Structural, Morphological and Optical Bandgap Analysis of Multifunction Applications of Y2O3 -ZnO Nanocomposites: Varistors and Visible Photocatalytic Degradations of Wastewater

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Structural, morphological and optical bandgap analysis of multifunction applications of Y$_2$O$_3$-ZnO nanocomposites: Varistors and visible photocatalytic degradations of wastewater

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Abstract

In this study, a combustion method as an efficient, easy, low-cost, and eco-friendly technique was used to synthesize nano-ZnO as a matrix with different yttrium doping ratios with different doping concentrations. Not only X-ray diffraction (XRD), but also scanning electron microscopy (SEM), and Fourier transformation Infrared spectroscopy (FT-IR) technique employed to characterize the structural and surface morphology of the Y$_2$O$_3$-ZnO nanocomposites. The obtained results supported ZnO’s growth from crystalline to satisfactory nanoparticle structure by changing the yttrium doping concentrations inside ZnO nanoparticles. Moreover, UV-Vis diffuse reflectance spectroscopy, AC electrical conductivity, and current-voltage characteristics were considered to characterize the effects of yttrium doping on the energy bandgaps and electrical/dielectric properties and discussed the parameters of the ceramic varistors of the studied Y$_2$O$_3$-ZnO nano-complex oxides. The photocatalytic degradation efficiency of phenol, Methylene Blue, and Rhodamine B was investigated using all prepared Y$_2$O$_3$-ZnO nanostructured samples. As the yttrium doping ratios increased, the photocatalytic efficiency increased. After the addition of moderate Y$^{3+}$ ions-doping, Further generation of hydroxyl radicals over ZnO. For Y$_2$O$_3$-ZnO (S5), the optimal photocatalyst is a
degradation of 100% of phenol, Methylene Blue, and Rhodamine B solutions compared to 80% of photocatalysis for ZnO stand alone. The prepared Y$_2$O$_3$-ZnO nanostructured materials are considered novel potential candidates in broad nano-applications ranging from biomedical and photocatalytic degradation for organic dyes and phenol to environmental and varistor applications.

**Keywords:**

Yttrium doping, Y$_2$O$_3$-ZnO nanocomposites, optical diffuse reflectance (ODR), optical bandgaps, electrical characterizations, and photocatalytic degradation.

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1. Introduction

Recently, the research focused on developing wastewater treatment, and human society has gained more attention. Phenolics are typical contaminants because those compounds are frequently utilized in the manufacture of various industrial products, such as textiles, pesticides, gunpowder, dyes, and plastics [1,2], where most of them have serious toxic damages on several biological fields [3]. It is challenging to depend on traditional organic treatment techniques to remove phenols due to their strong stability and toxicity [4]. Scientific studies have to pay more emphasis to ZnO, taking advantage of its amazing properties, including excellent chemical stability, high electrochemical coupling coefficient, small dielectric constant, high exciton binding energy (about 60 meV), broad bandgap (around 3.37 eV at room temperature) as well as sufficient thermal conductivity, antibacterial, binding, and UV-protection [5,6]. Besides, ZnO films are considered high transparency materials ranging from infrared (IR) to visible regions with significant refractive constants. As a result, all those characteristic behaviors are potentially broadening the ZnO technological applications, such as in UV-light emitters, solar cell windows, thin-film transistors, biological and chemical gas sensors, and biomedical sensors varistors [7].

Among these properties, the extremely photocatalytic characteristic with ultraviolet (UV) light, ZnO displayed excellent potentials for photocatalyst applications in wastewater treatments [8,9]. However, the photoinduced recombination process of the hole and electron in ZnO happens quickly, which restricts ZnO in industrial applications [10]. To enhance the ZnO photocatalytic behavior, scientific researchers have inspected various synthesizing methods, including sol-gel [11], solid-state reaction [12], and solvothermal [13]. On the other side, the ZnO optical, chemical, and physical properties were improved through doping ZnO with either non-metal or metal elements, for example, doping with sulfur that can increase the ZnO lattice constants as well as to enlarge the ZnO oxygen vacancy [14], gold could obstruct the holes and electrons recombination, and doping with chromium can rise the visible light absorption and reduce the ZnO bandgap [15,16]. Nevertheless, the ZnO doped with rare earth elements (REEs) such as yttrium (Y) has also been studied because the Y’s ionic radius is very close to ZnO [17]. The yttrium (Y) element has a single filled $4d$-orbital, which creates some electron configurations. Its oxides possess numerous benefits, including strong selectivity of adsorption and various types of crystallinity, as well as good electronic conductivity and thermal stability.
Currently, $Y^{3+}$-doping has been utilized to enhance the photocatalytic properties of different metal oxides, such as PbYO [20], $Y^{3+}/TiO_2$ [21], InYO$_3$ [22], and $Y^{3+}/Bi_5Nb_3O_{15}$ [23]. Importantly, the combination of ZnO with $Y^{3+}$-ions as ZnO: Y nanostructures are deliberated to enhance photocatalytic activities, display transparent coatings, improve UV-emission in photoluminescence (PL), etc. [24,25]. There are several research studies considering yttrium ($Y^{3+}$-ions) as a rare earth element to be used in enhancing the optical properties of ZnO [26]; however, to the best of the current knowledge, there aren’t many studies focus on $Y_2O_3$-ZnO being utilized as a photocatalyst, and varistors ceramic devices.

In this present study, $Y^{3+}$-ions (at different concentrations) were doped with ZnO using the combustion method, which is a considerably low cost, simple, and effective technique. The prepared $Y_2O_3$-ZnO nanostructures are smart and multifunctional materials to be applied in various technological, environmental, and electronic applications, including varistors, and photocatalysis of waste materials. Here, X-ray diffraction (XRD) and scanning electron microscopy (SEM) was applied to characterize the structural and surface morphology of the $Y_2O_3$-ZnO nanocomposite materials. The enhancements in the optical properties of ZnO with yttrium (Y) with different concentrations were examined using UV-Vis optical diffuse reflectance spectroscopy (ODR) and Fourier transformation Infrared spectroscopy (FT-IR). Besides, studying the electrical behaviors of $Y_2O_3$-ZnO nanocomposite materials as nanoscale ceramic varistors were investigated through current-voltage measurements and dielectric analysis. Visible photodegradation concerning illumination time of phenol, Rhodamine B, and Methylene Blue were used to evaluate ZnO and $Y_2O_3$-ZnO photocatalytic performance.

2. Experimental techniques.

2.1. Synthesis of $Y_2O_3$-ZnO nanocomposites.

The combustion method was used to prepare ZnO nanoparticles (NPs) doped with rare-earth yttrium ($Y^{3+}$-ions). First, 5 g of Zn(NO$_3$)$_2$·6H$_2$O was mixed and grinding well in ceramic crucibles with one gram of gum acacia. Eight different yttrium ($Y^{3+}$-ions) of different concentrations ranging from 0.001 g to 5 g (i.e., named as So, to S7 as illustrated in Table.1), respectively, were added separately to the previous mixture and dissolved in 5 mL of distilled water. The prepared mixtures of $Y_2O_3$-ZnO nanostructured were heated at 600 °C for 2 hours and then left to cool down to room temperature. In this preparation technique, gum acacia is considered a fuel to support the formation of ZnO nanostructure conversion from high crystallinity to nanoscale by enlarging their constituents inside the ZnO matrix. The final
obtained materials of ZnO-nanoparticles doped with yttrium-ions at various concentrations are shown in Fig. 1.

