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Bandgap Energy of TiO_2/M-Curcumin Material (M = Na^+, Mg^{2+}, Cu^{2+})

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Abstract

Bandgap energy (E_{gap}) of TiO_2/curcumin as well as TiO_2/M-curcumin (M = Na^+, Mg^{2+}, Cu^{2+}) was determined. The material was prepared on transparent conductive oxide as TiO_2 film. Then, the curcumin and curcumin derivatives were adsorbed on TiO_2 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_{gap} using the Tauc plot method. The calculation gave the E_{gap} of TiO_2 of 3.27 eV that lowers after being deposited with curcumin and metal-curcumin compounds. The E_{gap} of TiO_2/curcumin was 2.82 eV, while TiO_2/Na^+-curcumin, TiO_2/Mg^{2+}-curcumin, and TiO_2/Cu^{2+}-curcumin were 2.36, 3.11, and 2.15 eV, respectively. Curcumin metal complexes, i.e., TiO_2/Cu^{2+}-curcumin, showed high molar absorptivity and effectively deposited on the TiO_2 lowers the bandgap energy of TiO_2 compared to free-curcumin on TiO_2.

1. Introduction

Curcumin (1,7-bis [4-hydroxy-3-methoxy-phenyl] -1,6-heptadien-3,5-dion) 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 β-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].

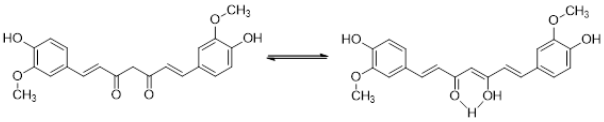

Figure 1. Keto-enol tautomerism of curcumin

Curcumin is an abundant natural compound colored due to the conjugated double bond structure that undergoes electronic transitions in the π-π^* and n-π^* 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_2 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_2 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 β-1,3-diketone group of curcumin have been reported [2, 3, 4]. Complexation of curcumin with metal ions, such as Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and 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 TiO_2 surface to provide TiO_2/M-curcumin materials (M= Na^+, Mg^{2+}, 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 TiO/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 (TiO_2) P_{25} 99.5% nanopowder 21 nm (Aldrich). Materials supplied by Merck were magnesium sulfate anhydrate ($MgSO_4$), NaCl, copper(II) chloride dihydrate ($CuCl_2.2H_2O$), 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. Sensitation of Curcumin and M-curcumin (M=Na^+, Mg^{2+}, Cu^{2+}) on TiO_2 Surface [14]

First, TiO_2 paste was prepared in which 2 g of the fine TiO_2 (P25) powder was mixed with 5 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 TiO_2 paste was deposited on the active glass surface with 1 cm x 1 cm of area. The TiO_2 film was dried under ambient temperature then calcined in a furnace at 450°C for 2 hours.

The compounds of M-curcumin (Na^+-cur, Mg^{2+}-cur, and Cu^{2+}-cur) were synthesized following the method previously reported [3]. Curcumin and the complexes (2 g) were dissolved in 50 cm^3 ethanol giving a 40 ppm concentration of the compounds. Curcumin and M-curcumin were sensitized on TiO_2 surfaces based on the adsorption process. Titanium dioxide film on TCO was immersed in 15 cm^3 of the curcumin solution for 24 hours under dark conditions. Similarly, 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 TiO_2 film.

The characterization of TiO_2, TiO_2/M-curcumin (M = Na^+, Mg^{2+}, and 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_{gap}). The E_{gap} value was calculated using the Tauc Plot method in which a linear graph of photon energy, hν (eV) on the *x*-axis, and the coefficient, $(Kh\nu)^2$ 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:

$$(Kh\nu)^{1/n} = K.E \tag{1}$$

$$(Kh\nu)^{1/n} = \frac{(1-R)^2}{2R} x \frac{hc}{\lambda} \tag{2}$$

Note:
R = reflectance
h = Plank constant (6,626 x 10^{-34} J/s)
c = the speed of light (3 x 10^8 m/s)
λ = wavelength (nm)
n = ½ (direct transition)

3. Results and Discussion

3.1. Electronic Spectra of Curcumin and M-Curcumin (M= Na^+, Mg^{2+}, 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.

