concentrations of ZrO_2–CuO increase in pure polyvinyl alcohol (PVA), the nanoparticles aggregate and form clusters within the polymer blend [29, 30]. At a high concentration of 6 wt.% of ZrO_2–CuO nanoparticles, the ZrO_2–CuO nanoparticles exhibit the formation of concentration network paths. These paths facilitate the passage of charge carriers, resulting in a modification of the material properties, as depicted in Fig. 2, *b*, *c*, and *d* [31, 32].

This study introduced an effective preparation technique that establishes optimal conditions for fabricating nanocomposite films.

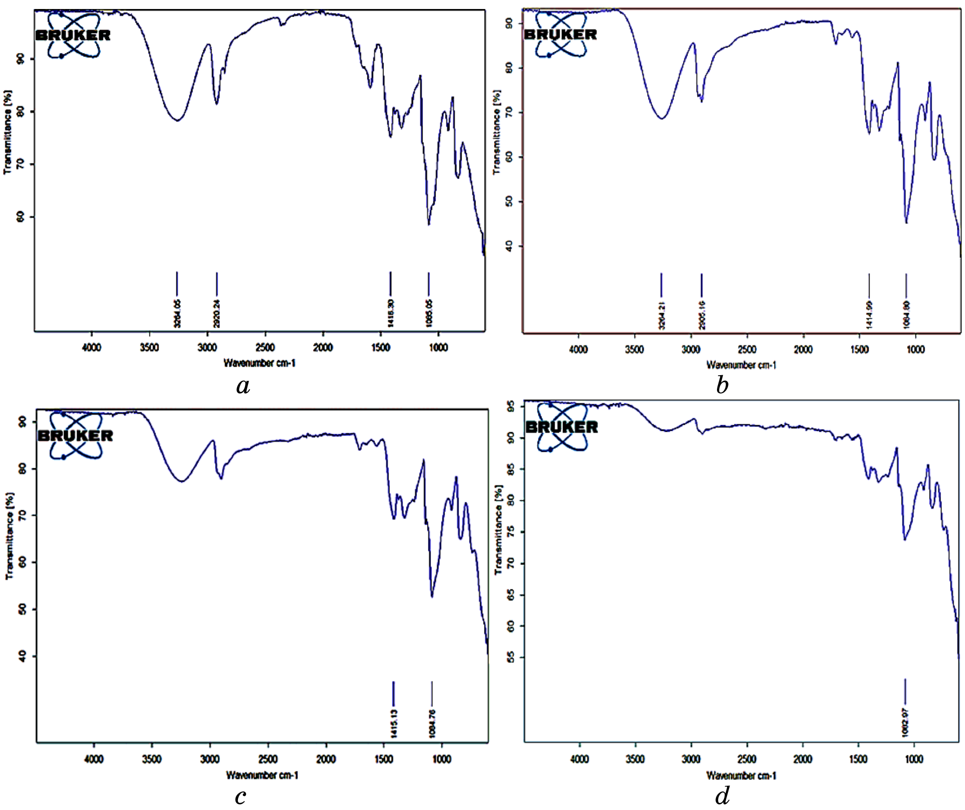

Fig. 1. FTIR spectra for PVA–ZrO_2–CuO nanocomposites: (*a*) for pure PVA; (*b*) for 2 wt.% ZrO_2–CuO; (*c*) for 4 wt.% ZrO_2–CuO; (*d*) for 6 wt.% ZrO_2–CuO.

3.3. The Optical Properties of PVA–ZrO_2–CuO Nanocomposites

Figure 3 illustrates the relationship between optical absorbance and wavelength for composites of polyvinyl alcohol–zirconium dioxide–copper oxide PVA–ZrO_2–CuO. Based on the data in Fig. 3, it can be observed that the spectra of all the films exhibit increased absorbance in the ultraviolet region. The phenomenon of composites displaying a diminished absorbance level within the visible spectrum can be attributed to their interaction with atoms, which subsequently leads to the transmission of photons [33, 34]. When the wavelength of incident photons decreases, particularly, in proximity to the fundamental absorption edge, there is a corresponding occurrence of interaction between the incident photon and the material. This interaction results in the absorption of the photon by the material [35, 36]. The intensity of the peak exhibits an increase while