**Table. 1.**
Sample code of pure and doped ZnO nanostructures with different doping concentrations of yttrium $Y^{3+}$-ions.

| Samples                  | Codes |
|--------------------------|-------|
| Pure ZnO                 | S0    |
| 0.001g Y-doped ZnO       | S1    |
| 0.01 g Y-doped ZnO       | S2    |
| 0.1 g Y-doped ZnO        | S3    |
| 0.5 g Y-doped ZnO        | S4    |
| 1 g Y-doped ZnO          | S5    |
| 2.5 g Y-doped ZnO        | S6    |
| 5 g Y-doped ZnO          | S7    |

**Fig. 1.** Synthesis procedures of ZnO nanoparticles with different doping ratios of yttrium (Y) rare earth element.

**2.2 Devices & Measurements.**

X-ray diffractometer (XRD) is a vital tool to investigate the prepared ZnO nanocomposites with different yttrium doping ratios. In this study, XRD analysis was achieved through Shimadzu LabX-XRD-6000, utilizing filtered radiation of $CuK_{\alpha}(\lambda = 1.5406 \text{ Å})$ at room
temperature. The recorded XRD data was matched with the attached software (pdf-2 library) in XRD Shimadzu, where the diffraction angle ($2\theta$) was between $5^\circ$ and $80^\circ$. Moreover, the scanning electron microscopy (SEM), which is JSM-6360 type with an operating voltage of 20 kV, was utilized to examine the morphology of the surface of all prepared Pr$_2$O$_3$–ZnO nanocomposites in power form.

Moreover, the UV-visible diffused reflectance spectra of as-prepared Y$_2$O$_3$–ZnO nanostructured materials was verified through an integrated sphere device coupled to a UV-3600 UV/Vis spectrophotometer (Shimadzu, Japan). Here, the wavelength ranged from 200 nm to 1600 nm, the step scan was 5 nm, and the reference material was barium sulfate.

DXR FT-IR Spectrometer, THERMO SCIENTIFIC, was used to measure the Fourier transform infrared (FT-IR) spectra of the Y$_2$O$_3$–ZnO nanocomposites within the wavenumber ranging from 400 cm$^{-1}$ to 4000 cm$^{-1}$. The Y$_2$O$_3$–ZnO nano-samples were subjected to the FT-IR analysis through principally preparing 100 mg of potassium bromide with 2 percent finely, where the mixtures crushed the Y$_2$O$_3$–ZnO nanopowders.

At a constant temperature of 25°C, the electrical properties were accomplished utilizing a computerized digital Keithley 4200-SCS with a wide range of frequency from 3 kHz to 10 MHz for the as-prepared Y$_2$O$_3$–ZnO nanostructured samples. A handheld hydraulic press was used to shape a pellet of 13 mm in diameter and 1 mm in thickness.

At room temperatures, the current-voltage was measured using the typical circuit controllable PID. The circuit involves a digital pico-ammeter that has the model of DPM-111/SVS labs Inc. USA, power supply with high-voltage from the model EHT-11/SVS labs Inc. USA, as well as PID controlled oven with the model of PID–200 that was linked to double probe holder, which was fixed in the oven that was attached to the operating system. The Y$_2$O$_3$–ZnO nanostructured was pressed on a solid disc in 10 tons with a 13 mm diameter and 1 mm thickness dimension.

The degradation process of photocatalytic was performed in a photoreactor planned by I.S. Yahia’s group in NLEBA at Ain Shams University in Egypt. The photoreactor holds eight visible light lamps with 18 W, 60 cm, and 420 nm wavelength. The Phenol (Ph), Rhodamine B (RhB), and Methylene Blue (MB) (100 ppm) were utilized for the photodegradation as waste materials. 0.01 g of undoped ZnO or Y$_2$O$_3$-doped ZnO nanocomposites have been dispersed in 200 mL of each waste materials’ solution. The mixture achieved adsorption equilibrium via 40 min dark stirring. Afterward, the mixture was irradiated through the designed photochemical reactor. To eliminate photocatalyst particles before examining phenol, Rhodamine B, and
Methylene Blue concentrations, 5 ml of the reaction mixture was extracted and centrifugated every 10 minutes. The concentration of Phenol (Ph), Rhodamine B (RhB), and Methylene Blue (MB) in the solution has been analyzed via the following absorbance at 269, 510, and 665 nm, respectively, using the JASCO V-550, Japan UV-Vis spectrophotometer in the wavelength range of (200-800 nm).

3. Results and discussion

3.1. Structural and morphological characterization of Y₂O₃-ZnO nanocomposites.

3.1.1. X-ray Diffraction patterns.

XRD patterns of Y₂O₃-ZnO nanocomposites with different doping ratios are illustrated in Fig. 1 at ambient temperature. All XRD spectra of pure ZnO and Y₂O₃-ZnO showed seven diffraction peaks predominantly due to the wurtzite ZnO phase (JSPDS 01- 075-0576) with weak lines related to the carbon phase (JSPDS 01-072-2091). The attained diffraction peaks of ZnO agree perfectly with the published results of the sol-gel Fe-ZnO samples by C. Aydın et. al [27]. Moreover, K.-S. Yu et.al studied the ZnO and Er:ZnO samples and XRD characterizations illustrated that the main sharp peaks of diffraction for ZnO phase positions at 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, 62.9°, 66.4°, which were corresponding to (100), (002), (101), (102), (110), (103), and (201) indices [28]. The prominent peaks were corresponding to (100) and (101) planes have been observed in all studied samples, which signposted the creation of undoped ZnO phase with wurtzite structure. Interesting features appear in the XRD spectra of the Y₂O₃-ZnO phase (JSPDS 01- 074-1828) with the indexed of (211), (222), (440), (422), and (136), where the main XRD peaks were comparable to ZnO sharp peaks and approved the ZnO hexagonal phase. A slight shift in 2θ value towards the left for the (002) plane has certainly been examined for the undoped ZnO material. XRD analysis reveals that yttrium doping content considerably affects the ZnO host matrix's crystalline structure and affects the formation of the Y₂O₃ phase, beginning to appear at the higher concentrations of Y³⁺-ions.

