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RESEARCH PAPER

Preparation and Characterization of ZnO, WO_3/ZnO Nanocomposites Using Hydrothermal Method

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ABSTRACT

In the present, nanocomposite with high photocatalytic degradation used in the removal pollutant. preparation by hydrothermal method was first used ZnO nanoparticles, and then a ZnO/WO_3 nanocomposite. Band gap energy (BG), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), field emission scanning electron microscopy (FE-SEM), and Fourier transform infrared spectra (FT-IR) were used to describe the products. The presence of WO_3, ZnO, and ZnO-WO_3 is indicated by the crystalline ZnO nanoparticle peaks at 32 °, 34 °, and 36 ° and the WO_3-ZnO nanoparticle peaks at 26 °, 27 °, 28 °, and 33 °. The band gap obtained from extrapolating this data after doping WO_3 onto ZnO nanoparticle is 2.81 eV, highlighting the possibility of WO_3-ZnO to be utilized in solar cell-based systems in the future in addition to their promise as efficient photo catalysts.

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INTRODUCTION

Industrial wastewater contains toxic organic chemicals that should be eliminated or changed into safe chemical compounds before being dumped into the environment [1]. Metallic oxide nanoparticles are well known for their intriguing applications in numerous industries. in the fields of optics, electronics, energy storage, ecological restoration, microbial inhibition, and medical implants. Consequently, the creation of metallic oxide nanoparticles has enormous potential during the current phase of urbanization and industrialization. Metal oxides are essential for long-term ecologically friendly repair [2].

In the last two decades, environmental and wastewater degradation brought on by textile effluents has been broken down utilizing semiconductor [3]. Organic contaminants from industries are currently a key source of concern for water resource contamination. Untreated industrial wastewater has a high concentration of organic contaminants that can have a permanent negative impact on the environment and human health [4]. Due to its aesthetic effects and toxicity on receiving waters, textile wastewater treatment is interesting. The threats to human and environmental health are decreased by cleaning wastewater before it is discharged into

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natural bodies of water [5, 6]. Several tried-and-true techniques have been used to treat waste water containing dyes, including the hydrothermal approach, the membrane process, chemical oxidation, microbial degradation, adsorption, and bio sorption [7, 8]. Hydrothermal is a phrase that has only geological origins. Hydrothermal processing is the term used to describe any heterogeneous reaction that occurs at high pressures and temperatures with aqueous solvents or mineralizers to dissolve and recrystallize (recover) materials that are ordinarily intractable [9]. Hydrothermal synthesis, commonly referred to as the "hydrothermal method," is a unique method for crystallizing substances from hot aqueous solutions at high vapor pressures. Hydrothermal synthesis, which is also known as the "hydrothermal method," is a unique method for crystallizing substances from hot aqueous solutions at high vapor pressures (Fig. 1) [10].

Because it doesn't utilize (organic solvents) or additional procedures like grinding and calcination, the hydrothermal technique is a straightforward and environmentally friendly procedure. When the substrate mixture is heated progressively to a temperature between 100 and 300 °C and left for additional days, this procedure calls for an autoclave space. As a result, (crystal nuclei) are produced with an increase in size after cooling. This procedure has a number of advantages, including the capacity to function at low temperatures and the dependence of crystal size and form on mixture composition, process temperature, and pressure [11]. Zinc oxide (ZnO) is utilized extensively in the photodegradation process because of its high stability, low cost, effectiveness, and environmental friendliness. Contaminants are effectively eliminated by the inclusion of ZnO and tungsten oxide (WO_3), which has special qualities as a stable semiconductor with a low bandgap of approximately (2.2-2.8) eV and strong chemical stability [12] .