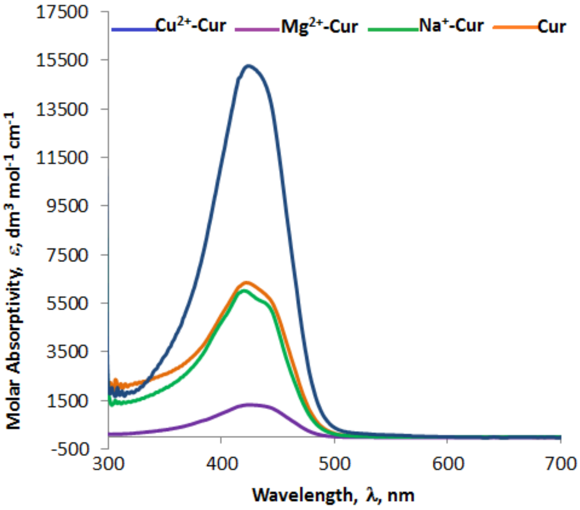

Figure 2. The UV-Vis spectra of curcumin and M-curcumin (M= Na^+, Mg^{2+}, Cu^{2+})

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^+-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^{2+}-curcumin demonstrates a drastic decrease in molar absorptivity with the maximum wavelength at 423 nm, shifting to a longer wavelength. Meanwhile, the Cu^{2+}-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^{2+}-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^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+} 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^+-curcumin, Mg^{2+}-curcumin, and Cu^{2+}-curcumin complexes prepared in this study.

3.2. Bandgap Energy of TiO_2/M-Curcumin (M= Na^+, Mg^{2+}, Cu^{2+})

The TiO_2 paste was deposited on the surface of the FTO glass to produce a film. The preparation of the TiO_2 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_2 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_2 surface. The highest decrease in the absorbance spectrum after adsorption is shown in Cu^{2+}-curcumin followed by Na^+-curcumin, then curcumin, and the least is Mg^{2+}-curcumin. It implies that the Cu^{2+}-curcumin compound was adsorbed more effectively on TiO_2 film than other compounds with the order of Cu^{2+}-curcumin > Na^+-curcumin > curcumin > Mg^{2+}-curcumin.

Table 1. The UV-Vis Absorbance of the Curcumin and M-Curcumin (M= Na^+, Mg^{2+}, Cu^{2+}) at λ_{max} Before and After Adsorption on TiO_2 Film

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

Bandgap energy of TiO_2 material is calculated based on the UV-Vis reflectance data using the Tauc plot equation. The diffuse reflectance-UV-Vis spectra of TiO_2, TiO_2/ curcumin, and TiO_2/ M-curcumin (M = Na^+, Mg^{2+}, and Cu^{2+}) are depicted in **Figure 3**, while the spectra that include Tauc plots are shown in **Figure 4**, and E_{gap} values are presented in **Table 2.**

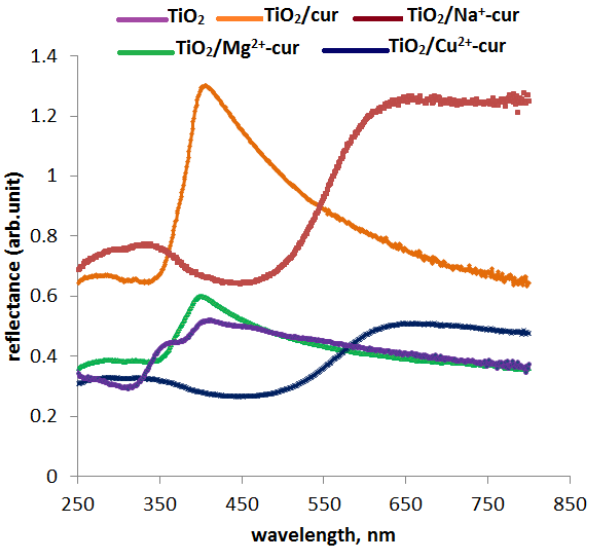

Figure 3. The diffuse reflectance-UV-Vis spectra of TiO_2, TiO_2/curcumin and TiO_2/M-curcumin (M= Na^+, Mg^{2+}, Cu^{2+})

These data show a decrease in the bandgap energy of the TiO_2 material after combining with both curcumin and curcumin complex compounds. The E_{gap} of TiO_2/curcumin (2.82 eV) was within the range of previously reported values [9, 20, 21]. The TiO_2/Mg^{2+}-curcumin material shows tremendous bandgap energy than TiO_2/curcumin, although it is still slightly smaller than TiO_2 itself. The most significant reduction in E_{gap} was seen in TiO_2/Cu^{2+}-

curcumin, then TiO_2/Na^+-curcumin. Similar observations have been reported for chlorophyll complexes, where the insertion of Cu^{2+}-chlorophyll and Fe^{3+}-chlorophyll compounds onto the surface of TiO_2 causes a decrease in the TiO_2 bandgap energy[14, 21].

