TiO$_2$–ZnO composites fabricated via sonication assisted with gelatin for potential use in Rhodamine B degradation

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ABSTRACT

Herewith we report a facile synthesis of zinc oxide doped with (5, 10, 15 and 20 wt%) titanium oxide nanocomposites in gelatin under ultra-sonication. The X-ray diffraction (XRD) data revealed the ZnO formation in addition to a rutile TiO$_2$ phase. The ZnO phase size decreased, while the rutile TiO$_2$ phase increased with a TiO$_2$ loading increment. The scanning electron microscopy (SEM) displayed a combination of spherical and hexagonal particles with 60–80 nm size distribution. The photocatalytic activity of the prepared nanostructures was assisted using Rhodamine B dye, where they showed enhanced photodegradation competence under visible light irradiation. The kinetics of photodegradation followed the first-order kinetics with the 20 wt% sample showing the maximum activity. The mechanistic investigation revealed the dominance of $h^+$ and $\cdot$O$_2^-$ species during the dye photodegradation. The results indicate the potential application of such gelatin-stabilized nanostructures for dye illumination from aqueous solutions under sunlight.

1 Introduction

Polymer stabilized nanocomposites are recently becoming of prime research interests by virtue of their value added benefits such as improved stabilizing, fictionalization, magnetic, thermal and mechanical qualities [1–3]. Being abundant, hydrophilic, biocompatible and biodegradable natural biopolymers are favored over the synthetic ones [4]. Gelatin obtained by denaturation of collagen is a form of a single sequence of amino acids. It is warm water soluble and gels when its concentration exceeds 1 wt% [2]. It has the ability to coordinate with metal ions due to the polar groups in its structure [5]. Gelatin was dissolved in the sol form and used as a structure-guiding agent to tailor the ZnO nanostructures morphology. For instance, ZnO nano-plates were developed from ZnO nanoparticles using...
gelatin [6], while Bauermann et al. fabricated hexagonal ZnO plates in a gelatin matrix [5]. Gelatin was employed to stabilize CdTe/CdS/ZnS (CSSG) core/double shell quantum dots (QDs) to advance their biocompatibility [7], copper NPs [8] and ZnO NPs [9].

The n-type and large bandgap semiconductors like ZnO, TiO$_2$ and SnO$_2$ have triggered the researchers curiosity persuading them to explore their properties and applications [10, 11]. To benefit from the ZnO flexibility in synthesis and morphologies and the stability of TiO$_2$, a coupling of TiO$_2$ and ZnO nanoparticles is a convenient approach to induce substantial effects on the morphologies, porosity, electronic and photo-electrochemical characteristics [12]. Morphological structures, crystallite size and crystallographic patterns greatly influence the properties of TiO$_2$–ZnO oxide binary systems [13, 14]. Due to the fact that the ZnO bandgap is marginally more negative than TiO$_2$ bandgap, the formation of TiO$_2$–ZnO oxide binary system facilitates the promotion of the ZnO conduction band electrons to the TiO$_2$ leading to a better charge carriers (electrons and holes) separation [15, 16]. The catalytic activity of TiO$_2$ was enhanced by adding ZnO [17] where the electron and hole transfer between their conduction and valence bands leads to a well separation of photogenerated charge carriers [17, 18]. Thus, coupling the two oxides into an integrated structure significantly enhances their properties and performance. For instance, TiO$_2$–ZnO oxide hybrids showed complete degradation of C.I. Basic Blue 9 within 25 min [19], and (TiO$_2$)$_{1-x}$–(ZnO)$_x$: thin films degrade MB [20] and TiO$_2$–ZnO nanofibers of Rhodamine B (RhB) under irradiation with 420 nm visible [21]. ZnO/TiO$_2$ nanocomposites were employed as photo-anode electrode for solid-state dye-sensitized solar cells that showed 6.5% conversion efficiency as explained synergetic effect between ZnO and TiO$_2$, which upsurges dye absorption, electron transport and electron lifetime [22]. Via dip coating, TiO$_2$ was incorporated into ZnO nanorods film and the obtained composite was found to establish a maximum photocurrent density of 19.78 mA/cm$^2$ with ~ 2.9% photoconversion efficiency under UV illumination and 14.75 mA/cm$^2$ - photocurrent density with photoconversion efficiency ~ 4.3% solar illumination [23]. The authors attributed that to Ti element inside TiO$_2$–ZnO nanorods film, which has played the role of a mediator to trap the photo-induced electrons and delay the recombination of charge carriers. Previous reported methods of ZnO–TiO$_2$ nanostructures synthesis included magnetron sputtering [24, 25], powders thermal processing [26], sol–gel [27, 28], chemical vapor deposition [29] and homogeneous hydrolysis [30]. As a gelling agent, gelatin can help size control and dispersion of nanostructures owing to its enlargement, while calcination can provide enduring stability by inhibiting particle agglomeration [31]. In addition, gelatin water solubility and binding with metal ions have been employed as a binder and gelling agent for porous ceramic shaping [32].

