

# Synergistic effect of TiO<sub>2</sub> and ZnO photocatalysts for 4-nitrophenol photodegradation under ultraviolet irradiation

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**Abstract.** Since phenolic compounds can seriously damage our health, their concentration in the industrial wastewater should be reduced before their disposal. A photodegradation process offers a green and simple process utilizing light irradiation in the presence of heterogeneous photocatalyst material. Titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO) materials have been reported for their remarkable photocatalytic activity under ultraviolet (UV) irradiation. However, the electron-hole recombination on these photocatalyst materials demarcates their photocatalytic efficiency. In the present work, we reported a synergistic effect of combined P25 TiO<sub>2</sub> and ZnO in the TiO<sub>2</sub>-ZnO composite for 4-nitrophenol degradation under UV irradiation. While it was obtained that the adsorption capability of TiO<sub>2</sub>-ZnO composite material (4.2%) toward 4-nitrophenol lay between those of the P25 TiO<sub>2</sub> (2.8%) and the ZnO (10%) materials, the TiO<sub>2</sub>-ZnO composite material exhibited a higher photocatalytic activity (65%) than both of the P25 TiO<sub>2</sub> (26%) and the ZnO (59%). The kinetic study showed that the TiO<sub>2</sub>-ZnO composite gave a higher reaction rate constant (0.197 h<sup>-1</sup>) than the P25 TiO<sub>2</sub> (0.047 h<sup>-1</sup>) and the ZnO (0.172 h<sup>-1</sup>) materials. From the fluorescence study, it was proposed that the electron transfer from the P25 TiO<sub>2</sub> to the ZnO was responsible for the photocatalytic activity enhancement.

## 1. Introduction

Environmental water pollution gives dangerous effects on human health. It has been known that water pollution caused by the phenolic-based compound is responsible for serious health disorders such as diarrhea, hemolytic anemia, nausea, irritation, and pulmonary edema [1]. Several techniques such as adsorption [2], bioremediation [3], and photocatalysis [4] have been reported for this water pollution treatment. Even though the adsorption technique is considered as the simplest and easiest way to overcome water pollution, this process generates the second waste of the used adsorbent material. Therefore, it is necessary to treat the used adsorbent materials for reusability purposes. In the bioremediation process, it often takes a long process for complete pollutant removal, which is unfavorable [5]. On the other hand, photocatalysis technique offers a promising way in the water remediation and the total degradation of the phenolic-based compound to less toxic compounds of water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) could be achieved in a short time reaction.

Metal oxide materials such as titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO) have been reported having good photocatalytic properties [6-13]. When these metal oxide materials adsorb a substrate from the system, the further photocatalytic process could be easily started by illuminating the mixture under ultraviolet (UV) light [6,7]. This photocatalytic process offers an environmental-friendly process and the photocatalyst material can be easily regenerated [8]. Particular attention is on the commercially available P25 TiO<sub>2</sub> nanomaterial, which has been reported for its promising photocatalytic degradation activity under UV light irradiation [9,10]. However, the fast rate of the electron-hole recombination process on this material limits the photocatalytic efficiency [11]. The fast recombination process could be reduced using a coupling method between two metal oxide materials. It has been reported that the enhancement in photocatalytic