Table 2. The E_{gap} Value for TiO_2, TiO_2/curcumin and TiO_2/M-curcumin Materials (M= Na^+, Mg^{2+}, Cu^{2+})

Compound	E_{gap} (eV), λ (nm)
TiO_2	3.27 (379)
TiO_2/curcumin	2.82 (440)
TiO_2/Na^+-curcumin	2.36 (525)
TiO_2/Mg^{2+}-curcumin	3.11 (399)
TiO_2/Cu^{2+}-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_2 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^{2+}-curcumin. Likewise, on the other hand, TiO_2/Mg^{2+}-curcumin shows the E_{gap} value is not much different from TiO_2 material, and the molar absorptivity of Mg^{2+}-curcumin is low. Another thing that can be seen from this experimental data is the higher number of sensitizer molecules adsorbed on the TiO_2 surface in line with the decrease in the sensitized-TiO_2 Egap. The Cu^{2+}-curcumin compound was adsorbed with the highest concentration compared to other compounds, showing the most significant decrease in E_{gap} of TiO_2/Cu^{2+}-curcumin. Meanwhile, the Mg^{2+}-curcumin compound was absorbed in the least, only slightly lowering the E_{gap} from 3.27 eV (TiO_2) to 3.11 eV (TiO_2/Mg^{2+}-curcumin).