In this study, gelatin-stabilized TiO$_2$–ZnO photocnomposites were synthesized via ultrasonic energy. A titanium oxide rutile phase has immerged and the morphology has altered as a result of doping. The optical properties and the employment of the photocnomposites to decolorize the RhB dye were investigated and the kinetics and mechanism of the process were probed.

2 Experimental methods

2.1 Preparation of TiO$_2$–ZnO photocnomposites

For the synthesis of TiO$_2$–ZnO photocnomposites at different TiO$_2$ nanoparticle contents (5, 10, 15 and 20 wt%), gelatin and ultra-sonication process was employed. The required amounts of TiO$_2$ and fixed amount of ZnO nanoparticles were dispersed in 100 ml of absolute ethanol and the mixture sonicated at room temperature for 30 min until a milky solution formed. The mixture obtained was added gradually to the 100 ml of a hot solution of gelatin under vigorous stirring. Next, the mixture was sonicated for 1 h at 0°C and oven dried at 120°C for 6 h. The dried samples were calcined at 650°C in air atmosphere for 1 h using muffle furnace. The samples were labeled as (TZO1, TZO2, TZO3 and TZO4).

2.2 Characterization of the photocnomposites

The crystalline structure of the powders was investigated by X-ray powder diffraction (XRD) using Bruker high-resolution diffractometer equipped with
Cu-Kα radiation (1.5418 Å), operating at 40 kV and 40 mA. Morphological images were recorded by field emission scanning electron microscopy (FE-SEM) using JEOL, JEM-2100. The Brunauer–Emmett–Teller (BET) specific surface area was assessed via N₂ adsorption–desorption isotherms by employed ASAP 2020 Micromeritics device. The optical properties were determined by means of diffuse reflectance spectroscopy (DRS) using JASECO V-770 spectrophotometer in the wavelength range 300–800 nm. Vibration and bending modes of the all samples were documented by means of Fourier Transform Infrared (FTIR) spectra (JASCO FI-IR 460 spectrometer) in the range 400–4000 cm⁻¹.

2.3 Photocatalytic efficacy of fabricated photocomposites

The photocatalytic competence of the as-fabricated photocomposites was assessed by monitoring the photodegradation of Rhodamine B dye under visible light illumination. In a typical test, 50 mg of the photocatalyst powder was dispersed in 100 ml aqueous solution of RhB dye concentration = 20 mg/L. Prior to the light illumination, the photocatalyst and the dye solution mixture was strongly magnetically stirred (400 rotation/min) in full darkness for 30 min under the ambient condition to achieve an adsorption/desorption equilibrium of dye on the photocatalyst surface. Then 5 ml of the mixture solution was withdrawn as an initial concentration (Cₒ) and exposed to visible light irradiation (OSRAM lamp 58 IM/W). Following the exposure to visible light, 5 ml suspension was withdrawn at different time intervals, centrifuged (5000 rpm for 10 min) to remove suspended photocatalyst and the absorbance was measured. Temporal concentration variations of RhB were measured via the change in the maximal spectra (λ_max = 525 nm) of the dye.