Table. 2 illustrated the calculated mean values of the grain size in nanometres, the dislocation density (η) in (nm)², and the lattice strain (ε) for all phases of the synthesized pure ZnO and as well Y₂O₃-ZnO nanostructured materials at different yttrium doping ratios. Here, the crystallinity size (D) of the prepared Y₂O₃-ZnO nanocomposites were evaluated through the following Scherrer’s equation, which was used to analyze the XRD data [29,30]:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta}, \]
Here, $\lambda$ is the X-ray wavelength in the unit of nm, $\theta$ is the diffraction angle in the degree unit, and $\beta$ is the full width at half maximum (FWHM) in the unit of a radian. Respectively, the values of dislocation density ($\eta$) and lattice strain ($\varepsilon$) of $\text{Y}_2\text{O}_3$–$\text{ZnO}$ nanocomposites were calculated from the following equations 2 and 3 [29,30]:

$$\eta = 1/D^2,$$  \hspace{1cm} (2)

$$\varepsilon = \beta \cos \theta / 4,$$  \hspace{1cm} (3)

**Table. 2.**

Calculated values of the grain size, dislocation density, and the lattice strain from XRD analysis, compared with the obtained SEM results for the as-prepared $\text{Y}_2\text{O}_3$–$\text{ZnO}$ nanocomposites at different yttrium concentrations.

| Samples | Phases                  | Mean values of the grain size, (nm) | Mean values of the dislocation, (nm)$^2$ | Mean values of the lattice strain, (nm) from SEM |
|---------|-------------------------|--------------------------------------|------------------------------------------|-----------------------------------------------|
| S0      | Phase 1 ZnO             | 39.759                               | 1.49E-03                                 | 1.22E-03                                      |
|         | Phase 2 carbon          | 18.555                               | 3.20E-03                                 | 1.93E-03                                      | 91.8571                                      |
| S1      | Phase 1 ZnO             | 40.905                               | 1.21E-03                                 | 1.03E-03                                      | 86.0625                                      |
|         | Phase 2 Carbon          | 17.614                               | 3.22E-03                                 | 1.97E-03                                      |
| S2      | phase 1 ZnO             | 33.700                               | 1.65E-03                                 | 1.33E-03                                      | 91.375                                       |
|         | Phase 2 Y$_2$O$_3$      | 13.714                               | 7.30E-03                                 | 2.82E-03                                      |
| S3      | Phase 1 ZnO             | 25.225                               | 2.41E-03                                 | 1.60E-03                                      | 54.88235                                     |
|         | Phase 2 Y$_2$O$_3$      | 27.176                               | 1.35E-03                                 | 1.28E-03                                      |
| S4      | Phase 1 ZnO             | 33.033                               | 1.81E-03                                 | 1.36E-03                                      | 74.9333                                      |
|         | Phase 2 Y$_2$O$_3$      | 16.284                               | 4.29E-03                                 | 2.22E-03                                      |
| S5      | Phase 1 ZnO             | 31.603                               | 1.87E-03                                 | 1.40E-03                                      |
It is noticeable from the data of Table 2 and Fig. 2 that the Y$_2$O$_3$ phase does not occur in low concentration doping and that phase occurs as increasing the dopant concentration. Dislocation density is an imperfection in a crystal associated with the misregister of the lattice in one part of the crystal concerning another part. Moreover, the average values of the crystallite size of all prepared Y$_2$O$_3$–ZnO nanocomposites are varied in the range from 13 nm to 40 nm with the difference in doping. Those obtained values were in great agreement with the published results of the mean grain size (4-40 nm) for yttrium oxide (Y$_2$O$_3$) thin films, which were synthesized and structurally characterized by V. H. Mudavakkat et.al [18].
Fig. 2. XRD patterns of the as-prepared Y$_2$O$_3$–ZnO nanocomposites at different yttrium concentrations.

3.1.2 Scanning Electron Microscopy.

In this study, scanning electron micrographs were applied to investigate the as-prepared Y$_2$O$_3$–ZnO nanocomposites at different yttrium concentrations growth topographies and surface morphology. Fig. 3 showed the SEM images of the studied Y$_2$O$_3$–ZnO nanocomposites at different yttrium doing ratios (i.e., So to S7). The changes in the structural morphology of the pure ZnO and yttrium doped ZnO nanocomposites were directly noticeable.
Fig. 3. SEM images of the as-prepared Y$_2$O$_3$–ZnO nanocomposites at different yttrium concentrations.

The SEM images of the studied Y$_2$O$_3$–ZnO nanocomposites showed mostly a uniform spherical nanoparticles distribution of Y$_2$O$_3$–ZnO nano-samples. It is clear that the yttrium ions create small-sized grains and encourage the crystal nucleation rate, while the trapping of yttrium grains prevents grain development. This issue could be due to the difference in ionic radius between zinc and yttrium [31].

As the yttrium doping concentrations increased, the shape and the size of the nanoparticles were varied. The obtained conclusion of SEM images agreed very well with the morphology characterizations of Y$^{3+}$-doped TiO$_2$ samples, a sol-gel prepared, by X. Niu et.al [21]. The grain sizes from SEM images were agreed well with the XRD results. The results of scanning electron microscopy (SEM) indicated that the crystalline size could be efficiently reduced with yttrium dopants [21].

3.2. Optical properties of Y$_2$O$_3$–ZnO nanocomposites.

3.2.1. Fourier transformation infrared (FT-IR) spectroscopy.

FT-IR spectroscopy was used to investigate the studied Y$_2$O$_3$–ZnO nanostructured samples' vibrational properties because the FT-IR is an extremely sensitive characterization technique and can contribute to XRD findings. The FT-IR spectra illustrate the relation between the light absorbance and the wavenumber within the wavenumber range from 400 cm$^{-1}$ to 7000 cm$^{-1}$ for the Y$_2$O$_3$–ZnO nanostructured at various doping concentrations, as shown in Fig. 4. It can be seen that the yttrium doping affects the shape and the intensity of the leading absorption bands, and the changes in the peak patterns were more noticeable in the Y$_2$O$_3$–ZnO curves than the undoped ZnO.

In the FT-IR spectral range, there is an overlapping of IR lines, which contributions to the phases of both ZnO and Y$_2$O$_3$. There were slight improvements in the optical transparency respecting the undoped ZnO sample in the samples of low yttrium concentrations. As the yttrium doping increased, the transmittance of ZnO-Y$_2$O$_3$ samples showed lower values, which might be due to the higher scattering. Therefore, the highest doping ratios of Y$_2$O$_3$ (i.e., S7) has the highest absorbance, which is in good agreement with the structure morphology results from both XRD, SEM analysis, and other published studies. K.-S. Yu et. al optically characterized pure ZnO and Er: ZnO, and they observed a maximum peak at 363 nm from the
ZnO absorption spectra [28]. The FT-IR results concluded that the absorption intensity increases as the dopant ratio increases, which was in excellent agreement with what was found in this proposed study.

![Absorbance vs Wavenumbers](image)

**Fig. 4.** FT-IR spectra of pure ZnO and Y$_2$O$_3$-ZnO nanocomposites at different yttrium doping ratios.

### 3.2.2. Optical band gap analysis using diffused reflectance spectroscopy.

The optical diffuse reflectance (ODR) measurement is considered a conventional technique applied to gather data on the studied Y$_2$O$_3$-ZnO nanostructured materials' absorption characteristics and their related parameters. The optical bandgaps and the absorption coefficient for organic and inorganic semiconductor materials are two parameters that can be obtained from ODR analysis. Respectively, Figs. (5&6) illustrated the optical diffused reflectance (ODR) and the absorption index ($k$) of the Y$_2$O$_3$-ZnO nanocomposites as a function
of light wavelength ranging from 200 nm to 700 nm. It is clear from Fig. 5 that there are many variations on the diffuse reflectance (DR) of the studied samples in the range between 200 nm and 370 nm. After that, the ODR observed a sharp increase within the wavelength ranges from 370 nm to 410 nm, forming the absorption edge, which related to the determining to the optical bandgap. The optical diffuse reflectance (ODR) spectra displayed almost straight curves with no changes within the wavelength ranges from 410 nm to 700 nm. The absorbed light via the deliberate samples generates the optical absorption bandgaps [32,33].