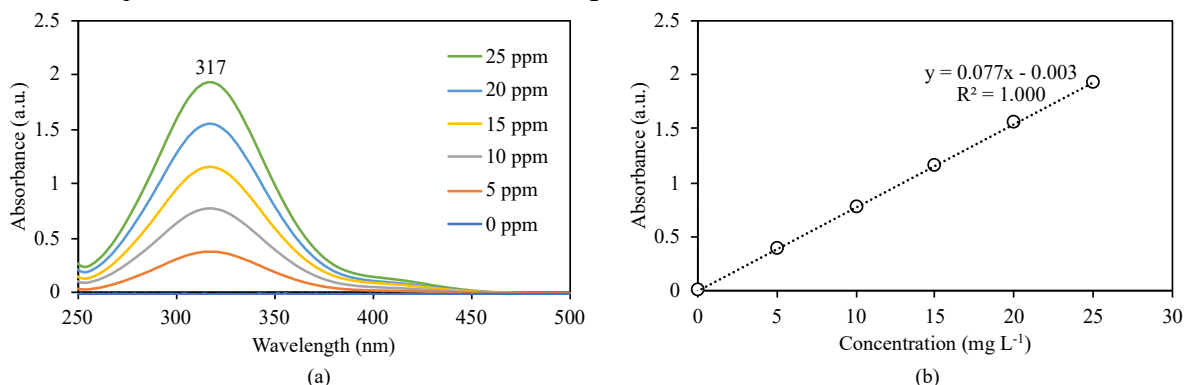
activity could be achieved by coupling the TiO<sub>2</sub> with the ZnO [7]. So far, the TiO<sub>2</sub>-ZnO composites were prepared by several methods, including sol-gel [11], impregnation [12], and solid-state sintering [13]. However, these three methods usually need several steps and pretreatment on the sample preparation as well as the use of the heating process. On the other side, a physical grinding technique is considered as the simplest and easiest way for the preparation of composite materials [14,15]. Unfortunately, despite its simplicity, this method is still rarely employed for the preparation of TiO<sub>2</sub>-ZnO composite as the photocatalyst.

In this work, we reported a synergistic effect on the photocatalytic activity enhancement on the TiO<sub>2</sub>-ZnO composite from a physical grinding of P25 TiO<sub>2</sub> and ZnO in 1:1 mass ratio. The TiO<sub>2</sub>-ZnO composite was characterized by diffuse reflectance ultraviolet-visible (DR UV-Vis), Fourier transform infrared (FTIR), and fluorescence spectroscopies. The photocatalytic activity of the TiO<sub>2</sub>-ZnO composite was then evaluated for the photocatalytic degradation of 4-nitrophenol as the model organic pollutant.

## 2. Experimental section

### 2.1. General

Commercial P25 TiO<sub>2</sub>, commercial ZnO, and 4-nitrophenol were purchased from Evonic Industries, DutaJaya, and Merck chemicals, respectively. The P25 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>-ZnO materials were characterized using a UV-Vis spectrophotometer (JASCO V-760), a Fourier transform infrared (FTIR) spectrophotometer (JASCO FTIR-6800), and a spectrofluorometer (JASCO FP-8500). The absorption of 4-nitrophenol was measured using a UV-Vis spectrophotometer (JASCO V-760) and its concentration was calculated from the calibration curve monitored at 317 nm. The UV-Vis spectra and the calibration curve of the 4-nitrophenol standard solution are shown in Figure 1.



**Figure 1.** (a) UV-Vis spectra and (b) calibration curve of 4-nitrophenol in distilled water at a various concentration (0–25 mg L<sup>-1</sup>)

### 2.2. Procedure

#### 2.2.1. Preparation and Characterizations of TiO<sub>2</sub>-ZnO Composite

The TiO<sub>2</sub>/ZnO composite material was prepared by a physical grinding of commercial P25 TiO<sub>2</sub> and commercial ZnO in a 1:1 mass ratio. In a typical preparation, 1.0 g of P25 TiO<sub>2</sub> and 1.0 g of ZnO were mixed in a mortar.

The prepared TiO<sub>2</sub>-ZnO composite materials were characterized using DR UV-Vis, FTIR and spectrofluorometer. The DR UV-Vis spectrum of the sample was measured in the Kubelka-Munk (KM) function from 200-800 nm. Meanwhile, the FTIR spectrum of the sample was obtained using Attenuated Total Reflection (ATR) method from 400-4000 cm<sup>-1</sup>. The fluorescence spectrum was recorded using a

spectrofluorometer through a solid sample measurement. For the comparison purpose, the P25 TiO<sub>2</sub> and ZnO were also characterized in a similar way to the composite.

