



## Bandgap Energy of TiO<sub>2</sub>/M-Curcumin Material (M = Na<sup>+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>)

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<https://doi.org/10.14710/jksa.25.1.1-6>

### Article Info

#### Article history:

Received: 3<sup>rd</sup> June 2021  
 Revised: 23<sup>rd</sup> January 2022  
 Accepted: 24<sup>th</sup> January 2022  
 Online: 31<sup>st</sup> January 2022

#### Keywords:

curcumin; TiO<sub>2</sub>; bandgap energy; Tauc plot method

### Abstract

Bandgap energy ( $E_{\text{gap}}$ ) of TiO<sub>2</sub>/curcumin as well as TiO<sub>2</sub>/M-curcumin (M = Na<sup>+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>) was determined. The material was prepared on transparent conductive oxide as TiO<sub>2</sub> film. Then, the curcumin and curcumin derivatives were adsorbed on TiO<sub>2</sub> surface by immersing the film in solution of the compounds. The diffuse reflectance UV-Vis spectra of the materials were recorded and utilized to calculate the  $E_{\text{gap}}$  using the Tauc plot method. The calculation gave the  $E_{\text{gap}}$  of TiO<sub>2</sub> of 3.27 eV that lowers after being deposited with curcumin and metal-curcumin compounds. The  $E_{\text{gap}}$  of TiO<sub>2</sub>/curcumin was 2.82 eV, while TiO<sub>2</sub>/Na<sup>+</sup>-curcumin, TiO<sub>2</sub>/Mg<sup>2+</sup>-curcumin, and TiO<sub>2</sub>/Cu<sup>2+</sup>-curcumin were 2.36, 3.11, and 2.15 eV, respectively. Curcumin metal complexes, i.e., TiO<sub>2</sub>/Cu<sup>2+</sup>-curcumin, showed high molar absorptivity and effectively deposited on the TiO<sub>2</sub> lowers the bandgap energy of TiO<sub>2</sub> compared to free-curcumin on TiO<sub>2</sub>.

## 1. Introduction

Curcumin (1,7-bis [4-hydroxy-3-methoxy-phenyl]-1,6-heptadien-3,5-dione) is a fascinating compound in terms of its structure and potential functions that have been reported and discussed in various research reports and reviews [1, 2]. The molecular structure of curcumin contains two phenolic groups with a group of  $\beta$ -1,3 diketone, which can act as a ligand like acetylacetone. The diketone group undergoes keto-enol tautomers, forming stable complex compounds (Figure 1) [3].

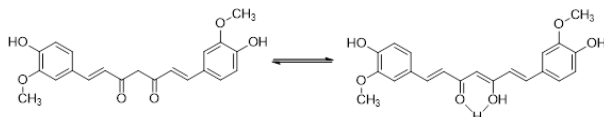


Figure 1. Keto-enol tautomerism of curcumin

Curcumin is an abundant natural compound colored due to the conjugated double bond structure that undergoes electronic transitions in the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  systems [4, 5]. This property can be exploited as a sensitizer in photovoltaic applications, for example, DSSC. In DSSC, dye is deposited on the TiO<sub>2</sub> layer surface, acting as a photosensitizer that absorbs photon energy from sunlight and generates excited electrons in the photoanode. The dye affects light absorption and the conversion of the light energy into electrical energy in

DSSC [6]. The application of various natural dyes as photosensitizers in DSSC has been reported [7].

Curcumin deposited on TiO<sub>2</sub> surface [8] or ZnO [9] tested for photosensitizers has been reported to widen the photon energy absorption range towards visible light compared to the metal oxides, which are photosensitive under UV light. Bandgap energy of curcumin-only was observed at about 2.30 eV [9, 10], while the electronic transition absorption of the molecule in solution is in the range of 300 – 600 nm, where the maximum wavelength is solvent dependent [5, 11]. The mixture of curcumin with copper oxide shows lower bandgap energy than curcumin-only from 2.30 eV (curcumin) to 2.27–2.16 eV getting smaller with increasing CuO concentration [10].

Light absorptivity and stability are two critical factors in the function of the dyes as a photosensitizer. The efficiency of light absorption can be improved by widening the absorption wavelength and increasing the light absorptivity of the dye [12]. The efficient sensitizer is expected to decrease the bandgap energy of materials which can be addressed by introducing the metals into the molecular structure of the dye. Complexes of curcumin from transition metals to the alkaline and alkaline earth groups coordinated through the  $\beta$ -1,3-diketone group of curcumin have been reported [2, 3, 4]. Complexation of

curcumin with metal ions, such as  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  improves their thermal stability and biological activity compared to the free-curcumin [4, 13]. The photostability of iron(III)-curcumin complex was also reported to be higher than that of the curcumin compound [11].