Tungsten trioxide (WO_3) has exceptional chemical stability in an acidic aqueous solution and great photo corrosion resistance [13]. It is frequently employed as an active visible light photocatalyst. However, WO_3's photoelectric performance needs to be enhanced for use in practical applications. The photoelectric performance of WO_3 has recently been the subject of considerable investigations that have implications for the use of solar energy and

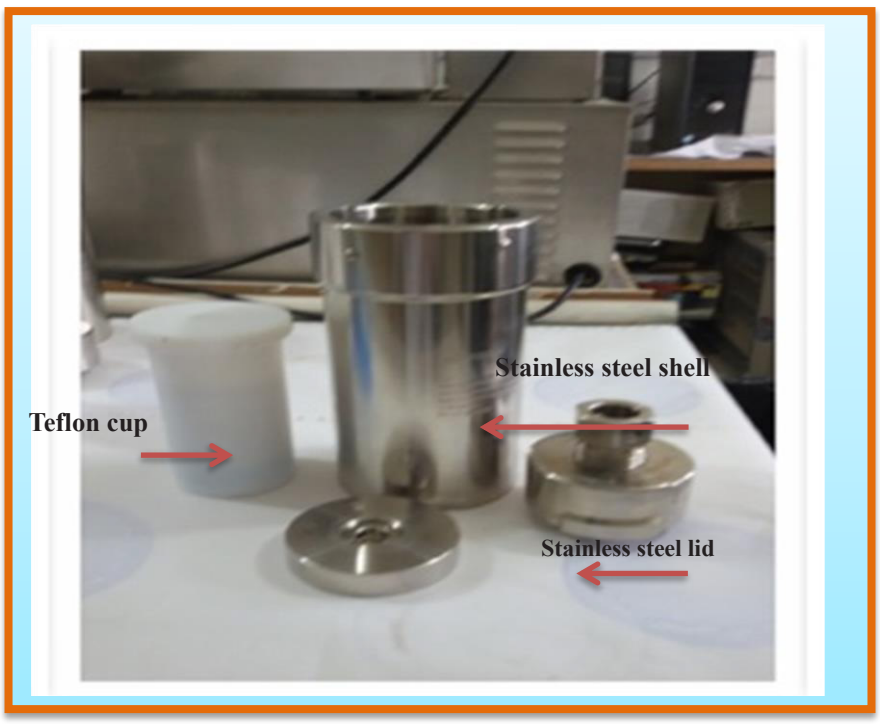

Fig. 1. Real image of autoclave with main compound, college of science for Women- University of Babylon.

photocatalytic systems [14]. Although WO_3-ZnO nanocomposites have been the focus of a few studies, their photocatalytic potential has received little attention. More crucially, little is known about the capacity of WO_3-ZnO composites to store energy [15]. WO_3 and ZnO nanoparticles are typical semiconductors. The potential energy storage system of ZnO when it is coupled with WO_3 and subjected to visible light is shown in Fig. 2 [16].

MATERIALS AND METHODS

Chemical and reagents

All of the analytical-grade chemicals and reagents utilized in this research were acquired from Alpha Chemika and Sigma-Aldrich-India. Milli pure water (Milli Pure Water System) was used for solution preparation.

Synthesis of ZnO nanoparticle

The hydrothermal technique was used to grow the ZnO nanoparticle in the initial step. Thus, a mixture of 4 grams of zinc acetate hex- hydrate and 5 grams of oxalic acid were agitated for one hour at 45 degrees Celsius. The combined mixture was then heated for 24 hours at 160°C in a 100 cc stainless steel autoclave lined with Teflon [17]. After the substrate had naturally cooled to ambient temperature, it was taken out of the autoclave and repeatedly washed with DW before being dried at 75 °C in air. Products were then further calcined in air for 1.5 hours at 500 °C; this preparation was described in Fig. 3.