**Fig. 5.** The optical diffused reflectance (ODR) versus the light wavelength of the studied Y$_2$O$_3$–ZnO nanostructured with different yttrium doping ratios.
Fig. 6. The absorption index ($k$) as a function of the light wavelength of the studied Y$_2$O$_3$–ZnO nanostructured with different yttrium doping ratios.

Fig. 6 demonstrates the studied Y$_2$O$_3$–ZnO nano-samples have slightly small absorption index values ($k$), between $1 \times 10^{-4}$ and $1 \times 10^{-3}$, due to the non-absorbent surface area, and the Y$_2$O$_3$–ZnO nanocomposites are predisposed to the incident light. Correspondingly, this figure shows the maximum absorption values at a light wavelength of around 380 nm, distinctive for electronic transitions from band to the band ($\pi \rightarrow \pi^*$) [34,35]. It was noted that the UV–vis diffuse reflectance measurements are in a great match with the J. Zhao et. al study of Y$^{3+}$-doped Bi$_5$Nb$_3$O$_{15}$, which was synthesized via the sol-gel approach [23]. The obtained results of UV–vis characterization displayed that the absorbance edges of Y$^{3+}$-Bi$_5$Nb$_3$O$_{15}$ noteworthy move to the visible-light range [23].

The optical bandgaps $E_g$ of the synthesized Y$_2$O$_3$–ZnO nanostructured were calculated using Tauc’s model, as in the following equations [36,37]:

\begin{align*}
F(R) &= \frac{(1-R)^2}{2R} = \frac{K}{S}, \\
\alpha &= \frac{F(R)}{t}, \\
(\alpha h \nu)^{1/n} &= A^{1/n}(h \nu - E_g)
\end{align*}
Here, \( F(R) \) represents the material reflectivity using the model of Kubelka-Munk, \( R \) is well-known as the optical diffuse reflectance (ODR) that is immediately recorded using the UV-Vis spectrophotometer, \( K \) is noted as the absorption index, \( S \) is identified as the scattering quantity.

In Eq. (2), \( \alpha \) is recognized as the absorption index, \( t \) is the thickness of the material, and as well as in equation (3), \( h\nu \) is the photon energy of electromagnetic (EM) radiation, \( \nu \) is the frequency, \( h \) is Planck constant, \( A \) is the band tailing factor, and its values ranged from \( 1 \times 10^5 \) to \( 1 \times 10^6 \) cm\(^{-1}\).eV\(^{-1} \) [38]. Therefore, the following formula is used to determine the material direct bandgap as illustrated below:

\[
(\alpha h\nu)^2 = A^2(h\nu - E_g), \quad (n = \frac{1}{2} \text{ for direct allowed transition}) ,
\]

(7)

While the following equation is expressed the material optical indirect bandgap as:

\[
(\alpha h\nu)^{1/2} = A^{1/2}(h\nu - E_g), \quad (n = 2 \text{ for indirect allowed transition}) ,
\]

(8)

where \( E_g \) is the optical bandgap energy of the studied material. Also, in the Eqs. (7&8), the values are either \( n = \frac{1}{2} \) for direct optical bandgaps or \( n = 2 \) for indirect bandgaps. Fig.7 and Fig.8 displayed the plotting of \( (\alpha h\nu)^{1/2} \) and \( (\alpha h\nu)^2 \) respectively as a function of the photon energy \( (h\nu) \) of electromagnetic (EM) radiation for all synthesized \( \text{Y}_2\text{O}_3-\text{ZnO} \) nanostructured samples at various yttrium concentrations. The direct and indirect optical bandgaps have been respectively obtained through the intercept line for the curves in Figs. (7&8), to the \( x \)-axis were \( \alpha^{1/2} \) and \( \alpha^2 \) reaches to zero.
Fig. 7. The optical allowed direct transition \(( \alpha h \nu)^2 \) versus the photon energy \(( h \nu)\) of the studied \( \text{Y}_2\text{O}_3-\text{ZnO} \) nanostructured with different yttrium doping ratios.

![Graph showing \(( \alpha h \nu)^2 \) vs. \(( h \nu)\) for different yttrium doping ratios.]

Fig. 8. Plotting of the optical allowed indirect transition \(( \alpha h \nu)^{1/2} \) versus the photon energy \(( h \nu)\) of the studied \( \text{Y}_2\text{O}_3-\text{ZnO} \) nanostructures with different yttrium doping ratios.

The direct optical bandgap's obtained values for the prepared \( \text{Y}_2\text{O}_3-\text{ZnO} \) nanocomposites range between 3.001 eV and 3.2 eV. On the other hand, the indirect allowed optical transition's determined values ranged from 3.36 eV to 3.25 eV. These attained values of optical bandgaps for the proposed \( \text{Y}_2\text{O}_3\)-doped \( \text{ZnO} \) nanostructures agree well with the published bandgaps for the Fe-doped \( \text{ZnO} \), which was prepared via the sol-gel method by C. Aydin et. al [37]. The calculated bandgap for pure \( \text{ZnO} \) semiconductor was around 3.19 eV, and as increasing Fe dopant concentration to 20% in the \( \text{ZnO} \) host matrix, the value of the energy bandgap decreases to reach 2.75 eV [37]. The optical bandgap is inversely proportional to the dopant concentration since new energy levels will be formed between the conduction and the valence bands as increasing the dopant ratios.

3.2.3 Dielectric properties and AC electrical conductivity of \( \text{Y}_2\text{O}_3-\text{ZnO} \) nanocomposites.

The dielectric function clarifies the material's direct response to electromagnetic radiation (EM) and controls EM waves' propagation behavior in the studied medium. Thus, it is very critical to distinguish the nature and the origin of the dielectric function. For the
considered materials $Y_2O_3$–$ZnO$, the complex dielectric function could be expressed through the following equations [39]:

$$\varepsilon^* (\omega) = \varepsilon_1 (\omega) + i\varepsilon_2 (\omega),$$  \(9\)

and

$$\varepsilon_1 (\omega) = \frac{C \times l}{\varepsilon_0 \times A}, \quad \text{and} \quad \varepsilon_2 (\omega) = \tan\delta \times \varepsilon' \quad \(10\)$$

The part of the dielectric constant here is $\varepsilon_1 (\omega)$, whereas $\varepsilon_2 (\omega)$ is the imaginary component. Furthermore, $\varepsilon_0$ is the permittivity of the free space, $A$ is the electrode area, $\tan\delta$ is the loss tangent, and $C$, $l$, and $Z$ are the capacitance, thickness, and the impedance of the tested sample, respectively. Figs. (9&10) illustrated the variation of both dielectric constant $\varepsilon_1 (\omega)$ and dielectric loss $\varepsilon_2 (\omega)$ versus the incident frequency ranging from $3 \times 10^3$ Hz to $10^7$ Hz. As shown in Fig. 9, in the lower regions of the applied frequency, the dielectric constants decline significantly as the frequency increases (for $\ln \omega$, it is up to 16). Following, the dielectric constants decrease marginally with the rise of frequency. Enhancing the dielectric constants with a frequency reduction discloses that the $Y_2O_3$–$ZnO$ nanostructures demonstrate a large interfacial polarization in the lower frequency region. The dielectric constant values increase and reach the maximum value (about 35) at the higher frequency region. The dielectric constant reduction is faster in the $Y_2O_3$–$ZnO$ nanostructures with higher doping ratios of the yttrium ions. Besides, the dielectric loss values reduce to the lowest possible point and then enlarge once more.
Fig. 9. Illustration of the dielectric constant as a frequency function of the studied Y$_2$O$_3$–ZnO nanostructured with different yttrium doping ratios.