### 2.2.2. Adsorption and Photocatalytic Degradation of 4-Nitrophenol

The adsorption of 4-nitrophenol was carried out in the dark condition for 1 hour. As much as 50 mg of the photocatalyst (P25 TiO<sub>2</sub> or ZnO or TiO<sub>2</sub>-ZnO) was added into 50 mL of 4-nitrophenol solution in distilled water at 50 mg L<sup>-1</sup> concentration. The mixture was stirred at room temperature and then was filtrated to obtain a clear filtrate which was free from the photocatalyst. The adsorption percentage of 4-nitrophenol was calculated using equation 1, where [4-NP]<sub>0</sub> and [4-NP]<sub>ads</sub> are the initial concentration and the concentration of 4-nitrophenol after the adsorption process, respectively.

$$\text{Adsorption (\%)} = \left( \frac{[4\text{-NP}]_0 - [4\text{-NP}]_{\text{ads}}}{[4\text{-NP}]_0} \right) \times 100\% \quad (1)$$

The photocatalytic degradation of 4-nitrophenol was conducted in the same conditions as the adsorption procedure, except for the use of the light source. After 1-hour adsorption in the dark condition, the mixture was illuminated using a UV lamp (UVLS-28 EL Series, 8 W) at a wavelength of 365 nm for 1, 2, 3, 4, 5, and 6 h. Finally, the phenol photodegradation percentage was estimated using equation 2, where [4-NP]<sub>ads</sub> and [4-NP]<sub>t</sub> are the concentrations of 4-nitrophenol after adsorption and UV illumination, respectively.

$$\text{Photodegradation (\%)} = \left( \frac{[4\text{-NP}]_{\text{ads}} - [4\text{-NP}]_t}{[4\text{-NP}]_{\text{ads}}} \right) \times 100\% \quad (2)$$

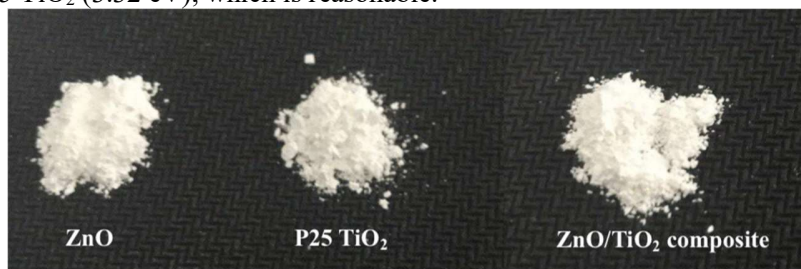
## 3. Results and discussion

### 3.1. Photocatalyst properties

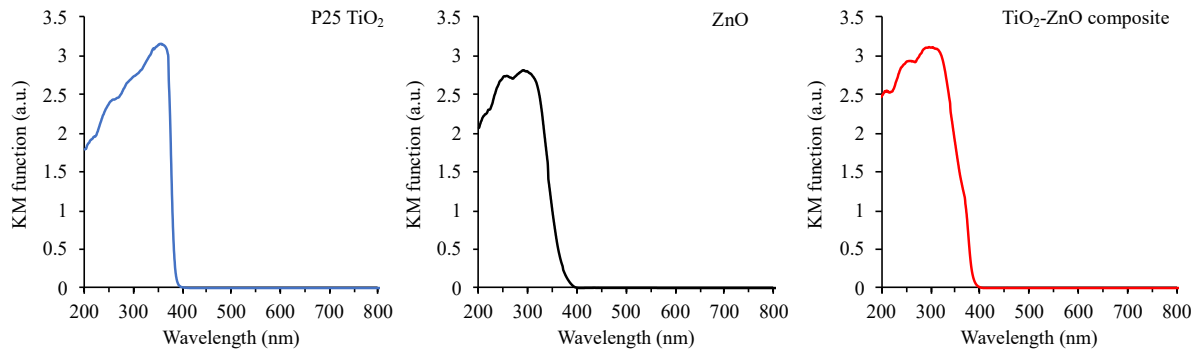
From a physical grinding of P25 TiO<sub>2</sub> and ZnO material in a 1:1 mass ratio, the TiO<sub>2</sub>-ZnO composite material was obtained as a white powder as shown in Figure 2. The DR UV-Vis spectra of P25 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>-ZnO composite are shown in Figure 3. As expected from the color appearances of these materials, the P25 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>-ZnO composite materials did not give any absorption signals in the visible region (400–800 nm). The absorption signal of the TiO<sub>2</sub>-ZnO composite in the UV region (200–400 nm) was similar to the absorption of combined P25 TiO<sub>2</sub> and ZnO material. Tauc plot shown in equation 3 was then used to calculate the bandgap energy of these materials.