Synthesis of WO_3-ZnO Nanocomposites

Thermal breakdown was used to create WO_3-ZnO Nanocomposites at a low cost [3]. Initially, 20 ml of distilled water was used to dissolve 6 gm of zinc acetate dehydrate and 3 gm of oxalic acid while stirring continuously. The nanocomposites were then created using 2 gm of sodium tungstate ($Na_2WO_4.2H_2O$), 4 gm of sodium sulfate (Na_2SO_4), and 1 gm of oxalic acid ($H_2C_2O_4$). This was accomplished by dissolving sodium tungstate, oxalic acid, and sodium sulfate in 60 ml of deionized water. When an aqueous solution became translucent, hydrochloric acid 4 M was slowly added. In this manner, the pH was tuned to 2.6 to appear yellow, and then was progressively added to the zinc acetate and oxalic acid mixed solution.

In a 100 ml Teflon-lined stainless steel autoclave, the aforementioned solution was heated for approximately 24 hours at 160 °C. The finished product was then cleaned with distilled water, and the cleaned material was overnight dried at 75 °C. Finally, the products underwent a 1.5-hour air calcination process at 500 °C [18]. Fig. 4 provides an explanation of this preparation.

RESULTS AND DISCUSSION

Characterization Techniques

X-ray diffraction (XRD)

X-ray diffraction is a highly effective non-destructive method for crystalline material characterization. Fig. 5 shows the XRD patterns

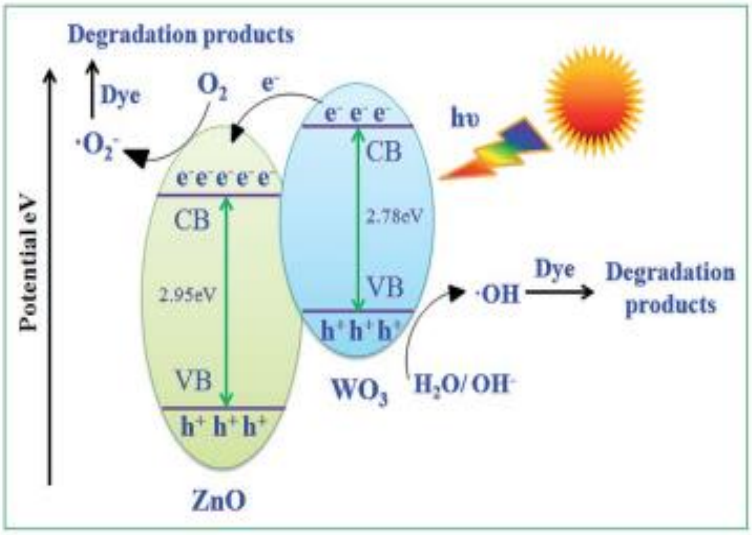

Fig. 2. Explained the WO_3-ZnO photocatalytic degradation process [16].

of pure ZnO and WO_3-ZnO Nanocomposites. The calcined ZnO, WO_3-ZnO, and ZnO at 500 °C XRD patterns. After calcination at 500 °C, impurities are removed and crystallinity is improved. At 500 °C, all of the ZnO peaks were discovered to be sharper, confirming that crystal formation occurs at higher calcination temperatures. The presence of no other contaminants in the diffraction patterns indicates that the produced nanomaterial was pure ZnO hexagonal quartzite., The existence of WO_3-ZnO is indicated by the WO_3-ZnO nanoparticle crystalline peaks at 26 o, 27 °, 28 °, and 33 °, as well as the ZnO nanoparticle crystalline peaks at 32 °, 34 °, and 36 °. However, EDX verified the existence of WO_3 and ZnO. Strong and precise diffraction peaks show that the nanocrystal line ZnO and WO_3-ZnO nanocomposites have good crystallinity [19].

EDX spectra shows that only Zn and O can be found in pure ZnO, whereas WO_3-ZnO nanocomposites may contain a third element, W. A semi-quantitative evaluation of the atomic concentration (atom%) shown in Table 1 shows that the products' W content increases from 0.5 to 1.8 at% depending on the levels of Na_2WO_4 addition [20]. But WO_3-ZnO Nanocomposites contain less W than the precursor solution does, indicating that part of the W.