Fig. 10. The dielectric loss plot versus photon frequency of the studied Y$_2$O$_3$–ZnO nanostructured with different yttrium doping ratios.
The values of the dielectric constant are larger than the dielectric loss because of the reliance on the \( k \) and \( n \) values. To demonstrate this, the dielectric constant and loss were small in the long frequency region, in the meanwhile they were high in the lower region, which perfectly agreed with the published conclusion by P. Maji et. al [40]. They investigated the dielectric permittivity of Zn (NO3)\(_2\) samples, where the dielectric constant was observed to decline with the polarization.

To emphasize, particular types of dielectric polarization appear as ionic, interfacial electronic, or dipolar polarization when an external electric field is applied to the Y\(_2\)O\(_3\)-ZnO nanostructured materials. Ionic and electronic polarizations are dominant in the higher frequency range. At a tiny frequency region, the maximum value of the dielectric loss \( \varepsilon_2(\omega) \) could be understood through the interfacial polarization mechanism due to the charge carriers, which establish and limited by defects and grouped in the dielectric medium. At the higher frequency, the \( \varepsilon_\ell(\omega) \) begins to rise, taking the advantages of the dipole oscillation, which can quickly rotate [41].

It is essential to consider the frequency effects on AC electrical conductivity to explain the electronic conduction mechanism of the Y\(_2\)O\(_3\)-ZnO nanostructured materials at different doping ratios of yttrium-ions. To evaluate the AC conductivity of the studied materials, the set of the following equations were applied as [42-45]:

\[
\sigma_{\text{Total,AC}}(\omega) = \frac{I}{ZA},
\]

\[
\sigma_{\text{Total,AC}}(\omega) = \sigma_{\text{DC}}(\omega \to 0) + \sigma_{\text{AC}}(\omega),
\]

\[
\sigma_{\text{AC}}(\omega) = A\omega^s,
\]

Here, the whole AC electrical conductivity is \( \sigma_{\text{Total,AC}}(\omega) \), the impedance is \( Z \), and \( A \) is a constant depends on temperature. Also, respectively, \( \sigma_{\text{DC}}(\omega \to 0) \) and \( \sigma_{\text{AC}}(\omega) \) are the DC and AC electrical conductivities, where the angular frequency is \( \omega \) and the frequency exponent is donated as \( (s) \). Semiconductor materials represent semiconducting compounds that display values of AC electrical conductivity in the range between \( 10^{-8} \) and \( 10^4 \ \Omega^{-1}.cm^{-1} \) [46]. The calculated values of \( \ln(\sigma_{\text{AC}}(\omega)) \) were illustrated in Fig.11 versus \( \ln(\omega) \) for the tested Y\(_2\)O\(_3\)-ZnO nanocomposites. The AC electrical conductivity values increase linearly with the incident frequency and with increasing the yttrium concentration in the ZnO host matrix materials.
room temperature, the frequency exponent ($s$) values were calculated from the slope of the obtained linear cures in the previous relation, as plotted in Fig. 11.

In this present study, $s$ values were estimated to be almost around one (0.92) [42]. Commonly, the AC electric conductivity depends strongly on the photon frequency for either disarranged or structured, and for organic or inorganic materials [46]. Eq. 13 suggests that AC electrical conductivity plays a significant role in the interaction of many-body, which clarify the universal behavior of the power-law. The frequency exponent ($s$) is a vital parameter that illustrates the multi interaction between the material impurities and charge carriers, where the ($s$) value depends not only on the applied frequency but also on the temperature, where its value ranges from zero to one; it is equal to one for standard Debye type media. Furthermore, the ($s$) frequency parameter is correlated to either charge carriers or inessential electrical dipoles resulting from impurities. For conducting disordered mediums, the values of the frequency exponent range between 0.6 to 0.8, and it was around one for highly disordered dielectric mediums [47,48].

![Fig. 11. AC electrical conductivity as a function of the applied frequency function of the studied Y$_2$O$_3$–ZnO nanostructured with different yttrium doping ratios.](image)

3.3. Electrical varistor applications of Y$_2$O$_3$-doped ZnO Nanocomposites.

Figs. 12(a–h) displayed the voltage-current ($V$–$I$) curves of the ZnO varistor ceramics with different yttrium contents. The curves show that the conduction characteristics are divided into two zones: a high impedance linear region below the knee-point voltage and a low
impedance nonlinear region above the knee point voltage. Nahm C. W. [49] studied the effect of sintering temperature on nonlinear electrical properties and stability against the DC accelerated aging stress of (CoO, Cr₂O₃, La₂O₃)-doped ZnO-Pr₆O₁₁-based varistors. It is known that the sharper the knee-point of the curves between the linear region and the breakdown field is, the better the nonlinear characteristic is, in other words, the threshold voltage $V_{ss}$, the nonlinear coefficient $\alpha$, the grain boundary resistance $R_{gb}$ from the Cole-Cole impedance measurements and the leakage current $I_R$ is determined by the $V-I$ curves.

Fig. 12(a-h). $V-I$ characteristics of the studied Y₂O₃–ZnO nanostructured with different yttrium doping ratios.

The AC impedance parameters have been analyzed the complex impedance ($Z^*=Z'+iZ''$) by the following functions [50]:

$$Z' = \frac{1}{\omega c_0} \left[ \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \right]; \quad Z'' = \frac{1}{\omega c_0} \left[ \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \right],$$

where $\omega$ is the chosen angular frequency, $(\varepsilon', \varepsilon'' = \varepsilon' \tan \delta)$ are the real and imaginary portions of the dielectric permittivity, and $c_0$ is the vacuum capacitance. The real and the imaginary components of this impedance were calculated as follows [50]:
The average square-method used for simulating the resistance $R_b$, the CPE value indicated by $Q$, and the parameter $c$ through the difference between experimental and theoretical results. The impedance of CPE is $Z_{CPE} = \frac{1}{A_0(i\omega)^c}$.

Figs. 13 (a&b) depicts the angular frequency-dependent of the complex impedance of the synthesized samples' real and imaginary parts with the various yttrium's compositions. The observed value of real impedance decreases gradually with an increase in both angular frequency and yttrium compositions. This decrease in real part impedance plots indicates an increase in the AC conductivity with angular frequency. Simultaneously, a quasi-peak is also visible in the imaginary part of the impedance plots for the sample at the (S6) yttrium composition, which indicates the relaxation process, which is a characteristic of the varistor semiconductors.