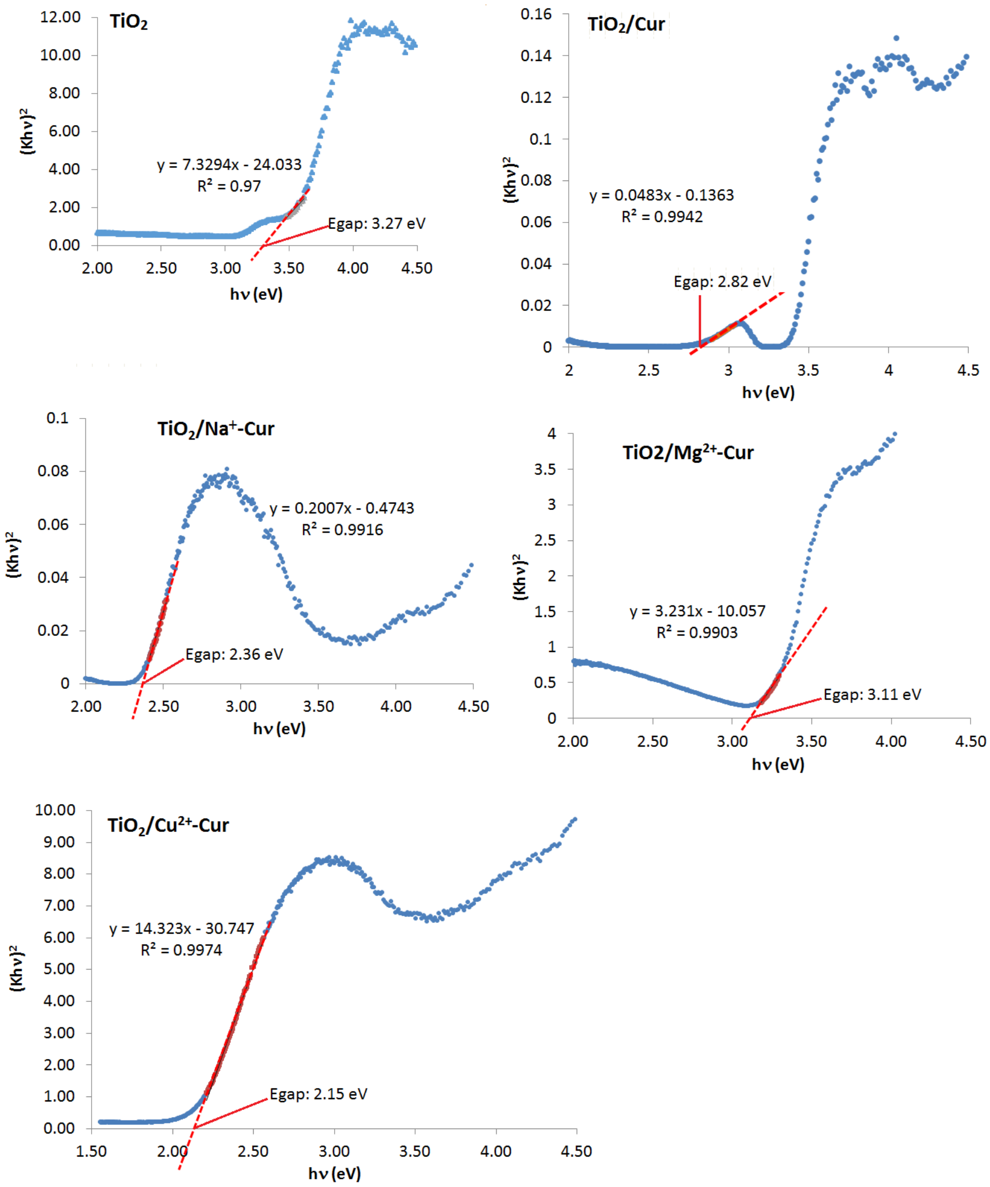

Figure 4. The diffuse reflectance-UV-Vis spectra of TiO_2, TiO_2/curcumin, and TiO_2/M-curcumin based on the equation of Tauc plot (M= Na^+, Mg^{2+}, Cu^{2+})

The introduction of metal into curcumin molecule that increases light absorption and is effectively adsorbed on the TiO_2 surface enlarges the light absorption spectrum towards visible light by decreasing the bandgap energy. The bathochromic shift occurs along with the interaction of TiO_2 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_2 conduction band. The excited electrons are injected into the TiO_2 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_2 was the Cu^{2+}-curcumin complex. This complex has a high light molar absorptivity and is most sensitized onto the TiO_2 surface compared to curcumin and the Na^+-curcumin and Mg^{2+}-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_2/curcumin and TiO_2/M-curcumin ($M = Na^+$, Mg^{2+}, Cu^{2+}) material was smaller than the TiO_2 material itself, namely 3.27 eV for TiO_2. In contrast, for TiO_2/curcumin, TiO_2/Na^+-cur, TiO_2/Mg^{2+}-cur, and TiO_2/Cu^{2+}-cur were 2.82, 2.36, 3.11 and 2.15 eV, respectively. The incorporation of curcumin onto the TiO_2 lowers the bandgap energy. However, the metal-curcumin complex, which has high molar absorptivity and is effectively adsorbed on the TiO_2 surface, reduced the bandgap energy of TiO_2 significantly. The stability of complex compounds, solubility, and optimization of the deposition of compounds on the TiO_2 still need to be analyzed, considering its function as a photosensitizer or photocatalyst.

References

[1] Yanan Zhang, Abdur Rauf Khan, Manfei Fu, Yujia Zhai, Aihua Yu, Guangxi Zhai, The progresses in curcuminoids-based metal complexes: especially in cancer therapy, *Future medicinal chemistry*, 11, 9, (2019), 1035-1056 https://doi.org/10.4155/fmc-2018-0190

[2] Simon Wanninger, Volker Lorenz, Abdus Subhan, Frank T. Edelmann, Metal complexes of curcumin–synthetic strategies, structures and medicinal applications, *Chemical Society Reviews*, 44, 15, (2015), 4986-5002 https://doi.org/10.1039/C5CS00088B

[3] Peni Peni, Risya Sasri, Imelda Hotmarisi Silalahi, Synthesis of Metal–Curcumin Complex Compounds ($M = Na^+$, Mg^{2+}, Cu^{2+}), *Jurnal Kimia Sains dan Aplikasi*, 23, 3, (2020), 75-82 https://doi.org/10.14710/jksa.23.3.75-82

[4] Moamen S. Refat, Synthesis and characterization of ligational behavior of curcumin drug towards some transition metal ions: Chelation effect on their thermal stability and biological activity, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 105, (2013), 326-337 https://doi.org/10.1016/j.saa.2012.12.041

[5] Bachar Zebib, Zéphirin Mouloungui, Virginie Noirot, Stabilization of curcumin by complexation with divalent cations in glycerol/water system, *Bioinorganic chemistry and applications*, 2010, (2010), Article ID 292760 https://doi.org/10.1155/2010/292760

[6] Jiawei Gong, K. Sumathy, Qiquan Qiao, Zhengping Zhou, Review on dye-sensitized solar cells (DSSCs): Advanced techniques and research trends, *Renewable and Sustainable Energy Reviews*, 68, (2017), 234-246 https://doi.org/10.1016/j.rser.2016.09.097

[7] Monishka Rita Narayan, Review: Dye Sensitized Solar Cells Based on Natural Photosensitizers, *Renewable and Sustainable Energy Reviews*, 16, 1, (2012), 208-215 https://doi.org/10.1016/j.rser.2011.07.148