Field emission scanning electron microscopy (FE-SEM)

The field emission scanning electron microscopy is an ideal analytical technique for characterizing and visualizing the elemental composition of a specimen (Fig. 6) [21,22]. WO_3-ZnO nanocomposites and pure ZnO are shown in pictures made with a FE-SEM. The pure ZnO

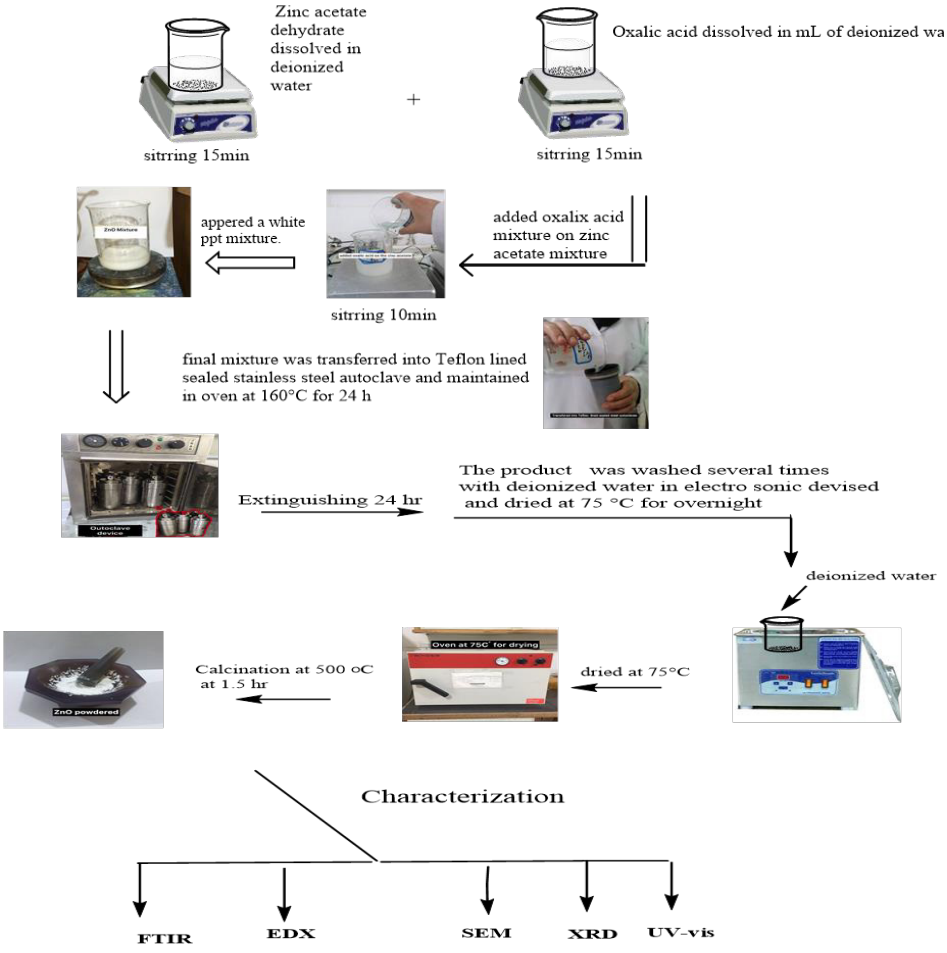

Fig. 3. Preparation of ZnO nanoparticle by hydrothermal method

particles have an aspect ratio of 7, with an average diameter and length of 36 nm and 253 nm, respectively. While the average diameter of pure ZnO particles is comparable to that of 1 mol% WO_3-ZnO particles, their lengths are more erratic, ranging from 96-422 nm [23, 24].