Fig. 13(c) showed the Nyquist diagram of studied samples based on varistor ceramics. It is noticed that the tested-ceramic varistor systems have a quasi-semicircle, which is related to the grain boundary contribution. Also, with increasing the yttrium doping, it is noticeable that it produces a decrease in the high-frequency quasi-semicircle and becoming almost imperceptible for the studied ceramic varistor systems. This change in high-frequency impedance data results from the increase of the ZnO matrix's charge carriers due to incorporating yttrium contents. In this way, the equivalent circuit model using the Eqs. (15&16) were used to determine the grain boundary resistance ($R_{gb}$) and capacitance ($Q$) in parallel.
So ZnO
S1 Y
S2 Y
S3 Y
S4 Y
S5 Y
S6 Y
S7 Y

\( \mathcal{Z}'(\omega) \)

\( \mathcal{Z}''(\omega) \)

(a) 

(b)
Figs. 13(a-c). (a) Real, (b) imaginary parts, and (c) nyquist diagram plots (the line represents the theoretical Cole-Cole fitting) of the studied $Y_2O_3$–ZnO nanostructured with different yttrium doping ratios.

Fig. 14 (a) shows the variation of the obtained grain boundary capacitance from the fitted impedance data vs. the yttrium doping levels of ZnO ceramic varistors. When yttrium composition is increased, it is observed that the grain boundary capacitance progressively decreases and remains increases above the composition up to (S5) yttrium content, which is related to the decrease in the defect density after the release of trapped charge carriers. The $V-I$ characteristics exhibited for the tested samples based on varistor ceramics consist predominantly of pre-breakdown, breakdown, and upturn regions [51].
Figs. 14 (a-c). Influence of yttrium contents on $V-I$ fitted parameters of the studied $Y_2O_3-ZnO$ nanostructured with different yttrium doping ratios.

The varistor action takes place in the breakdown region. In this region, the applied voltage is a highly nonlinear function of the current and can be described by the empirical law [52]:

$$I = KV^\alpha,$$

where $V$ is the applied voltage, $I$ is current, $K$ is a constant depending on the geometry and manufacturing process, and $\alpha$ is the nonlinear coefficient. The value of nonlinear coefficient $\alpha$ is obtained from the inverse of the $\ln V-\ln I$ curves' slope at any voltage value, as shown in Fig.15. The effect of yttrium doping contents on the nonlinear coefficient of $ZnO$ based ceramic varistors is very complicated. With the increase of the yttrium's level doping, an increase in the nonlinear coefficient $\alpha$ is observed from (So) to (S2) yttrium contents, producing more grain
boundaries in the specimen (see Fig. 14(b)). A graphical description of the nonlinear coefficient $\alpha$ and the threshold voltage $V_{ss}$ according to ZnO varistors' yttrium contents is illustrated in Fig. 14 (c).

![Graphical description](image)

**Fig. 15.** Illustration of the linear relation between $\ln I$ and $\ln V$ of the studied Y$_2$O$_3$–ZnO nanostructured with different yttrium doping ratios.

The correlation between the composition and electrical characteristics leads to the following that there is no significant increase in the threshold voltage. An increase of its values is observed for the addition of (S5) yttrium content sample. The substituting reaction of yttrium materials is responsible for improving the nonlinear coefficient influencing the potential barrier's characteristics formed on the grain boundary. From (S2) further to 0. (S4) with increasing the yttrium contents, the nonlinear coefficient $\alpha$ decreased, which attributed to the increasing of the insulator layer's width so-called tunneling process as a result was reported by Levinson et al. [53]. Another reason for decreasing $\alpha$ in specimens with 0.01 (S2), (S3), and (S4) with increasing the yttrium doping levels are reducing the microstructure's homogeneity.

The high value of $\alpha$ of the 5 (S7) yttrium doping level signifies a better protective function of the ceramic varistors. It was possible to obtain only the grain boundary resistance $R_{gb}$ of the investigated varistor since the impedance spectroscopy technique allows the separation of the resistive contribution from the grain boundary and the trap level. The grain boundary resistance $R_{gb}$ obtained from the relevant impedance data, and the leakage current for the studied ceramic
varistor systems as represented in Fig. 14(b). The leakage current results from most of the electrons passing over the Schottky barrier at the grain boundaries. With increasing the yttrium contents from (S3) to (S7) with increasing yttrium contents, the leakage current is very low and only shows little change. It is believed that the decrease in the leakage current can be attributed to an increase in the average energy needed for electrons to overcome the Schottky barrier and the homogeneous distribution in the ceramic varistor samples. As a result, it is necessary to ensure a high level of practical barriers to the grain boundaries, increase its resistance, and avoid leakage currents to achieve higher values with a nonlinear coefficient. Reducing the leakage current of Y2O3–ZnO ceramic-based varistors can make these materials an excellent candidate in power systems.

3.4. Photocatalytic degradation of color and colorless using Y2O3-doped ZnO Nanocomposites.

3.4.1. Kinetic Studies.

The concentration of phenol (Ph), Methylene Blue (MB), and Rhodamine B (RhB) and decline with visible light irradiation using the only ZnO, and Y2O3-doped ZnO nanoparticles as shown in Figs. 16 (a-c). The photocatalytic degradation % of the synthesized ZnO is reached 91%, 94%, and 97% within 90 min for phenol, MB, and RhB, respectively. The incorporation of Y3+-ions has improved the ZnO photocatalytic performance. Figs. 17 (a-c) showed that 98% degradation of phenol, MB, and RhB solutions were obtained after 40 minutes using 1% Y2O3-doped ZnO (S5) under visible illumination. This reaction obeys the Langmuir–Hinshel model that is symbolized as:

\[
\ln\left(\frac{C_t}{C_o}\right) \rightarrow k_t, \quad (18)
\]

The initial concentration \(C_o\), concentration is \(C_t\) at time \(t\) with constant rate \(k\).

The kinetic rate is attained through a plot of Ph, MB, and RhB concentration versus time of exposure, as shown in Figs. 18 (a-d). Table. 3 also showed that the rate constant was affected by yttrium dopant concentration. The kinetic rate using pure ZnO is 0.00262, 0.00112, and 0.00178 min\(^{-1}\) for phenol, MB, and RhB solutions. It was 0.01079, 0.00887, and 0.01061 min\(^{-1}\) of phenol, MB, and RhB solution, respectively, using 1% Y2O3-doped ZnO. These findings reveal that Y2O3-doped ZnO has greater photocatalytic activity than pure ZnO. As the number of oxygen vacancies and surface defects increases, electron-hole regeneration, and charge trapping efficiency will be high. As the photocatalytic operation of ZnO-ion doping is boosted, there is no distinct phase at the lower concentration of Y3+-ions as the Y-dissolution
will occur in the ZnO lattice [54]. On the other side, Y$^{3+}$-distorts the crystallinity of ZnO at high concentrations of more than 1% [55]. Photocatalytic activity of the tested samples is increasing by doping as shown in Fig. 17. Hemalatha et al. revealed the increasing photocatalytic efficiency of Y-doped ZnO because the electron-holes produced are weakly recombined, leading to subsequent growth in activity centers [56]. Such factors help to improve the operation of photocatalysis.

Fig. 16. Concentration vs. Time for the photodegradation of a) Phenol, b) MB, and dye c) RhB dye of Y$_2$O$_3$-ZnO nanocomposites with different concentrations of Y$^{3+}$-ions under visible light.
Figs. 17(a-c). % degradation vs. time for photodegradation of a) Phenol, b) MB dye, and c) RhB dye of $Y_2O_3$-ZnO nanocomposites with different concentrations of $Y^{3+}$-ions under visible light.
Figs. 18(a-c). Plots of $lnC/C_0$ vs. Time for photodegradation of a) Phenol, b) MB dye, and c) RhB dye of Y$_2$O$_3$-ZnO nanocomposites with different concentrations of Y$^{3+}$-ions under visible light.