In this study, the electronic transition of curcumin complex compounds of metal ions, i.e., sodium(I), magnesium(II), and copper(II), was observed. The complex compounds were deposited onto the  $\text{TiO}_2$  surface to provide  $\text{TiO}_2/\text{M}$ -curcumin materials ( $\text{M} = \text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ), then the bandgap energy value of the materials was analyzed based on diffuse reflectance UV-Vis spectroscopic data. The electronic properties shown by the  $\text{TiO}_2/\text{M}$ -curcumin materials are the basis for its use as a photocatalyst or photosensitizer in DSSC. The selection of the three metals is based on the expansion of metal diversity, including light metals from the main group and metal representing transition metals. The preparation of these three types of metal curcumin compounds has been reported and characterized based on FTIR analysis [3].

## 2. Methodology

### 2.1. Equipment and Materials

The equipment used was a set of glassware, chromatography column, hotplate, UV lamp (254 nm), analytical balance (Mettler Toledo AE 60), magnetic stirrer, rotary evaporator, furnace, Perkin Elmer infrared spectrophotometer, Perkin Elmer Atomic Absorption Spectrophotometer (AAS), UV-Visible spectrophotometer (UV-Vis) Shimadzu UV 2600, and Shimadzu 2450 Diffuse Reflectance UV-Vis (DR/UV-Vis) spectrophotometer.

The materials used in this study were transparent conducting oxide (TCO), fluorine tin oxide (FTO), curcumin obtained from Sigma-Aldrich, titanium(IV) oxide ( $\text{TiO}_2$ ) P<sub>25</sub> 99.5% nanopowder 21 nm (Aldrich). Materials supplied by Merck were magnesium sulfate anhydrate ( $\text{MgSO}_4$ ), NaCl, copper(II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), TLC plate silica gel 60 Å pore size, silica gel for column chromatography pore size 60 Å, 99.7% glacial acetic acid, 99.8% acetonitrile, dichloromethane 99.8%, ethanol 98%, methanol 99.8%. All reagents are analytical grade and used directly without further treatment.

### 2.2. Sensitization of Curcumin and M-curcumin ( $\text{M} = \text{Na}^+$ , $\text{Mg}^{2+}$ , $\text{Cu}^{2+}$ ) on $\text{TiO}_2$ Surface [14]

First,  $\text{TiO}_2$  paste was prepared in which 2 g of the fine  $\text{TiO}_2$  (P25) powder was mixed with 5  $\text{cm}^3$  of glacial acetic acid and ten drops of acetonitrile while stirring with a magnetic stirrer form a paste. Transparent conductive oxide (TCO) was cleaned using ethanol; then, the  $\text{TiO}_2$  paste was deposited on the active glass surface with 1 cm x 1 cm of area. The  $\text{TiO}_2$  film was dried under ambient temperature then calcined in a furnace at 450°C for 2 hours.

The compounds of M-curcumin ( $\text{Na}^+$ -cur,  $\text{Mg}^{2+}$ -cur, and  $\text{Cu}^{2+}$ -cur) were synthesized following the method previously reported [3]. Curcumin and the complexes (2 g) were dissolved in 50  $\text{cm}^3$  ethanol giving a 40 ppm

concentration of the compounds. Curcumin and M-curcumin were sensitized on  $\text{TiO}_2$  surfaces based on the adsorption process. Titanium dioxide film on TCO was immersed in 15  $\text{cm}^3$  of the curcumin solution for 24 hours under dark conditions. Similarly,  $\text{TiO}_2$  films were also immersed in each curcumin complexes. After that, the films were dried in the oven to remove the solvent. The UV-Vis spectra of curcumin and M-curcumin solutions were recorded before and after the adsorption process to measure the percentage of compounds adsorbed on the  $\text{TiO}_2$  film.

The characterization of  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{M}$ -curcumin ( $\text{M} = \text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Cu}^{2+}$ ) materials was done using a Diffuse Reflectance UV-Vis (DR-UV-Vis) spectrophotometer, and the reflectance data obtained were analyzed by using the Tauc plot method to determine the change in bandgap energy ( $E_{\text{gap}}$ ). The  $E_{\text{gap}}$  value was calculated using the Tauc Plot method in which a linear graph of photon energy,  $h\nu$  (eV) on the x-axis, and the coefficient,  $(\text{Kh}\nu)^2$  on the y-axis were drawn. The bandgap energy is the photon energy value from the x-axis intersection obtained from the regression equation [15, 16].