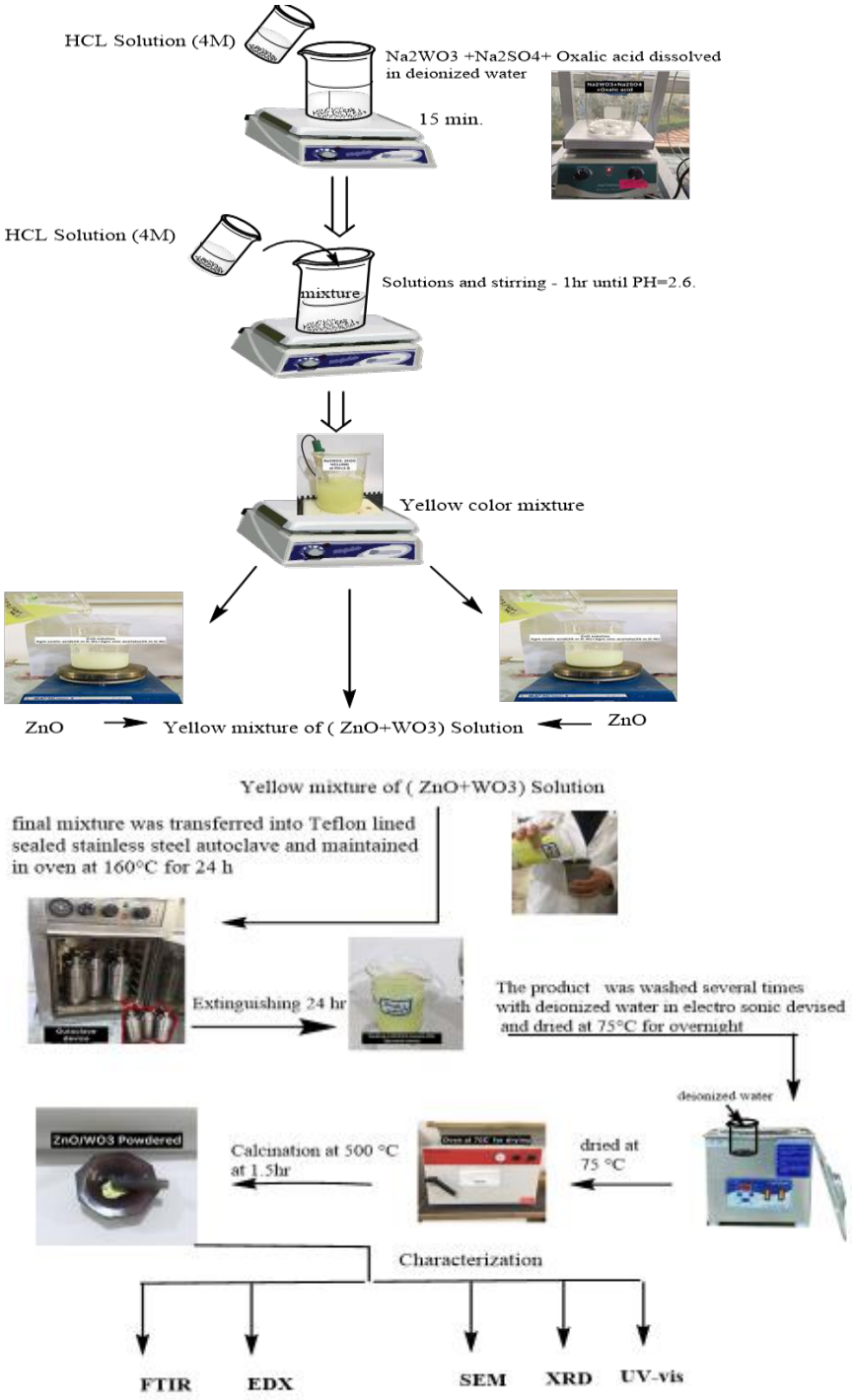

Fig. 4. Synthesis of WO_3 -ZnO Nanocomposites by hydrothermal method.