[8] Khalil Ebrahim Jasim, Seamas Cassidy, Feryad Zaki Henari, Akil Aziz Dakhel, Curcumin dye-sensitized solar cell, *Journal of Energy and Power Engineering*, 11, (2017), 409-416 http://dx.doi.org/10.17265/1934-8975/2017.06.006

[9] D. Sinha, D. De, A. Ayaz, Performance and stability analysis of curcumin dye as a photo sensitizer used in nanostructured ZnO based DSSC, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 193, (2018), 467-474 https://doi.org/10.1016/j.saa.2017.12.058

[10] Kokkarachedu Varaprasad, Matias López, Dariela Núñez, Tippabattini Jayaramudu, Emmanuel Rotimi Sadiku, Chandrasekaran Karthikeyan, Patricio Oyarzúnc, Antibiotic copper oxide-curcumin nanomaterials for antibacterial applications, *Journal of Molecular Liquids*, 300, (2020), 112353 https://doi.org/10.1016/j.molliq.2019.112353

[11] Fatima Mohammed, Fiza Rashid-Doubell, Seamas Cassidy, Fryad Henari, A comparative study of the spectral, fluorometric properties and photostability of natural curcumin, iron-and boron-complexed curcumin, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 183, (2017), 439-450 https://doi.org/10.1016/j.saa.2017.04.027

[12] Mian-En Yeoh, Kah-Yoong Chan, Recent advances in photo-anode for dye-sensitized solar cells: a review, *International Journal of Energy Research*, 41, 15, (2017), 2446-2467 https://doi.org/10.1002/er.3764

[13] Samya Banerjee, Akhil R. Chakravarty, Metal complexes of curcumin for cellular imaging, targeting, and photoinduced anticancer activity, *Accounts of chemical research*, 48, 7, (2015), 2075-2083 https://doi.org/10.1021/acs.accounts.5b00127

[14] Muhammad Yusprianto, Titin Anita Zaharah, Imelda Hotmarisi Silalahi, Bandgap Energy of TiO_2/M-Chlorophyll Material ($M=Cu^{2+}$, Fe^{3+}), *Jurnal Kimia Sains dan Aplikasi*, 24, 4, (2021), 126-135 https://doi.org/10.14710/jksa.24.4.126-135

[15] Jonathan P. Blitz, Diffuse Reflectance Spectroscopy, in: F.M. Mirabella (Ed.) *Modern Techniques in Applied Molecular Spectroscopy*, John Wiley & Sons, Inc, New York, 1998,

[16] Patrycja Makuła, Michał Pacia, Wojciech Macyk, How to Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV–Vis Spectra, *The Journal of Physical Chemistry Letters*, 9, 23, (2018), 6814-6817 https://doi.org/10.1021/acs.jpclett.8b02892

[17] M. A. Subhan, K. Alam, M. S. Rahaman, M. A. Rahman, R. Awal, Synthesis and characterization of

metal complexes containing curcumin ($C_{21}H_{20}O_6$) and study of their anti-microbial activities and DNA-binding properties, *Journal of Scientific research*, 6, 1, (2014), 97-109 http://dx.doi.org/10.3329/jsr.v6i1.15381

[18] Quang Hieu Tran, Thanh Thao Doan, A novel study on curcumin metal complexes: solubility improvement, bioactivity, and trial burn wound treatment in rats, *New Journal of Chemistry*, 44, 30, (2020), 13036-13045 https://doi.org/10.1039/D0NJ01159B

[19] William Meza-Morales, Mirian Estevez, Yair Alvarez-Ricardo, Marco Obregón, Julia Cassani, María Apan, Carolina Escobedo, Manuel Soriano, William Reynolds, Raul Enriquez, Full Structural Characterization of Homoleptic Complexes of Diacetylcurcumin with Mg, Zn, Cu, and Mn: Cisplatin-level Cytotoxicity in Vitro with Minimal Acute Toxicity in Vivo, *Molecules*, 24, 8, (2019), 1598 http://dx.doi.org/10.3390/molecules24081598

[20] Z. M. Abou-Gamra, M. A. Ahmed, Synthesis of mesoporous TiO_2–curcumin nanoparticles for photocatalytic degradation of methylene blue dye, *Journal of Photochemistry and Photobiology B: Biology*, 160, (2016), 134-141 https://doi.org/10.1016/j.jphotobiol.2016.03.054

[21] Azadeh Haghighatzadeh, Comparative analysis on optical and photocatalytic properties of chlorophyll/curcumin-sensitized TiO_2 nanoparticles for phenol degradation, *Bulletin of Materials Science*, 43, 1, (2020), 52 https://doi.org/10.1007/s12034-019-2016-9