2.4 Radical scavenger experiment

To probe the photocatalytic mechanistic activity of the photocomposites, the effective reactive species (holes and radicals) were identified using radical scavenging test method. In this method, the valence band holes (h⁺), conduction band electrons (e⁻), hydroxyl radical (·OH) and superoxide radical (·O₂⁻) were monitored by adding EDTA (h⁺) [33], silver nitrate (e⁻) [34], isopropanol (·OH) [33] and ascorbic acid (·O₂⁻) [34] to the reaction solution, individually, through the process of photocatalytic degradation of RhB dye. In a typical procedure, 50 mg of photocomposite and 10 mM of radical scavengers were placed in 100 ml of 20 mg/L RhB dye solution; then the mixture was illuminated utilizing the visible light at the same time after adsorption equilibrium. Ultimately, the degradation rate of the dye was calculated to highlight the main role of active species.

3 Results and discussion

3.1 XRD analysis

The XRD patterns of the TiO₂–ZnO photocomposites sketched in Fig. 1a reveal sharp and distinct diffraction peaks with relative high intensity and broadening, as a clue of the development of nano-crystalline structure of high crystallinity [35]. The peaks at 2θ = 31°, 34°, 36°, 47°, 56°, 62°, 66°, 68° and 69° that can be assigned to the (100), (002), (101), (102),(110), (103), (200), (112), (201), (004) and (202) planes of the wurtzite hexagonal ZnO structure in accordance with JCPDS card No. 36-1451 can be observed. In addition, extra peaks correspond to 2θ = 28°, 35°, 42°, 53° and 62° delineating the (110), (101), (200), (211) and (310) planes of the TiO₂ rutile phase in agreement with JCPDS card No. 21-1276 [36–38]. It can be noticed that the intensities of the peaks corresponding to the rutile phase increase proportional to the TiO₂ ratio in the sample (Fig. 1b) which is an expected consequence of the ZnO % lowering in the precursor powders [39]. A noticeable decrease in the FWHM with increase of Ti loading is an indication of improved crystallinity [40]. The Scherrer equation [41] was used to compute the crystallite size of the photocomposites:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

where β is the full width at half maximum (FWHM) of the XRD peak (in radians), the constant, k value of 0.90, θ is diffraction angle and λ is the wavelength of the Cu-Kα (1.5418 Å). The crystallite size for ZnO wurtzite was estimated taking the most intense peak (101), while the peak (110) was used for the TiO₂ rutile phase. The crystallite size of the wurtzite ZnO [D(ω)] exhibits a decrease with the addition of more TiO₂ [42], while a reverse trend is shown by the rutile phase crystallite size [D(φ)]. From the XRD findings,
a successful synthesis of nanocomposites comprising rutile TiO$_2$ and wurtzite ZnO can be confirmed. The d-spacing, lattice parameters and the unit cell volumes were estimated by the expressions:

$$d = \frac{\lambda}{2\sin \theta}$$  
$$a = \frac{\lambda}{\sqrt{3\sin \theta}}$$ and $$c = \frac{\lambda}{\sin \theta}$$

$$V = 0.866 \times a^2 \times c.$$  

The microstrain is estimated via the expression $\varepsilon = \frac{\beta}{4\tan \theta}$ and the stress $\sigma$ (GPa) in the crystallite’s plane is computed:

$$\varepsilon = \frac{\beta}{4\tan \theta}$$

$$\sigma = 233 \left( \frac{c_{\text{bulk}} - c}{c_{\text{bulk}}} \right),$$

where $c$ and $c_{\text{bulk}}$ are the measured lattice parameter and the strain-free lattice parameter of ZnO (5.2061 Å), respectively. The Zn–O bond length ($L$) was calculated using the equation:

$$L = \sqrt{\frac{a^3}{3} + (0.5 - u)^2 \times c^2},$$

where $u = \frac{\beta}{\lambda} + 0.25$.