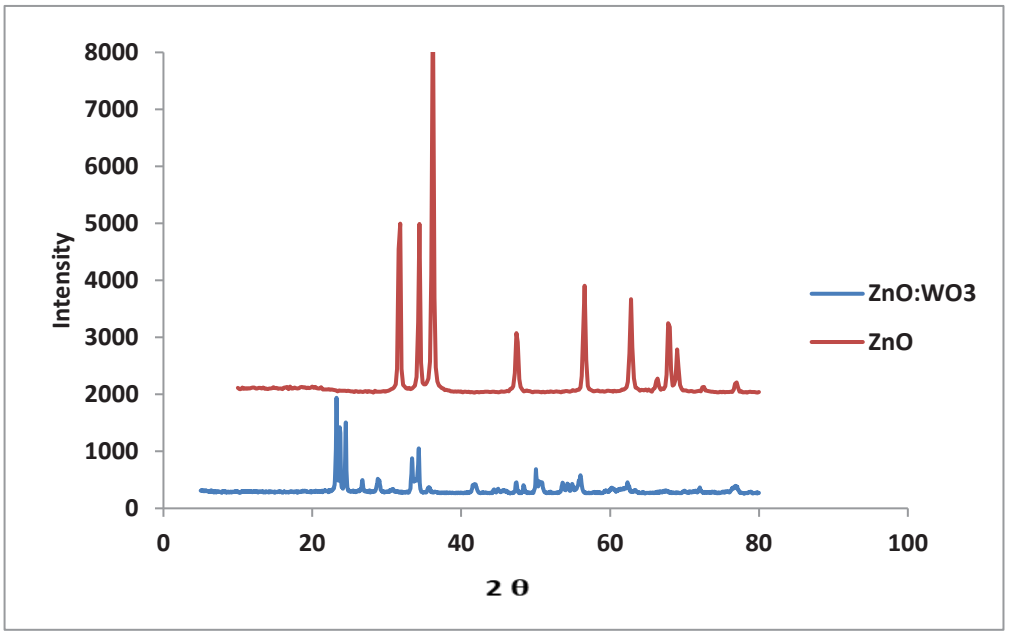

Fig. 5. WO_3-ZnO nanocomposites and pure ZnO XRD patterns.

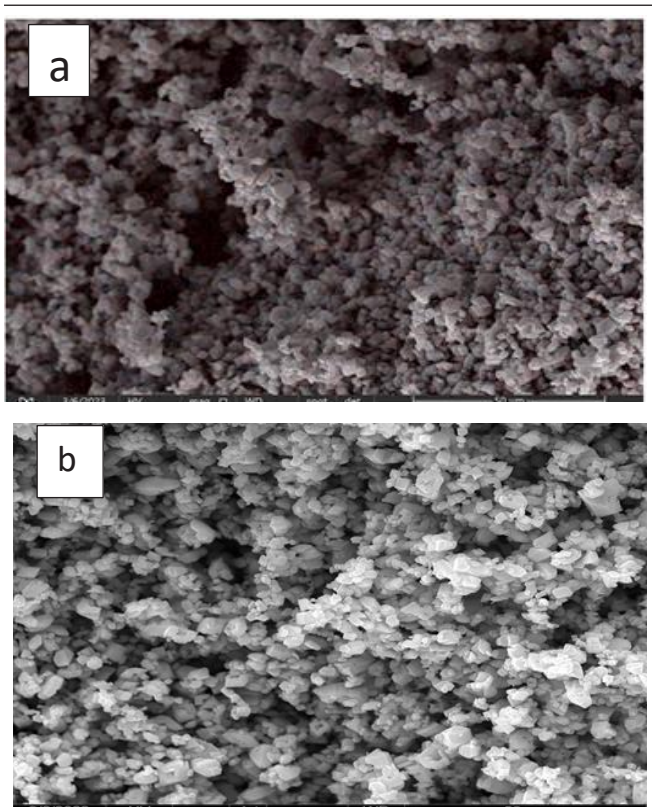

Fig. 6. Pure (a) ZnO and (b) WO_3/ZnO nanocomposites are depicted in FESEM pictures.