The Tauc plot equation is as follows:

$$(\text{Kh}\nu)^{1/n} = K \cdot E \quad (1)$$

$$(\text{Kh}\nu)^{1/n} = \frac{(1-R)^2}{2R} \times \frac{hc}{\lambda} \quad (2)$$

Note:

R = reflectance

h = Plank constant ( $6,626 \times 10^{-34}$  J/s)

c = the speed of light ( $3 \times 10^8$  m/s)

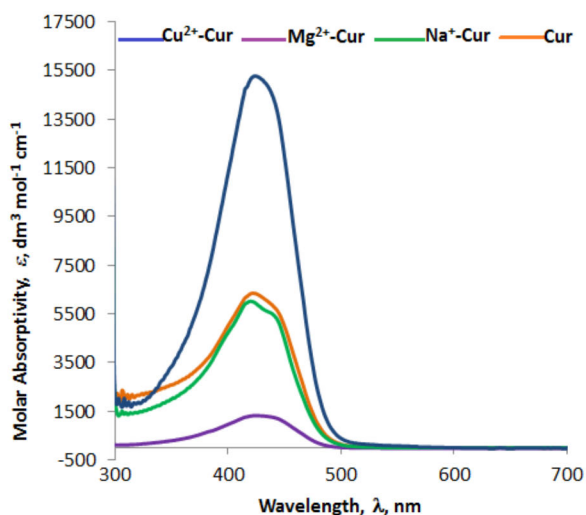
$\lambda$  = wavelength (nm)

n = 1/2 (direct transition)

## 3. Results and Discussion

### 3.1. Electronic Spectra of Curcumin and M-Curcumin ( $\text{M} = \text{Na}^+$ , $\text{Mg}^{2+}$ , $\text{Cu}^{2+}$ )

The electronic spectra of curcumin and M-curcumin measured in ethanol at room temperature are shown in Figure 2. The UV-Vis spectrum of curcumin shows absorption at 300–500 nm with a maximum wavelength of 420 nm with a shoulder at 443 nm. The absorption is attributed to the electronic transition of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  systems that are associated with the conjugated double bond structure in the curcumin molecule. Similar results were previously reported where the maximum wavelength was at 420 nm in methanol with a shoulder at longer wavelengths [17, 18], while in DMSO, the maximum wavelength was at 430–435 nm [4, 17]. The UV-Vis electronic transition in the system was influenced by the solvent. The polar solvent stabilized the polar chromophore of the keto-enol group in the curcumin molecule in both the ground state and the excited state through electrostatic interactions so that the transition energy of  $\pi \rightarrow \pi^*$  decreases while the transition energy of  $n \rightarrow \pi^*$  increases in polar solvents such as methanol [17]. This effect caused the two transition peaks to be close together in the polar solvents.



**Figure 2.** The UV-Vis spectra of curcumin and M-curcumin (M= Na<sup>+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>)

The metalation of curcumin with three metals from different groups appeared to change the electronic transition properties of curcumin differently, as shown in **Figure 2**. The Na<sup>+</sup>-curcumin spectrum shows a maximum peak at 420 nm with a shoulder at 443 nm slightly higher molar absorptivity than curcumin. The spectrum of Mg<sup>2+</sup>-curcumin demonstrates a drastic decrease in molar absorptivity with the maximum wavelength at 423 nm, shifting to a longer wavelength. Meanwhile, the Cu<sup>2+</sup>-curcumin shows a significant increase in molar absorptivity, three times higher than curcumin with a maximum wavelength that appeared only at 424 nm, experiencing a redshift (bathochromic).

The shift of the maximum peak and the appearance of one maximum peak indicate the metalation of curcumin in the β-1,3-diketone system, which is most evident in the Cu<sup>2+</sup>-curcumin spectrum. A similar observation was previously reported for Ca-curcumin complex showing the maximum peak at 430 nm, 433 nm for copper (II)-curcumin, and 446 nm for iron (III)-curcumin complex [18]. Complexation of diacetylcurcumin with metal ions Mg<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Mn<sup>2+</sup> also causes a shift in the maximum wavelength to a longer direction [19]. The properties of metal ions affect the shift in the wavelength of curcumin and light absorptivity. For example, complexation with transition metals such as chromium (II) and palladium (II) ions causes a more extended shift than that with the main group and rare earth metal ions [19]. This phenomenon was also observed in the Na<sup>+</sup>-curcumin, Mg<sup>2+</sup>-curcumin, and Cu<sup>2+</sup>-curcumin complexes prepared in this study.