The tabulated values (Table 1) of the d-spacing, $a$, $c$, $V$ and $L$ reveal a decrease with the increment of titanium in the nanocomposites. This may be attributed to the substitution of larger radius Zn$^{2+}$ (74 pm) by the smaller radius Ti$^{4+}$ (68 pm) [42]. The stress ($\sigma$) in the nanocomposites can be estimated by the expression $\sigma = -233(c_0 - c)/c_0$, where $c$ and $c_0$ are the lattice constants calculated from XRD data the lattice constant of the pure ZnO (0.5206 nm) respectively [45]. It is evident that the samples containing titania have a negative or very less stress that points to a compressive stress. Thus, the minor shrinkage in the lattice parameters can be ascribed to a compressive stress as a result of the partial displacement of the large Zn$^{2+}$ by the small Ti$^{4+}$ in the structures [46, 47]. Using the formula $\varepsilon = \beta/4 \tan \theta$, the microstrain ($\varepsilon$) was calculated and tabulated (Table 1). As can be observed, the microstrain decreased monotonously with the increase in titania loading which may be attributed to the atom diffusion [48] during the Ti$^{4+}$ substitution of Zn$^{2+}$ during composite formation. From Table 1, it is evident that the preferred orientation has changed from (002) to the (101) plane as titanium loading is increased as reflected by the increase in ($I_{101}/I_{002}$) ratio. This may be attributed to the effect of Zn and Ti atoms that reduce the surface free energy of the (101) which might have changed the plane of minimum surface free energy from (002) to (101) [49].

The formation of a single TiO$_2$ rutile phase even at low temperature might be attributed to the gelatin addition. It has been previously reported that organic additives such as $N,N'$-dicyclohexylcarbodiimide and l-serine have enabled the formation of a single rutile phase TiO$_2$ hollow spheres [50]. In addition, an effective rutile phase transformation at 300 °C was achieved by adding hexylene glycol to the titanium alkoxide solution. This was attributed to the
formation of a bidentate ligand between the hexylene glycol and titanium and it was argued that the bidentate binding has promoted the rutile phase formation at such a low temperature [51]. Similarly, we presume that the amine pendant groups on the gelatin have led to the development of gelatin-stabilized stable rutile TiO₂ phase within the nanocomposites. In addition, the high temperature due the ultrasonic probe may also contribute to the stabilization of rutile form [53].

### 3.2 Morphological investigations and elemental mapping distribution

The SEM images of the prepared nanocomposites are depicted in Fig. 2a–d. The TZO1 sample (Fig. 2a) reveals a blend of spherical and hexagonal particles with a size distribution 60–80 nm. In the TZO2 and TZO3 specimens’ images (Fig. 2b, c), the nanoparticles are transformed into fused oval shapes with size distribution 40–80 nm. In the TZO4 sample Fig. 2d, the nanoparticles are turning into more hexagonal shape with less fusion and reduced size. The decrease in particle size of the highest Ti ratio sample may be attributed to the substitution of the Zn²⁺ (74 pm) with smaller radius Ti⁴⁺ (64 pm) [54].

The TEM image of TZO4 photocomposite (Fig. 3a) reveals spherical-shaped particles with a nanoscale size, as confirmed by SEM image, as shown in Fig. 2d. The EDS image of TZO4 photocomposite (Fig. 3b and c) reveals the existence of O, Ti and Zn to determine the development of TiO₂–ZnO photocomposite as well as weight percentage composition. Besides, in order to examine the homogeneity of element distribution TZO4, EDS elemental mapping was employed, as illustrated in Fig. 3d–f. O, Ti and Zn are displayed in distinct colors to know their distribution within the nanocomposite (Fig. 3d–f). A brighter domain in the elemental map designates a greater concentration of the identical element. It can be noted that all elements O, Ti and Zn are regularly distributed over all the examined particles, which gives evidence for the successful fabricated of homogeneous photocomposite.