$$(\alpha h\nu)^2 = A(E_g - h\nu) \quad (3)$$

The A, E<sub>g</sub>, h, ν, and α are referred to as the slope of Tauc plot, bandgap energy, Planck constant, light frequency, and absorption coefficient of the materials, respectively. The bandgap energy values of the P25 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>-ZnO composite were determined to be 3.32, 3.19, and 3.20 eV, respectively. It was noted that the calculated bandgap energy of TiO<sub>2</sub>-ZnO composite was between the bandgap energy of ZnO (3.19 eV) and P25 TiO<sub>2</sub> (3.32 eV), which is reasonable.

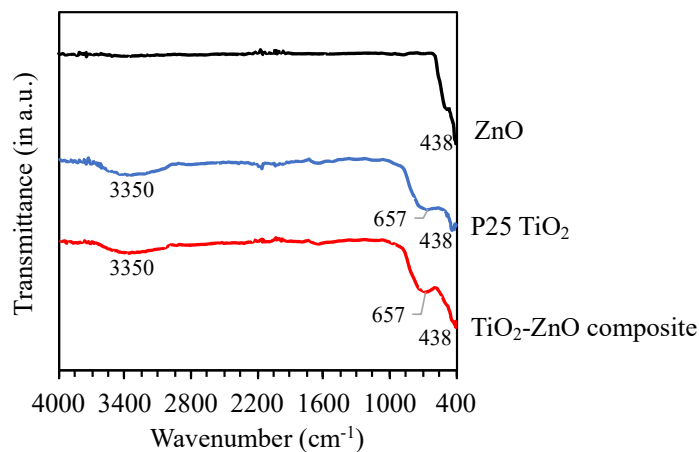


**Figure 2.** Photograph images of P25 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>-ZnO composite



**Figure 3.** DR UV-Vis spectra of P25 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>-ZnO composite

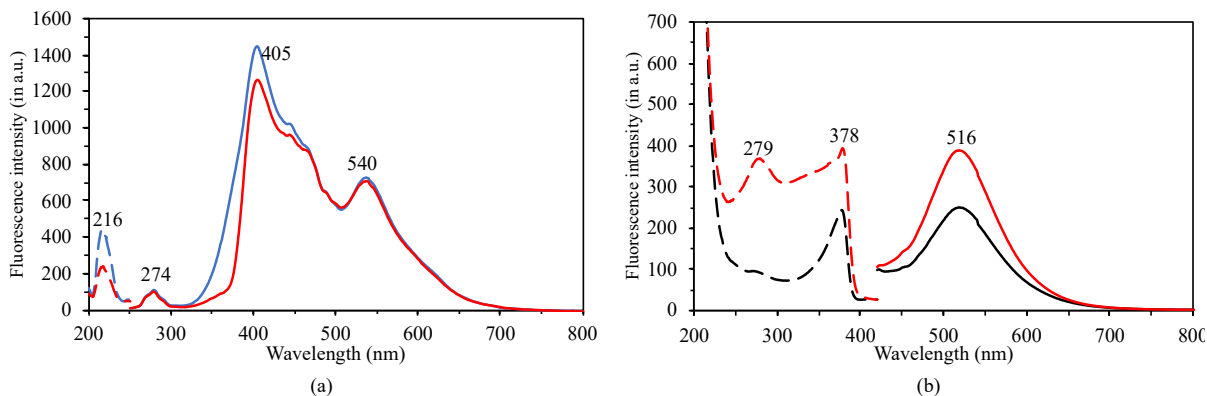
The P25 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>-ZnO composite were further characterized using FTIR and fluorescence spectrometers. Figure 4 shows the FTIR spectra of the P25 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>-ZnO composite materials. The P25 TiO<sub>2</sub> showed the absorption signals of O–H, Ti–O–Ti, and Ti–O functional groups at 3350, 657, and 438 cm<sup>-1</sup>, respectively [16], while the ZnO showed an absorption signal of Zn–O functional group at 438 cm<sup>-1</sup> [17]. The TiO<sub>2</sub>-ZnO composite showed the characteristic absorption of both P25 TiO<sub>2</sub> and ZnO, where the O–H, Ti–O–Ti, and M–O (M = Ti or Zn) functional groups were observed at 3350, 657, and 438 cm<sup>-1</sup>, respectively. The TiO<sub>2</sub>-ZnO composite exhibited a stronger absorption of M–O linkages (M = Ti or Zn), but a lower absorption of the O–H functional group than that of the P25 TiO<sub>2</sub>, which would be due to the presence of ZnO in the composite.