### 3.2. Bandgap Energy of TiO<sub>2</sub>/M-Curcumin (M= Na<sup>+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>)

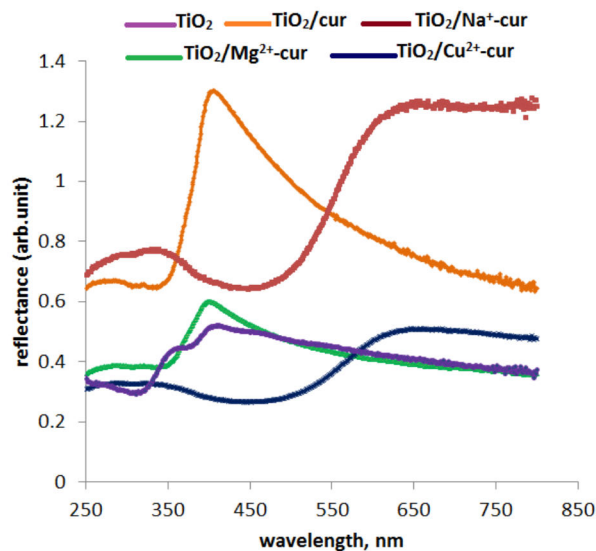
The TiO<sub>2</sub> paste was deposited on the surface of the FTO glass to produce a film. The preparation of the TiO<sub>2</sub> film was carried out where homogeneity of the particles and the surface area were considered so that it did not lose the ability to adsorb the sensitizer, i.e., curcumin and its derivatives, and accommodate the movement of electrons efficiently. The TiO<sub>2</sub> film was then sensitized by following the adsorption method of curcumin molecules and

curcumin complex compounds in solution. The concentration measured as absorbance in the UV-Vis spectra before and after adsorption shown in **Table 1** indicates the adsorption of compounds on the TiO<sub>2</sub> surface. The highest decrease in the absorbance spectrum after adsorption is shown in Cu<sup>2+</sup>-curcumin followed by Na<sup>+</sup>-curcumin, then curcumin, and the least is Mg<sup>2+</sup>-curcumin. It implies that the Cu<sup>2+</sup>-curcumin compound was adsorbed more effectively on TiO<sub>2</sub> film than other compounds with the order of Cu<sup>2+</sup>-curcumin > Na<sup>+</sup>-curcumin > curcumin > Mg<sup>2+</sup>-curcumin.

**Table 1.** The UV-Vis Absorbance of the Curcumin and M-Curcumin (M= Na<sup>+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>) at λ<sub>max</sub> Before and After Adsorption on TiO<sub>2</sub> Film

Compound	λ (nm)	Absorbance		Adsorption percentage
		Before adsorption	After adsorption	
Curcumin	420	0.687	0.678	1.31%
Na <sup>+</sup> -curcumin	420	0.782	0.768	1.79%
Mg <sup>2+</sup> -curcumin	423	0.871	0.862	1.03%
Cu <sup>2+</sup> -curcumin	424	0.992	0.957	3.52%

Bandgap energy of TiO<sub>2</sub> material is calculated based on the UV-Vis reflectance data using the Tauc plot equation. The diffuse reflectance-UV-Vis spectra of TiO<sub>2</sub>, TiO<sub>2</sub>/curcumin, and TiO<sub>2</sub>/M-curcumin (M = Na<sup>+</sup>, Mg<sup>2+</sup>, and Cu<sup>2+</sup>) are depicted in **Figure 3**, while the spectra that include Tauc plots are shown in **Figure 4**, and E<sub>gap</sub> values are presented in **Table 2**.