### 3.3 Surface properties analysis

Surface area and pore size of nanocatalysts are among the vital parameters that determine the quality of adsorbents due to their direct effect on the adsorbate retention aptitudes. The adsorption desorption isotherms (Fig. 4 and Table 2) of the samples are of Type IV as categorized by the IUPAC [55] with a type H3 hysteresis loop. This hysteresis at P/P₀ from 0.4 to 1 is attributed to the capillary condensation in the mesopores associated with the cavities between the powder particles [56]. The point, at the beginning of the linear middle part of the graph, marks the stage where the monolayer coverage is complete and multilayer adsorption commences [57]. The large BET surface area of bare ZnO was decreased from 20 to 15 m²/g as TiO₂ is incorporated into the lattice. Besides that, the pore volume and pore diameter of pure ZnO reduced from 0.053 cm³/g and 18 nm to 0.027 cm³/g and 15 nm when the maximum TiO₂ was uploaded although the crystallite size is decreased. This anomaly may be ascribed to the nonconformity of pore geometry with the spherical shape. As per de Boer, the H4 type hysteresis loop is made by flatter or tubular pores that have a narrow constriction and/or closed pores of the ink bottle type [58]. Some pores exhibit ellipsoidal or cylindrical morphology due to the contraction of the original spherical pore [59]. An inverse relation between the crystallite size and porosity was reported in the literature for ceramic foams [60].

| Samples | β      | 2θ (0) | D (nm) | Lattice parameter (Å) | I₁₀₁/I₀₀² | σ (× 10⁻³) | ε (× 10⁻³) | d-spacing | V   | u   | L   |
|---------|--------|--------|--------|-----------------------|-----------|-------------|-------------|------------|-----|-----|-----|
| TZO1    | 0.2317 | 36.232 | 43.0   | 3.253                 | 5.210     | 0.268       | 1.78        | 3.08       | 2.4768 | 47.7 | 0.3799 | 1.9796 |
| TZO2    | 0.2231 | 36.285 | 37.5   | 3.248                 | 5.202     | 0.555       | -2.55       | 3.00       | 2.4741 | 47.5 | 0.3799 | 1.9757 |
| TZO3    | 0.2202 | 36.262 | 38.4   | 3.249                 | 5.205     | 1.044       | -0.44       | 2.93       | 2.4741 | 47.6 | 0.3799 | 1.9772 |
| TZO4    | 0.2183 | 36.235 | 37.3   | 3.252                 | 5.208     | 1.805       | 0.89        | 2.91       | 2.4755 | 47.7 | 0.3799 | 1.9790 |
Fig. 2  SEM of TZO1 (a), TZO2 (b), TZO3 (c) and TZO4 (d)

Fig. 3  a TEM, b EDS and c weight percentage (d–f) elemental composition mapping for TZO4 photocomposite
Fig. 4 Adsorption–desorption isotherms of N₂ at 77 K (inset pore size distribution) of all samples
3.4 Optical properties

3.4.1 UV–visible and bandgap determination

The optical properties the TiO$_2$–ZnO composites with varying Ti percentages were probed by UV–Vis and their respective spectra are shown in Fig. 5a. The graph reveals a maximum absorption at 373, 373, 369 and 370 nm for the TZO1, TZO2, TZO3 and TZO4, respectively. The bandgap energy ($E_g$) was estimated from the $(\alpha h\nu)^{1/2}$ versus $h\nu$ graph (Fig. 5b) using the Tauc equation [61, 62]:

$$ (\alpha h\nu)^{1/2} = A(h\nu - E_g), $$

where $h$, $\nu$, $\alpha$ and $E_g$ stand for the Planck’s constant, frequency, absorption coefficient and the bandgap energy, respectively, whereas $A$ is a proportionality constant, and $n$ designates the nature of electron transition (for directly allowed transitions, $n = 1/2$). The energy bandgap values of were found to be 3.218, 3.212, 3.227 and 3.237 eV the TZO1, TZO2, TZO3 and TZO4 samples, respectively. The $E_g$ of the nanocomposites makes them a promising candidate for different photo-applications [63, 64]. During the doping process and the Ti$^{4+}$ ion replacement of Zn$^{2+}$ ions at substitution sites [65], an increase in the number of the free charge carriers prevails which considerably distresses low-energy excitations. Such a situation may lead to the semiconductor’s conduction band Fermi level expansion and a consequent optical bandgap widening, in accordance with the Burstein–Moss shift [66, 67]. Analogous blue shift phenomenon of optical bandgaps in Ti-doped ZnO films [46, 68] and Ti-doped ZnO nanoparticles [69] has been reported earlier.