**Figure 4.** FTIR spectra of P25 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>-ZnO composite

The fluorescence spectra of P25 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>-ZnO composite are shown in Figure 5. Figure 5(a) shows the excitation and emission spectra of the P25 TiO<sub>2</sub> and the TiO<sub>2</sub>-ZnO composite, which were measured at the emission and excitation wavelengths of the P25 TiO<sub>2</sub>, respectively. The P25 TiO<sub>2</sub> was shown to have an excitation peak at 216 nm and emission peaks in the UV region at 274 nm [18] as well as in the visible region at 405 and 504 nm. The TiO<sub>2</sub>-ZnO composite exhibited similar fluorescence spectra to the P25 TiO<sub>2</sub> due to the presence of TiO<sub>2</sub>. However, the fluorescence intensity of the composite (red line) was lower than that of the P25 TiO<sub>2</sub> (blue line). The lower intensity suggested the possible reduced electron-

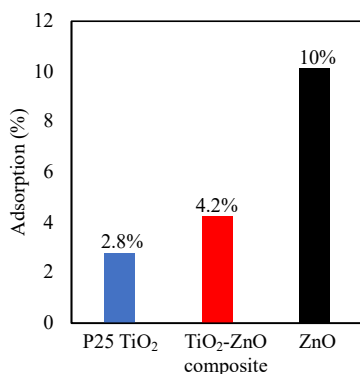
hole recombination in the composite. Figure 5(b) shows the excitation and emission spectra of the ZnO and the TiO<sub>2</sub>-ZnO composite when they were monitored at the emission (516 nm) and excitation (378 nm) wavelengths of the ZnO, respectively. The ZnO gave excitation peaks around 200, 279, and 378 nm, and one emission peak at 516 nm, which were similar to the reported one [19]. In contrast to Figure 5(a), the composite (red line) gave higher intensity than the ZnO (black line). Based on these results, it could be proposed that there was a charge transfer from the TiO<sub>2</sub> to the ZnO as evidenced in the decreased fluorescence intensity of P25 TiO<sub>2</sub> and the increased fluorescence intensity of ZnO in the TiO<sub>2</sub>-ZnO composite.



**Figure 5.** Excitation (dash line) and emission spectra of (a) P25 TiO<sub>2</sub> (blue line) and TiO<sub>2</sub>-ZnO composite (red line), and (b) ZnO (black line) and TiO<sub>2</sub>-ZnO composite (red line).

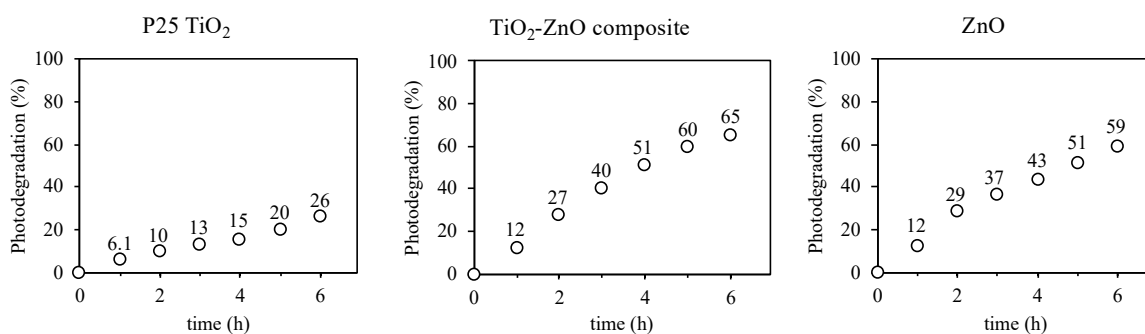
### 3.2. Adsorption and photocatalytic degradation of 4-nitrophenol