Table 3.

| Samples | $K$, min$^{-1}$ | Phenol | MB | RhB |
|---------|----------------|--------|----|-----|
| So      |                | 0.0026 | 0.0011 | 0.0018 |
| S1 Y    |                | 0.0014 | 0.0018 | 0.00135 |
| S2 Y    |                | 0.0024 | 0.0030 | 0.0019 |
| S3 Y    |                | 0.0049 | 0.0071 | 0.0028 |
| S4 Y    |                | 0.0090 | 0.0065 | 0.0100 |
| S5 Y    |                | 0.0108 | 0.0089 | 0.0106 |
| S6 Y    |                | 0.0064 | 0.0014 | 0.0043 |
| S7 Y    |                | 0.0046 | 0.0016 | 0.0019 |

3.4.2 Comparative Study Between Rare Earth Doped ZnO Photocatalysts

For enhancing the properties of ZnO nanostructures, we have to add impurity or defect at the time of synthesis of nanoparticles. The addition of foreign atoms or impurities (doping) to a compound by creating a defect that can enhance its physical properties. Here, doping is required to modify the physical properties of nanostructures [57,28]. In ZnO nanostructures, there are two types of defects: intrinsic defects and extrinsic defects. The intrinsic or native point defects concerned with ZnO are the interstitial of oxygen, vacancies, and zinc at a bonding between zinc and oxygen. The oxygen vacancies and zinc interstitials are the dominant native or relevant donor. And in this, the formation of donor levels may be probable when the band of Fermi energy becomes equivalent to the valence band [58]. Extrinsic defects are classified into two types: n- and p- types. The n-type ZnO is obtained via Group (III) doping elements like Al, In, Ga, etc., transition metal elements as Pb, Mn, Fe, Ni, Co, [59–61] and rare earth metals as Eu, Y, Gd, [61–63], etc. These elements incorporate on the zinc lattice site and become shallower effective mass donors. The free electron concentration of n-type is obtained...
via hydrogen support. The p-type ZnO construction has proven very hard and has been a bottleneck in producing ZnO-based devices for functional and industrial applications due to the asymmetrical limitations in doping in ZnO nanostructures [64]. For n-type doping of ZnO, by rare earth elements', the optical and high conductivity features, can be considered as dopants [65,59-61]. In-display applications involving photocatalytic degradation of contaminants, rare-earth metals doping to decrease the electron-hole recombination is continued to be of interest. This modification displays less thermal emission quenching than pure semiconductors. The rare-earth elements such as Tb-doped ZnO as a green luminescence and Eu-doped ZnO's as red luminescence suggest that such materials may be useful also in optoelectronic applications [66,67]. Korake et al. [68] studied the doped ZnO as a photocatalyst using the assisted microwave process with a range of Eu contents.

By studying the efficiency of degradation, it was found to have a critical role in photocatalytic operation when preparing Y doped ZnO nanoparticles. Doping of ZnO with rare-earth has a great influence on ZnO’s photocatalytic efficiency [69–71]. The photocatalytic activity of Eu-doped ZnO nanorods has been evaluated for methyl orange degradation. The photodegradation efficiency has been enhanced up to 91% within 180 min by increasing catalyst loading under UVA-radiation (at 365 nm) [69]. Furthermore, the Gd-doped ZnO NPs showed ferromagnetism, which can be applied in spintronic applications. Niaz et al. used the sol-gel process to synthesize ZnO and Gd-doped ZnO for the Gd$^{3+}$ impact on structural and physical characteristics of ZnO. These particles are wurtzite of 14.46 nm average crystallite size and 76 nm grain size [72]. Moreover, Gd-doping significantly impacts the particle size, and Gd-doping ZnO has a much smaller particle size than ZnO. In the photocatalytic process, the aqueous solutions of methyl blue (MB) under the sunlight are applied for degradation by ZnO and Gd-doped ZnO nanocrystalline powders. These results showed that an increase in photocatalytic activity by increasing Gd-loading [73].

The photocatalytic behavior of zinc oxides was improved also by neodymium doping as proved by Jheng et al. who studied their photocatalytic efficiency on Methyl orange solution degradation [74,75]. The photocatalytic operation is enhanced upon increase the doping of Nd into ZnO to an ideal level of 3% of doping [75–77]. An increase in electron-hole pairings induced defects due to the presence of Nd which induced the apparent light emissions to increase photocatalytic performance. In the case of controlling electrons - hole paired through adding intrinsic defects by Nd doping [78,79], the enhanced photocatalytic behavior is obtained [80,81]. Yayapao et al. [80] also demonstrated their photocatalytic activity of methylene blue
through using Nd-doped ZnO under UV-illumination. Their research showed 1% Nd-doped ZnO with 2.5 times the pure ZnO with 92% for 300 minutes. Ce-doped ZnO-NPs have been synthesized and observed by Kumear et al. [82] to aid a solution combustion process. In only 70 minutes, the photocatalytic degradation was achieved by reaching an optimum Ce-doping concentration of up to 99.5%. The improved photo-catalytical efficiency in the Ce-dopped ZnO could be attributed to an expansion of ZnO’s bandgap energy versus ZnO only, resulting in an increase of electron-hole stability and leading to the photocatalytic capacity.

Thus, changes in ZnO-nanostructures, by doping-transition metals or rare-earth metals, are commonly demonstrated to enhance their properties [62-64]. Thus, ZnO’s properties depend on their morphology, crystalline structure surface defects, and size. Once modified by incorporating dopant ions, the ZnO NPs photocatalytic performance has been increased and enhanced. In ZnO NPs, the doping of metal ions will result in such effects as improvement/decline of fluorescence and regulation of surface deficiency concentration [59].

Additionally, the photodegradation of organic compounds by modified doped-ZnO with materials that contain higher oxygen defects is outstanding. The ferromagnetic characteristics of rare-earth-doped ZnO are determined by the energy level or charge transfer between states [67].

### 3.4.3 Photodegradation Mechanism

The proposed Y₂O₃-doped ZnO photocatalytic mechanism is visible irradiation is presented via scheme 1. As light is emitted, holes and electrons are formed on the Y₂O₃-doped ZnO surface. The electrons excited from the valence to the conducting band contribute to hole creation. The electron-hole recombination occurred, causing the heat release. Afterward, the excited electrons react with the adsorbed oxygen, leading to O₂⁺, while the valence band hole with OH⁻ or H₂O molecules leads to the hydroxyl radical’s formation [83,84]. The HO₂⁺ is then generated due to the conjunction between H⁺ and O₂⁺. The organic molecules are immediately oxidized by these OH⁺, HO₂⁺, and O₂⁺ reactive species. The Y-doped ZnO possesses reliable photocatalytic degradation efficiencies because the Y³⁺-serves as electron scavengers to react with superoxides to prevent the electron-hole's recombination.
Scheme 1. Mechanism of photodegradation of Phenol, MB dye, and RhB dye using Y$_2$O$_3$-ZnO nanocomposites with different concentrations under visible light.