3.4.2 FTIR study

FTIR spectra conducted in the variety of 400–4000 cm$^{-1}$ for all as-prepared nanocomposites are presented in Fig. 6. The broad peak at $\approx$ 3500 cm$^{-1}$ might be assigned to the O–H stretching vibration hydroxyl groups of the nanocomposites surface [70]. The vibration mode of Zn–O–Ti is indicated by the at the 800 cm$^{-1}$ region peaks [71]. The peaks at 1160 and 1080 cm$^{-1}$ might be attributed to the Ti–OH bond, whereas the peaks at 500–700 cm$^{-1}$ might present the symmetric stretching vibration of the Ti–O–Ti bond and the flexion vibration of the O–Ti–O, correspondingly [72, 73].

3.5 Photocatalytic activity of composites

The photocatalytic performance of the as-synthesized nanocomposites was assessed by the RhB dye decomposition under visible light illumination. As presented in Fig. 7a, RhB dye has achieved poor

| Samples | $S_{BET}$ | $E_g$ (eV) | Pore volume | Pore diameter |
|---------|----------|-----------|-------------|--------------|
| TZO     | 20.3     | 3.196     | 0.0528 cm$^3$/g | 18.2497 nm   |
| TZO1    | 14.7     | 3.222     | 0.0223 cm$^3$/g | 13.1817 nm   |
| TZO2    | 14.9     | 3.226     | 0.0237 cm$^3$/g | 11.2235 nm   |
| TZO3    | 15.3     | 3.232     | 0.0251 cm$^3$/g | 13.3149 nm   |
| TZO4    | 15.5     | 3.245     | 0.0273 cm$^3$/g | 14.7948 nm   |

Figs. 5a UV–Vis absorbance and b the bandgap energy of TiO$_2$–ZnO composites

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photocatalytic activity in the presence of pure ZnO under visible light illumination, which was a result of the fast recombination of photogenerated electron–hole pairs [74]. On the other hand, the TiO$_2$–ZnO samples demonstrated improved photocatalytic performance (Fig. 7b). With increasing TiO$_2$ content, the photodegradation competence of the nanocomposites has markedly improved [75]. Among them, TZO4 exemplified the best performance with a dye photodegradation rate of 97% within 180 min (Fig. 8a). Due to a heterojunction formation at the ZnO–TiO$_2$ interface, a possible electron transfers from the TiO$_2$ valence band to ZnO conduction band leading to lower the recombination rate of photogenerated charge carriers [76]. This phenomenon subsequently increases the positive hole centers on the surface of TiO$_2$ and enhances its oxidizing power [77].

The kinetics of the photodegradation significantly fits the first-order kinetics as indicated by the linear $\ln \frac{C_0}{C_t}$ vs $t$ plots (Fig. 8b) and the regression values ($R^2 \approx 1.0$) [78, 79]. The rate constant and half-life values (Table 3) clearly confirm the highest photodegradation capacity of the TZO4 sample.

### 3.5.1 Influence of radicals’ scavengers on the photocatalytic activity

Oxygen species are reactive radicals that are usually involved in the photodegradation process. In order to verify the operative entities, the scavengers EDTA, isopropanol, silver nitrate and ascorbic acid are employed to monitor the effects of positive holes, hydroxyl radicals, electrons and superoxide radicals, respectively, on TiO$_2$–ZnO composite activity. The photodegradation ($C_t/C_0$) percentage variation with scavengers is displayed in Fig. 9. It can be seen that photodegradation yields are 10%, 5%, 15% and 30% due to the addition of EDTA ($h^+$ scavenger) [80] and ASC ($O_2^-$ scavenger) [81] as compared to IPA ($OH$ scavenger) [81] and AgNO$_3$ ($e^-$ scavenger), respectively. This implies that the $h^+$ [82] and $O_2^-$ [83] radicals have more contribution to the dye photodegradation compared to $OH$ and $e^-$ that show less impact on the photodegradation process by the TiO$_2$–ZnO photocomposite.