To evaluate the photocatalytic activity of TiO<sub>2</sub>-ZnO composite material, the 4-nitrophenol was selected as the model organic pollutant. The adsorption percentage of 4-nitrophenol was calculated using equation (1) from the adsorption experiment of 50 mL 4-nitrophenol solution in distilled water using 50 mg of the photocatalyst material. It was obtained that as much as 4.2% of 4-nitrophenol was adsorbed at dark conditions on the TiO<sub>2</sub>-ZnO composite material. As shown in Figure 6, this adsorption percentage was higher than the 4-nitrophenol adsorption percentage of the P25 TiO<sub>2</sub> (2.8%) but lower than the 4-nitrophenol adsorption percentage of ZnO (10%).

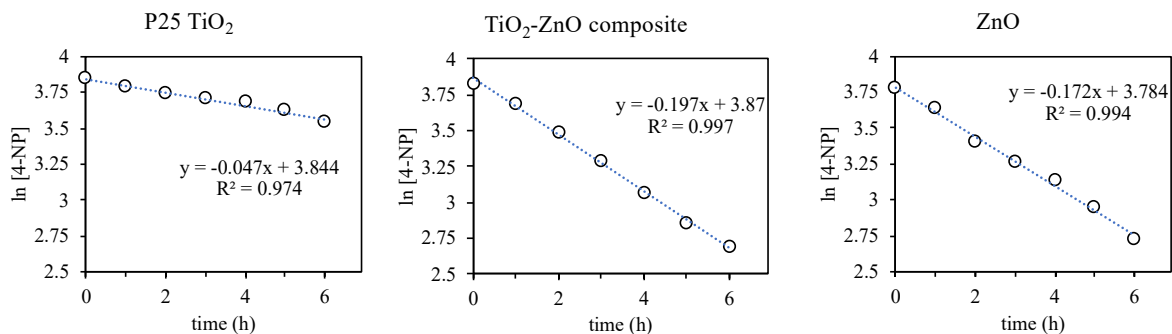


**Figure 6.** Adsorption of 4-nitrophenol on the P25 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>-ZnO composite

The profiles of 4-nitrophenol photocatalytic degradation are shown in Figure 7. After 6 h-reaction under UV light irradiation, the P25 TiO<sub>2</sub> material was only able to degrade the 4-nitrophenol up to 26%. Meanwhile, the ZnO material degraded up to 59%. Interestingly, the TiO<sub>2</sub>-ZnO composite exhibited a higher 4-nitrophenol photodegradation percentage (65%) than both P25 TiO<sub>2</sub> and ZnO materials. The 4-nitrophenol photocatalytic degradation on all photocatalysts followed the first-order kinetic model as indicated by the high correlation factor ( $R^2 = 0.974-0.997$ ) as shown in Figure 8. From the first-order kinetic model, the reaction rate constant was determined for each photocatalyst. The TiO<sub>2</sub>-ZnO composite material showed the highest rate constant ( $0.197 \text{ h}^{-1}$ ), followed by the ZnO ( $0.172 \text{ h}^{-1}$ ), and P25 TiO<sub>2</sub> ( $0.047 \text{ h}^{-1}$ ). This result clearly showed the synergistic effect of TiO<sub>2</sub> and ZnO in the composite, which resulted in better photocatalytic activity. The order of the photocatalytic activity did not match the order of adsorption capability, suggesting that the adsorption capability might not be the main parameter affecting the photocatalytic activity. The higher photocatalytic activity shall be due to the reduced charge recombination on the P25 TiO<sub>2</sub>.