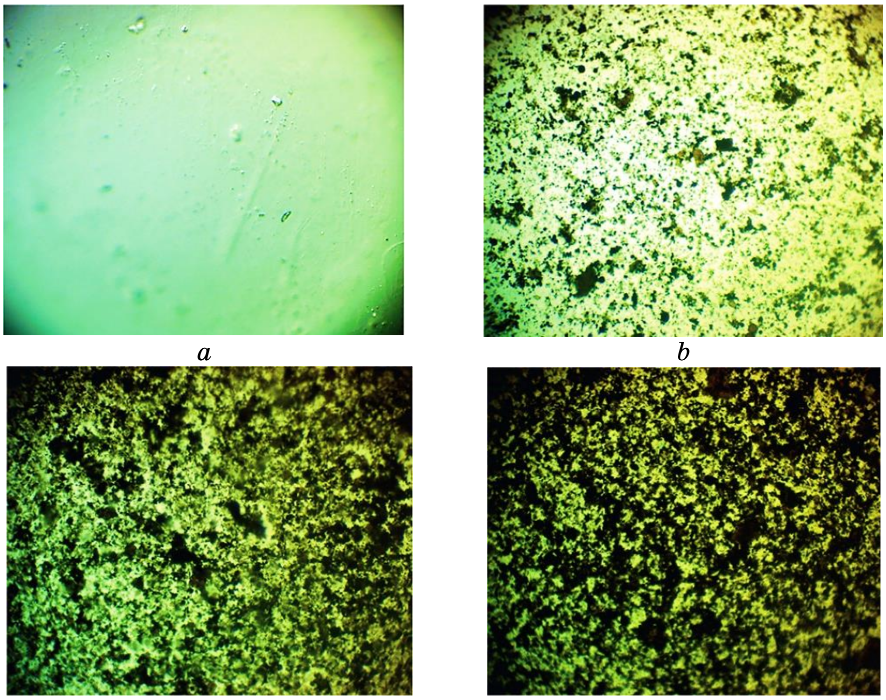

Fig. 2. Photomicrographs ×10 for PVA–ZrO_2–CuO NCs: (*a*) for pure PVA; (*b*) for 2 wt.% ZrO_2–CuO; (*c*) for 4 wt.% ZrO_2–CuO; (*d*) for 6 wt.% ZrO_2–CuO).

the position of the peak remains unchanged. The observed absorbance demonstrates a positive correlation with the weight percentages of the materials. This phenomenon can be attributed to the absorption of incident light by free electrons [37, 38].

Figure 4 depicts the transmittance values of the nanocomposites PVA–ZrO_2–CuO and pure PVA. The provided figure demonstrates a notable enhancement in transmittance for the pure polymer and the nanocomposites within the visible spectrum, in contrast to the observed transmittance intensity in the ultraviolet (UV) region. Furthermore, the reduction in transmittance intensity becomes increasingly noticeable as the proportion of nanoparticles in the nanocomposites increases [39, 40]. This phenomenon can be ascribed to the nanoparticles' heightened absorption of incident light [41].

Figure 5 depicts the relationship between the square root of the absorption edge $(\alpha h\nu)^{1/2}$ and the photon energy for nanocomposites comprising polyvinyl alcohol–zirconium dioxide–copper oxide (PVA–ZrO_2–CuO). By extrapolating a linear segment from the upper portion of the curve towards the *x*-axis, specifically at the point

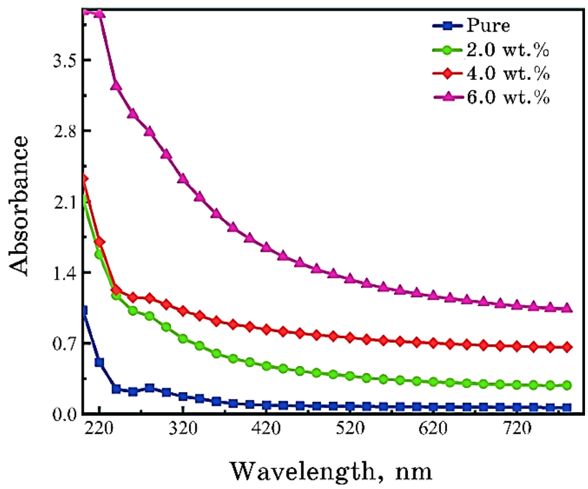

Fig. 3. Absorbance of PVA–ZrO_2–CuO NCs as a function of wavelength.

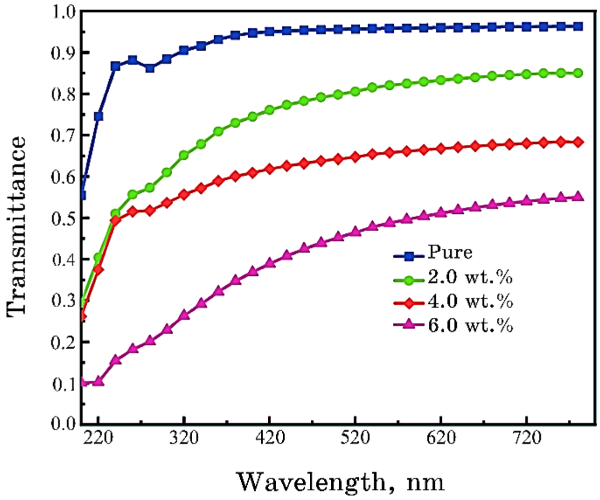

Fig. 4. The transmission spectra of PVA–ZrO_2–CuO NCs as a function of wavelength.

where the square root of $\alpha h\nu$ equals zero, we can ascertain the energy difference linked to the allowable indirect transition.