### 3.5.2 Mechanism of Photocatalysis

Electrons get excited due to ultraviolet of visible light irradiation electrons and are then promoted from valence band (VB) to conduction band (CB) of ZnO NPs creating a positive holes ($h^+$) behind [84]. The
powerful oxidizing $O_2^-$ resulting an electron and an O$_2$ reaction do combine with hole ($h^+$) to generate the peroxide $H_2O_2$ ($O_2 + 2h^+ + 2e^- \rightarrow H_2O_2$) that triggers chain reactions with electrons to the produce the active -OH radicals ($H_2O_2 + e^- \rightarrow OH^- + -OH$). Similarly -OH can be generated from the $h^+$ reaction with surface-adsorbed H$_2$O molecules [85]. The photodegradation reaction proceeds due to the continuous bouts on the organic dye by -OH radicals ($R + -OH \rightarrow R' + H_2O$) or $h^+$ ($R + h^+ \rightarrow R'^+$ -> degradation products [86].

The conduction band (CB) and valence band (VB) of samples can be calculated according to [74]:

$$E_{CB} = X - E^c - 0.5E_g$$  (9)
$$E_{VB} = X - E^c + 0.5E_g,$$  (10)

where $E_{CB}$, $E_{VB}$ are the CB and VB edge potential, respectively; $X$ is the electronegativity of the semiconductor, obtained from the geometric mean of the electronegativity of the constituent atoms (The $X$ values of ZnO and TiO$_2$ are 5.95 and 5.81 [33]); $E^c$ is the energy of free electrons on the hydrogen scale (4.5 eV); and $E_g$ is the bandgap energy of the semiconductor (The $E_g$ values of ZnO and TiO$_2$ are calculated to be 3.21 and 3.27 eV as shown in Fig. 5, respectively.). Consistent with the above relation, the $E_{CB}$ values of ZnO and TiO$_2$ are calculated to be $-1.48$ and $-0.31$ eV, while the $E_{VB}$ are $4.048$ and $2.95$ eV, respectively [33].

As TiO$_2$ cannot be activated under visible light, RhB can absorb photons and then the excited molecule transfers the LUMO electrons to the conductive band of TiO$_2$ and ultimately to the CB of ZnO [87]. Thus, the CB of ZnO and TiO$_2$ can function as a pool to contain the photo-induced $e^-$s and hinder their recombination with the $h^+$s. Thereafter, the conductive electron reacts with pre-adsorbed oxygen molecules to produce active oxygen species [88, 89]. Based
on the following mechanism proposed by Liang et al. [90], the RhB degradation can be proposed.

\[
\text{RhB} + h\nu \rightarrow \text{RhB}^* \\
\text{RhB}^* + \text{TiO}_2 - \text{ZnO} \rightarrow \cdot\text{RhB}^* + \text{TiO}_2 - \text{ZnO}(e^-) \\
\text{TiO}_2 - \text{ZnO}(e^-) + \text{O}_2 \rightarrow \text{O}_2^- \\
\text{O}_2^- + h^+ \rightarrow \text{OOH}^+ \\
\text{OOH}^* + \text{O}_2^- + h^+ \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2
\]

- \text{RhB}^* + \text{ROS} \rightarrow \text{Degraded products.} \quad (17)

As can be deduced from the proposed mechanism, the most active photo-species are the \( h^+ \) and \( \text{O}_2^- \) in agreement with the radical scavengers results. Figure 10 is a graphical description for a photodegradation scheme.

Table 4 shows a comparison of the photocatalytic competence of TZnO4 with other photocatalysts from the literature. The data undoubtedly exhibit the higher performance of the photocatalyst to decolorize RhB in aqueous solutions.
4 Conclusion

Visible light-driven photocatalytic degradation of RhB dye was achieved using ZnO/TiO\textsubscript{2} composites stabilized by gelatin under ultra-sonication. The optical properties revealed higher absorbance for the TZO\textsubscript{4} sample with a bandgap energy of 3.23 eV. The excellent performance of the composites is attributed to the excellent charge carrier separation and the development of impurity level in the binary system. Based on the results presented in this research, TiO\textsubscript{2}/ZnO composites are effective photocatalyst for organic pollutant degradation.

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