**Figure 3.** The diffuse reflectance-UV-Vis spectra of TiO<sub>2</sub>, TiO<sub>2</sub>/curcumin and TiO<sub>2</sub>/M-curcumin (M= Na<sup>+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>)

These data show a decrease in the bandgap energy of the TiO<sub>2</sub> material after combining with both curcumin and curcumin complex compounds. The E<sub>gap</sub> of TiO<sub>2</sub>/curcumin (2.82 eV) was within the range of previously reported values [9, 20, 21]. The TiO<sub>2</sub>/Mg<sup>2+</sup>-curcumin material shows tremendous bandgap energy than TiO<sub>2</sub>/curcumin, although it is still slightly smaller than TiO<sub>2</sub> itself. The most significant reduction in E<sub>gap</sub> was seen in TiO<sub>2</sub>/Cu<sup>2+</sup>-

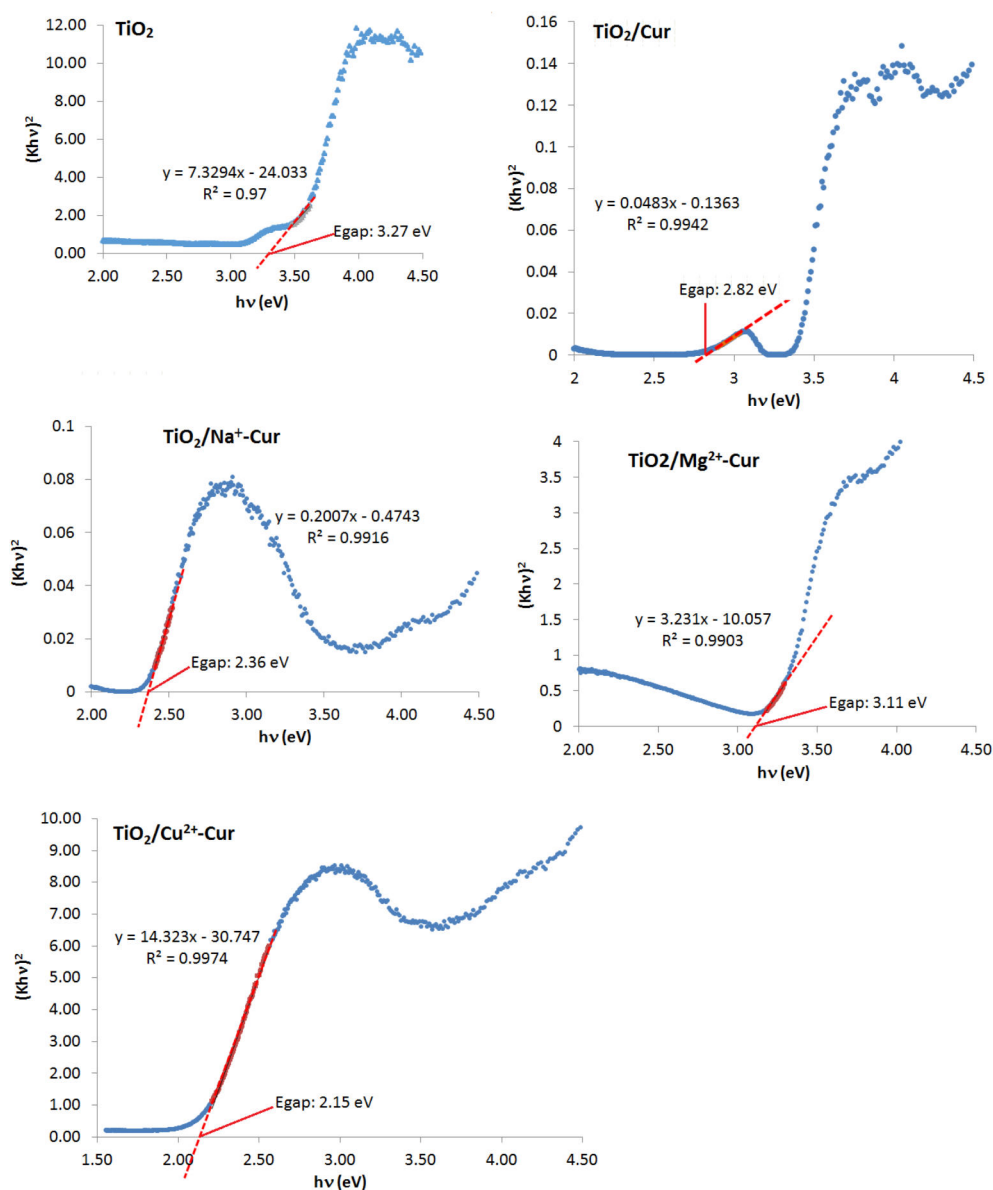
curcumin, then TiO<sub>2</sub>/Na<sup>+</sup>-curcumin. Similar observations have been reported for chlorophyll complexes, where the insertion of Cu<sup>2+</sup>-chlorophyll and Fe<sup>3+</sup>-chlorophyll compounds onto the surface of TiO<sub>2</sub> causes a decrease in the TiO<sub>2</sub> bandgap energy [14, 21].