The maximum values of the diameter and length of the 3 mol% WO_3-ZnO particles are, respectively, 0.38 mm and 1.14 mm. The ultrasonic treatment may result in some recognizable fragments prior to FESEM testing. It is apparent that the presence of the secondary oxide (WO_3) affects the particle size and shape [25].

Band gap energy measurements

The bandgap energy for ZnO and WO_3/ZnO nanoparticles was determined from the UV-Vis reflectance spectrum using the Tauc relationship. The influence of the UV absorption spectrum on scattering is greater than that of the UV reflection spectrum. The fact that the optical bandgap coincides to a wavelength where there is a substantial drop in light reflection suggests that the molecules are almost uniformly distributed throughout the sample. The reflection data are used to calculate the direct bandgap energy (Eg) for ZnO nanoparticles by fitting them to the direct transition equation:

$\alpha h = ED (h - Eg)^{½}$

where (h) is the photon energy, (ED) is a constant, (Eg) is the direct bandgap, and is the optical absorption coefficient. (h) was plotted for the sample's ZnO and WO_3-ZnO nanoparticles as a function of h [26]. Fig. 7 shows the linearity suggesting the direct transition of semiconducting WO_3-ZnO. The band gap of 2.81 eV obtained from extrapolating this data after doping WO_3 onto ZnO nanoparticles demonstrates the promise of WO_3-ZnO as efficient photo catalysts as well as their potential to be utilized in solar cell-based systems in the future. The significant reduction in band gap brought on by WO_3 doping in ZnO may be due to the oxygen vacancy, which makes it easier for electrons to move between the valence and conduction bands [27].

FTIR Spectroscopy

Fig. 8 displays the FTIR spectra of the aforementioned materials, which were collected between 400 and 4000 cm^{-1}. It is evident that when WO_3 concentration rises, a widening WO_3 specific absorption band appears at 816 cm^{-1}. As WO_3 and ZnO's unique bands gradually overlap at

Table 1. The WO_3-ZnO nanocomposites' composition.

Element	Atomic %	Atomic % Error	Weight %	Weight % Error
Zn	40.5	0.3	75.7	0.5
O	84.3	0.11	33.5	0.4
W	17.8	0.4	73.3	1.8

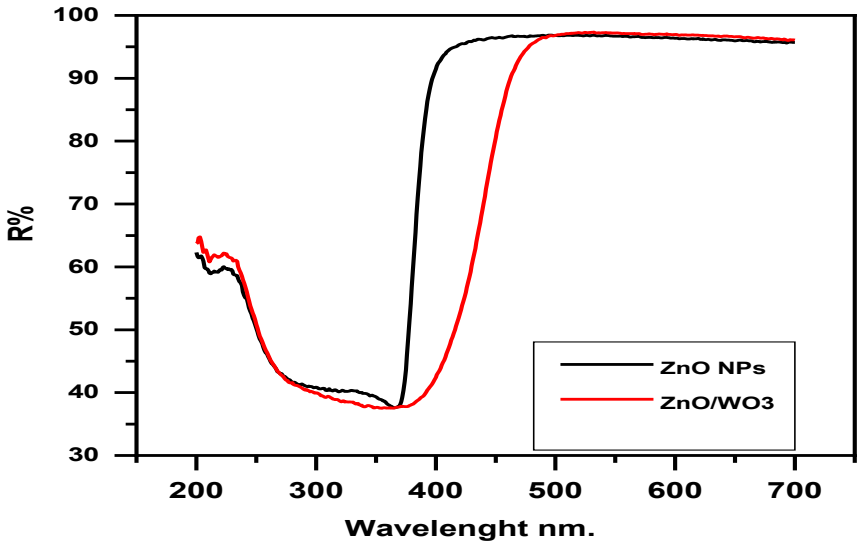

Fig. 7. The WO_3-ZnO band gap is made smaller by the energy levels between the two materials.