Table illustrates a decline in the energy gap values with increasing weight percentages of zirconium oxide (ZrO_2) and copper oxide (CuO) nanoparticles. This phenomenon is responsible for forming localized states within the energy gap prohibited for electronic transitions. The transfer process occurs biphasically, wherein elec-

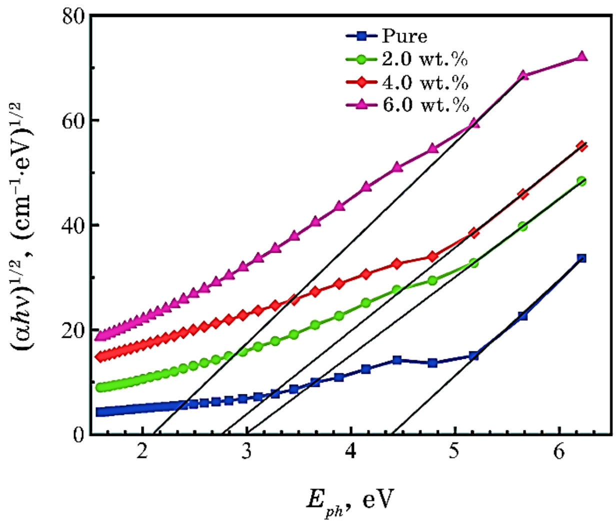

Fig. 5. Difference of $(\alpha h\nu)^{1/2}$ for PVA–ZrO_2–CuO NCs with photon energy.

TABLE. Values of energy gap for indirect transitions (forbidden and allowed) in the PVA–ZrO_2–CuO nanocomposites.

Content of PVA–ZrO_2–CuO nanoparticles wt.%	Indirect energy gap (allowed), eV	Indirect energy gap (forbidden), eV
0	4.37	3.76
2	2.98	1.85
4	2.76	1.64
6	2.11	0.74

tron transitions from the valence band to the localized energy levels and subsequently progresses to the conduction band. This phenomenon corresponds with a rise in the weight percentage of nanoparticles composed of zirconium oxide (ZrO_2) and copper oxide (CuO). The observed phenomenon can be explained by the diverse composition of nanocomposites, where the flow of electrons depends on the amount of additional components present. The study revealed a direct correlation between the concentration of ZrO_2–CuO nanoparticles and the density of localized states [42, 43].

Figure 6 illustrates the correlation between the quantity $(\alpha h\nu)^{1/3}$ $[cm^{-1}\cdot eV]^{1/3}$ and the photon energy of nanocomposites. The presented figure illustrates a decreasing trend in the energy gap values for forbidden indirect transitions as the concentration of ZrO_2–CuO nanoparticles increases. Moreover, the magnitudes of forbidden indirect transitions are relatively lower when compared to those of al-

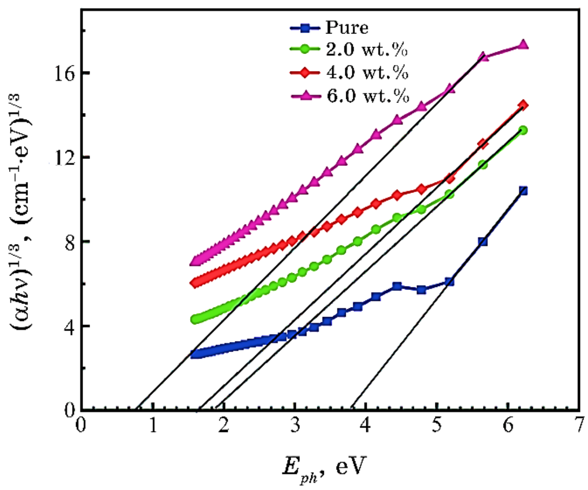

Fig. 6. Difference of $(\alpha h\nu)^{1/3}$ of PVA–ZrO_2–CuO NCs with photon energy.

lowed indirect transitions [44, 45].

4. CONCLUSION

The current study involves the production of nanostructured films composed of PVA–ZrO_2–CuO through the solution casting method. The investigation focused on analysing the structural and optical characteristics of nanostructures composed of PVA–ZrO_2–CuO. The Fourier transform infrared (FTIR) analysis revealed notable alterations in the infrared spectra' peak position, shape, and intensity when comparing the polymer blend with nanoparticles to pure polyvinyl alcohol (PVA). These changes indicate no chemical interaction between the polymer blend and the nanoparticles. The optical microscope images provide evidence of the uniform dispersion of ZrO_2–CuO additives, with the nanoparticles forming a cohesive network within the polymer blend. The augmentation in the concentration of nanoparticles comprising zirconium dioxide (ZrO_2) and copper oxide (CuO) results in an elevation in the absorbance of nanocomposites (NCs) composed of polyvinyl alcohol (PVA), zirconium dioxide (ZrO_2), and copper oxide (CuO). Incorporating nanofiller consisting of ZrO_2–CuO at a concentration of 6 wt.% results in a reduction in the energy gap associated with indirect transitions, including both permissible and impermissible transitions. The energy gap related to allowable transitions experienced a decrease from 4.37 eV to 2.11 eV. In contrast, the energy gap for non-permissible transitions reduced from 3.76 eV to 0.74 eV. Moreover, an augmentation in the ratios of ZrO_2/CuO leads to a reduction in the extent of transmittance.

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