**Table 2.** The  $E_{gap}$  Value for TiO<sub>2</sub>, TiO<sub>2</sub>/curcumin and TiO<sub>2</sub>/M-curcumin Materials (M= Na<sup>+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>)

Compound	$E_{gap}$ (eV), $\lambda$ (nm)
TiO <sub>2</sub>	3.27 (379)
TiO <sub>2</sub> /curcumin	2.82 (440)
TiO <sub>2</sub> /Na <sup>+</sup> -curcumin	2.36 (525)
TiO <sub>2</sub> /Mg <sup>2+</sup> -curcumin	3.11 (399)
TiO <sub>2</sub> /Cu <sup>2+</sup> -curcumin	2.15 (578)

Based on the observational data in this study, it can be seen that the trend of decreasing the bandgap energy

of TiO<sub>2</sub> seems the same as the light absorption value of the sensitizer molecules in solution in which the material indicates the highest decrease in the  $E_{gap}$  value with the highest ability to absorb light, namely Cu<sup>2+</sup>-curcumin. Likewise, on the other hand, TiO<sub>2</sub>/Mg<sup>2+</sup>-curcumin shows the  $E_{gap}$  value is not much different from TiO<sub>2</sub> material, and the molar absorptivity of Mg<sup>2+</sup>-curcumin is low. Another thing that can be seen from this experimental data is the higher number of sensitizer molecules adsorbed on the TiO<sub>2</sub> surface in line with the decrease in the sensitized-TiO<sub>2</sub>  $E_{gap}$ . The Cu<sup>2+</sup>-curcumin compound was adsorbed with the highest concentration compared to other compounds, showing the most significant decrease in  $E_{gap}$  of TiO<sub>2</sub>/Cu<sup>2+</sup>-curcumin. Meanwhile, the Mg<sup>2+</sup>-curcumin compound was absorbed in the least, only slightly lowering the  $E_{gap}$  from 3.27 eV (TiO<sub>2</sub>) to 3.11 eV (TiO<sub>2</sub>/Mg<sup>2+</sup>-curcumin).



**Figure 4.** The diffuse reflectance-UV-Vis spectra of TiO<sub>2</sub>, TiO<sub>2</sub>/curcumin, and TiO<sub>2</sub>/M-curcumin based on the equation of Tauc plot (M= Na<sup>+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>)

The introduction of metal into curcumin molecule that increases light absorption and is effectively adsorbed

on the TiO<sub>2</sub> surface enlarges the light absorption spectrum towards visible light by decreasing the bandgap

energy. The bathochromic shift occurs along with the interaction of TiO<sub>2</sub> with the curcumin complex molecule, where the molecule absorbs photons. The photon absorption causes electrons to be excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), which have a higher energy level than the TiO<sub>2</sub> conduction band. The excited electrons are injected into the TiO<sub>2</sub> conduction band to decrease the bandgap energy. This condition was observed in the curcumin molecule and the three curcumin complexes, but the most effective at reducing the bandgap energy of TiO<sub>2</sub> was the Cu<sup>2+</sup>-curcumin complex. This complex has a high light molar absorptivity and is most sensitized onto the TiO<sub>2</sub> surface compared to curcumin and the Na<sup>+</sup>-curcumin and Mg<sup>2+</sup>-curcumin complexes.

#### 4. Conclusion

Based on the research and discussion that has been done, it can be concluded that the bandgap energy of the TiO<sub>2</sub>/curcumin and TiO<sub>2</sub>/M-curcumin (M = Na<sup>+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>) material was smaller than the TiO<sub>2</sub> material itself, namely 3.27 eV for TiO<sub>2</sub>. In contrast, for TiO<sub>2</sub>/curcumin, TiO<sub>2</sub>/Na<sup>+</sup>-cur, TiO<sub>2</sub>/Mg<sup>2+</sup>-cur, and TiO<sub>2</sub>/Cu<sup>2+</sup>-cur were 2.82, 2.36, 3.11 and 2.15 eV, respectively. The incorporation of curcumin onto the TiO<sub>2</sub> lowers the bandgap energy. However, the metal-curcumin complex, which has high molar absorptivity and is effectively adsorbed on the TiO<sub>2</sub> surface, reduced the bandgap energy of TiO<sub>2</sub> significantly. The stability of complex compounds, solubility, and optimization of the deposition of compounds on the TiO<sub>2</sub> still need to be analyzed, considering its function as a photosensitizer or photocatalyst.

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