3.4.5 Reusability Studies

The recovered catalyst 1g of Y (S5) doped ZnO was reused for photodegradation of phenol, MB, and RhB. This process has been repeated for 4 cycles. The findings are represented in Figs. 19 (a-d). The reusability of the catalysts occurs as the photocatalytic efficiency of the catalysts, especially ZnO, decreases during re-use due to photo-corrosion [85,86]. Since 1 g Y doped ZnO ~ 98% activity (S5) didn’t decrease significantly after four cycles, it was confirmed that Y$^{3+}$-doping improved the stability and anti-photo-corrosive nature of ZnO. Particularly ZnO, photocatalytic efficiency decreases because of photo-corrosion throughout reusing [85,86]. On the contrary, 1g Y$_2$O$_3$ doped ZnO -98% (S5) was no longer significantly reduced after 4 cycles by the action of 1 g of Y$^{3+}$ (S5). These data revealed the stability and anti-photo-corrosive quality of ZnO by Y$_2$O$_3$ doping.
Fig. 19. Recycling for the photodegradation of a) Phenol, b) MB dye, and c) RhB dye in the presence of 1g Y$_2$O$_3$-doped ZnO nanocomposites under visible light.

Table 4.
The rate of photodegradation and comparative analysis of different phenols and dyes using ZnO doped with rare-earth elements.
| Samples                  | Pollutant         | Method of synthesis | Synthesis conditions                                      | % of degradation | Photocatalytic conditions | Refs.       |
|-------------------------|-------------------|---------------------|-----------------------------------------------------------|-----------------|---------------------------|-------------|
| 1g Y-doped ZnO (S5)     | Phenol            | solution combustion | heated at 600 °C for 2 hours then left to dry at room   | 98.5%           | under a Visible light     | Present work|
|                         |                   | method              | temperature                                               |                 | source within 40 min      |             |
| 1 g Y-doped ZnO (S5)    | Methylen e Blue  | solution combustion | heated at 600 °C for 2 hours then left to dry at room   | 98.36%          | under a Visible light     | Present work|
|                         |                   | method              | temperature                                               |                 | source within 40 min      |             |
| 1g Y-doped ZnO (S5)     | Rhodamine B       | solution combustion | heated at 600 °C for 2 hours then left to dry at room   | 89.5%           | under a Visible light     | Present work|
|                         |                   | method              | temperature                                               |                 | source within 40 min      |             |
| 0.2 % Eu-doped ZnO      | methyl orange     | Co-precipitation    | Stirring for 4 hrs. at 60 °C, dried at 200 C             | 91%             | under UV light (365 nm)   | [87]        |
|                         |                   | method              |                                                           |                 | within 180 min            |             |
| Ag-doped ZnO            | M-violet          | coprecipitation     | 4.5 × 10⁻⁴ M of dye concentration with 1 g/l of catalyst load | 83%             | under sunlight for 3 hours| [88]        |
4. Conclusion

It is found that using the combustion method is a very reasonable, low cost, effective, and eco-friendly approach for successful preparing nano-ZnO doped with yttrium element of different concentrations. Both X-ray diffraction (XRD) and scanning electron microscopy (SEM) was applied to investigate the structural morphology of Y$_2$O$_3$-ZnO nanocomposites', which revealed an enhancement in the grain size as the yttrium doping ratio increased. Besides, UV-Vis diffuse reflectance spectroscopy (DR) and Fourier transformation Infrared spectroscopy (FT-IR) were used to examine the optical properties of the Y$_2$O$_3$-ZnO nanostructured materials. The optical energy bandgaps of the Y$_2$O$_3$-ZnO samples were between 3.001 eV and 3.2 eV, indicating the catalyst's absorption edge depends on ZnO's structure. Moreover, the electrical behaviors of the as-prepared ZnO doped with the yttrium at the nanoscale for ceramic varistors were investigated through the current-voltage measurements and dielectric analysis. ZnO material's photocatalytic properties as a host matrix can be...
improved via the doping process by a reasonable amount of yttrium. The study reveals that photocatalytic degradation performance enhances as yttrium load increases. This indicating the promising photocatalytic performance of synthesized $\text{Y}_2\text{O}_3$-doped ZnO towards phenol and organic dyes degradation. The synthesis of $\text{Y}_2\text{O}_3$-ZnO nanostructures, smart, and multifunctional materials are promising candidates for wide-scale technological, environmental, and biomedical applications, such as ceramic varistors and photocatalysis.

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**Competing interests:**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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Figures

Figure 1

Synthesis procedures of ZnO nanoparticles with different doping ratios of yttrium (Y) rare earth element.
Figure 2
XRD patterns of the as-prepared Y2O3–ZnO nanocomposites at different yttrium concentrations.

Figure 3
SEM images of the as-prepared Y2O3–ZnO nanocomposites at different yttrium concentrations.
Figure 4

FT-IR spectra of pure ZnO and Y2O3-ZnO nanocomposites at different yttrium doping ratios.
Figure 5

The optical diffused reflectance (ODR) versus the light wavelength of the studied Y2O3–ZnO nanostructured with different yttrium doping ratios.

Figure 6
The absorption index (k) as a function of the light wavelength of the studied Y2O3–ZnO nanostructured with different yttrium doping ratios.

Figure 7

The optical allowed direct transition \((\alpha h \nu)^2\) versus the photon energy \((h \nu)\) of the studied Y2O3–ZnO nanostructured with different yttrium doping ratios.
Figure 8

Plotting of the optical allowed indirect transition $(ahv)^{1/2}$ versus the photon energy $(hv)$ of the studied Y2O3–ZnO nanostructures with different yttrium doping ratios.

Figure 9

Illustration of the dielectric constant as a frequency function of the studied Y2O3–ZnO nanostructured with different yttrium doping ratios.
The dielectric loss plot versus photon frequency of the studied Y2O3–ZnO nanostructured with different yttrium doping ratios.

Figure 10

Figure 11
AC electrical conductivity as a function of the applied frequency function of the studied Y2O3–ZnO nanostructured with different yttrium doping ratios.

Figure 12

V-I characteristics of the studied Y2O3–ZnO nanostructured with different yttrium doping ratios.
Figure 13

(a) Real, (b) imaginary parts, and (c) nyquist diagram plots (the line represents the theoretical Cole-Cole fitting) of the studied Y2O3–ZnO nanostructured with different yttrium doping ratios.
Figure 14

(a-c). Influence of yttrium contents on V–I fitted parameters of the studied Y2O3–ZnO nanostructured with different yttrium doping ratios.
Figure 15

Illustration of the linear relation between lnI and ln V of the studied Y2O3–ZnO nanostructured with different yttrium doping ratios.
Figure 16

Concentration vs. Time for the photodegradation of a) Phenol, b) MB, and dye c) RhB dye of Y2O3-ZnO nanocomposites with different concentrations of Y3+-ions under visible light.
Figure 17

% degradation vs. time for photodegradation of a) Phenol, b) MB dye, and c) RhB dye of Y2O3-ZnO nanocomposites with different concentrations of Y3+ ions under visible light.
Figure 18

Plots of ln(Ct/Co) vs. Time for photodegradation of a) Phenol, b) MB dye, and c) RhB dye of Y2O3-ZnO nanocomposites with different concentrations of Y3+-ions under visible light.
Figure 19

Recycling for the photodegradation of a) Phenol, b) MB dye, and c) RhB dye in the presence of 1g Y2O3-doped ZnO nanocomposites under visible light.

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