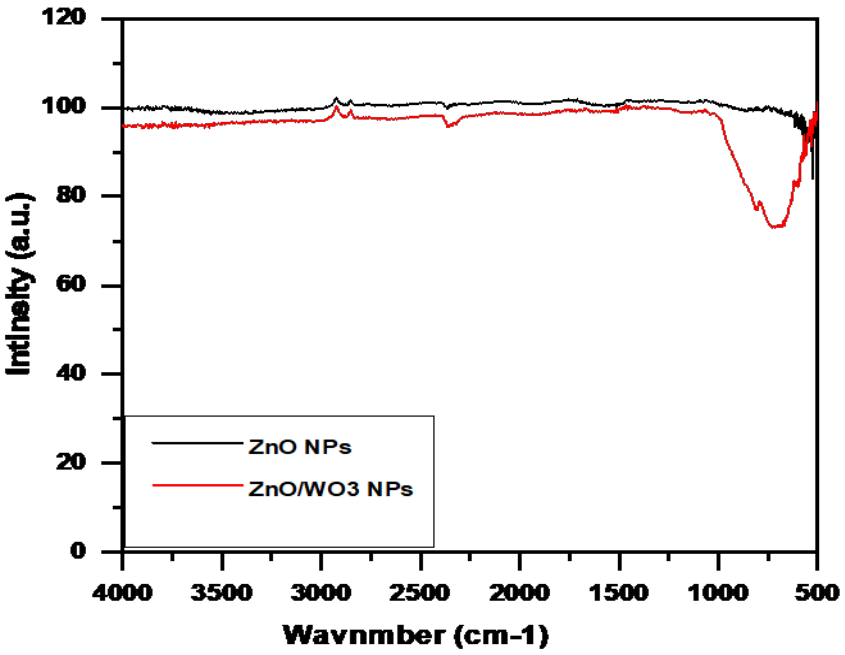

Fig. 8. FTIR spectra of pure ZnO and WO_3–ZnO composites.

500 cm^{-1}, the usual ZnO absorption band quickly broadens. The stretching vibration of water, which can be observed at 3444 cm^{-1}, and the bending vibration of water, which can be seen at 1635 cm-, are caused by water adsorbed on the surface of the sample [15].

Two factors in particular account for WO_3/ZnO Nanocomposites' higher photocatalytic activity than pure ZnO. First, the energy level difference between WO_3 and ZnO causes the band gap of WO_3-ZnO nanocomposites to be smaller., increasing the efficiency of light use and widening the optical absorption spectrum. Second, when exposed to UV-Vis light, ZnO and WO_3 both undergo synchronous interband transitions. Because the valence and conduction bands are located differently, excited electrons in the ZnO conduction band can easily transfer to the WO_3 conduction band, but excited holes in the WO_3 valence band can also transfer to the ZnO valence band. The lifetime of the electron-hole pairs increases as a result of the decreased recombination of the photo-induced carriers. The reduced recombination of the photo-induced carriers causes an increase in the lifespan of the electron-hole pairs. An excessive amount of WO_3 would hurt the dispersion of WO_3 in ZnO, and redundant WO_3 would act as recombination hubs for electron-hole pairs, which might lessen the efficiency of electron-hole separation [20].

CONCLUSION

The hydrothermal method is an effective technique for producing WO_3-ZnO. By combining the previously prepared materials with the ZnO, using ultrasound irradiation to prepare them, and using staleness, binary nanocomposites were created. In the process of reducing heat, a steel autoclave. Additionally, XRD spectroscopy was used to study nanocomposites that were created, and the radiation revealed that the materials had a distinct crystalline phase. as metal was photo-deposited on ZnO, the band gap values fell. Finally, the generated materials with distinct peaks of WO_3-ZnO were identified using FTIR spectra, and the exterior morphology and layer thickness of the recorded material were studied using EDX-FESEM.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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