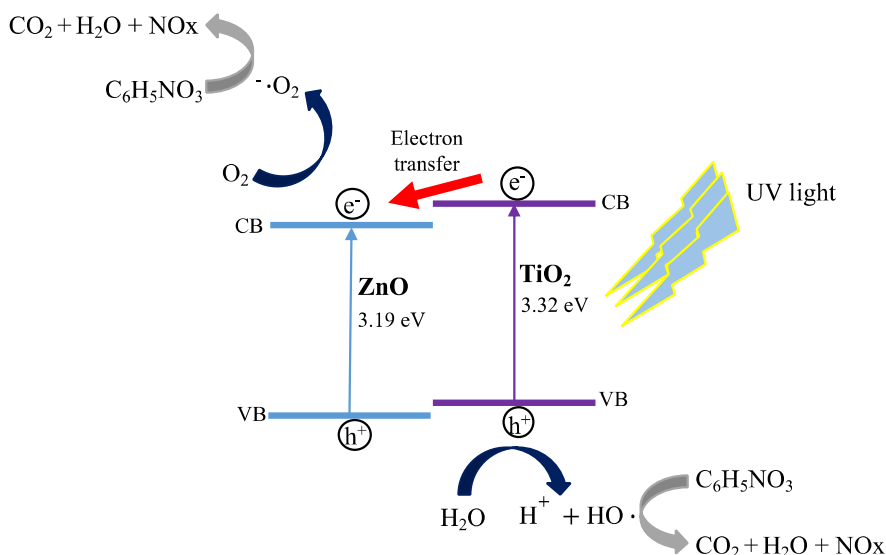
**Figure 7.** Photocatalytic degradation of 4-nitrophenol on the P25 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>-ZnO composite



**Figure 8.** First-order kinetic profiles of 4-nitrophenol photocatalytic degradation on the P25 TiO<sub>2</sub>, ZnO, and TiO<sub>2</sub>-ZnO composite

As shown and discussed in Figure 5, the fluorescence spectra of the composite showed that the electron-hole recombination on the P25 TiO<sub>2</sub> was suppressed, which shall occur via the electron transfer from the TiO<sub>2</sub> to the ZnO. Based on this result and photocatalytic activity achievement, the mechanism of 4-nitrophenol photocatalytic degradation under UV irradiation on the TiO<sub>2</sub>-ZnO composite could be proposed and illustrated in Figure 9. Since the electron transfer process occurred from the conduction band (CB) of TiO<sub>2</sub> to the CB of ZnO, the photoreduction of the oxygen molecule would mainly occur at the CB of ZnO,

and the generated superoxide radical ion ( $\text{O}_2^{\cdot-}$ ) would oxidize the 4-nitrophenol to  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{NO}_x$  molecules. Meanwhile, the holes could be generated at both valence band (VB) of  $\text{TiO}_2$  and  $\text{ZnO}$ , which could directly oxidize the 4-nitrophenol, or via the formation of hydroxyl radicals ( $\text{HO}\cdot$ ) from water to produce  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{NO}_x$  molecules.



**Figure 9.** Proposed mechanism of the photocatalytic degradation of 4-nitrophenol on the  $\text{TiO}_2$ - $\text{ZnO}$  composite under UV irradiation.

#### 4. Conclusions

We observed a synergistic effect of  $\text{TiO}_2$  and  $\text{ZnO}$  in the  $\text{TiO}_2$ - $\text{ZnO}$  composite to enhance the 4-nitrophenol photocatalytic degradation. The  $\text{TiO}_2$ - $\text{ZnO}$  composite was prepared by a physical grinding of P25  $\text{TiO}_2$  and  $\text{ZnO}$  in a 1:1 mass ratio. The bandgap energy of the  $\text{TiO}_2$ - $\text{ZnO}$  composite was calculated to be 3.20 eV and that value was between the bandgap energy values of  $\text{ZnO}$  (3.19 eV) and P25  $\text{TiO}_2$  (3.32 eV). The FTIR spectra of the  $\text{TiO}_2$ - $\text{ZnO}$  composite gave three main absorption signals of O–H, Ti–O–Ti, and M–O (M = Ti or Zn) groups. The fluorescence intensity of the  $\text{TiO}_2$ - $\text{ZnO}$  composite was lower than that of the P25  $\text{TiO}_2$  but higher than that of  $\text{ZnO}$ . This result demonstrated that the electron-hole recombination on the P25  $\text{TiO}_2$  was reduced and the electron transfer occurred from the P25  $\text{TiO}_2$  to the  $\text{ZnO}$ . Such a synergistic effect resulted in the enhancement of photocatalytic activity in the  $\text{TiO}_2$ - $\text{ZnO}$  composite (65%) as compared to the bare P25  $\text{TiO}_2$  (26%) and  $\text{ZnO}$  materials (59%).

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