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Optical Properties of *Citrus hystrix* and *Curcuma*-Incorporated Micro- and Nano-TiO_2 Films for Dye-Sensitized Solar Cell Photoanodes

Musyarofah[1*], Bellia Prafilta Enggar Sasmita[1], Fadli Robiandi[1], Nurrisma Puspitasari[2], Budi Prayitno[3*]

[1] *Department of Physics, Institut Teknologi Kalimantan, Indonesia*
[2] *Department of Physics, Institut Teknologi Sepuluh Nopember, Indonesia*
[3] *Department of Mechanical Engineering, Universitas Balikpapan, Indonesia*

Corresponding Authors E-mail: musyarofah@lecturer.itk.ac.id, budi.prayitno@uniba-bpn.ac.id

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Abstract

Natural-dye-sensitized TiO_2 films are promising photoanode materials for dye-sensitized solar cells (DSSCs) because natural dyes provide visible-light absorption and offer an environmentally friendly alternative to synthetic sensitizers. This study investigated the influence of sensitizer type, co-sensitization, and TiO_2 crystallite size on the optical absorption properties and apparent optical band gap of dye-sensitized TiO_2 films. Micro- and nano-TiO_2 films sensitized with Citrus hystrix, Curcuma sp., and mixed-dye sensitizers were deposited on indium tin oxide (ITO) substrates by spin-coating. The optical responses of the films were analyzed using UV-Vis spectroscopy, and the apparent optical band gap energies were determined using the Tauc plot method. The research revealed that both sensitizer type and TiO_2 crystallite sizes influenced the optical properties of the samples. Films containing Citrus hystrix exhibited higher optical absorption than those containing Curcuma sp. in both micro- and nano-TiO_2 systems. The apparent optical band gap ranged from 2.82 to 3.68 eV. Of all the samples investigated, the nano-TiO_2/Citrus hystrix films showed the least apparent optical band gap of 2.82 eV, revealing the most extended optical response toward low photon energies. Although co-sensitization extended the absorption profile, it did not yield lower apparent optical band-gap energies than those of the Citrus hystrix films. These results suggest that the optical behavior of dye-incorporated TiO2 films depends on the sensitizer-TiO2 combination. Each film configuration was fabricated and measured once; therefore, the reported values represent individual measurements without replicate-based statistical uncertainty. The results shed light on the production of TiO_2-based photoanodes that are environmentally friendly for DSSC applications.

Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable attention as an alternative photovoltaic technology because of their relatively low production cost, simple fabrication process, and potential for operation under diffuse-light conditions [1], [2]. In DSSCs, the photoanode plays a crucial role in harvesting solar energy and transporting photo-generated electrons [3], [4]. The device's overall performance is therefore strongly influenced by both the optical properties of the sensitizer and the characteristics of the semiconductor material [2]. Consequently, considerable efforts have been devoted to developing photoanode systems that extend light absorption into the visible region while maintaining efficient electron transfer.

Among various sensitizers, natural dyes have emerged as environmentally friendly alternatives to conventional ruthenium-based complexes. Natural pigments derived from plants are attractive because they are abundant, biodegradable, inexpensive, and non-toxic [5], [6], [7]. Numerous studies have investigated chlorophyll- [8], [9], anthocyanin- [10], [11], [12], carotenoid- [13], [14], and curcuminoid- [15], [16], [17] containing extracts as DSSC sensitizers, demonstrating their ability to enhance visible-light absorption through photosensitization of TiO_2. However, the optical performance of natural dyes varies significantly with pigment composition, extraction source, and interactions with the semiconductor surface. Therefore, identifying and optimizing suitable natural sensitizers remains an important challenge in the development of sustainable DSSC materials.

Co-sensitization, a process in which multiple sensitizers are employed to expand the photoanode's range of absorbing the sunlight, has recently emerged as a highly promising concept for photovoltaic devices [18]. A few studies showed that light trapping by co-sensitization could be increased by combining two absorption bands from different dyes [19]. The problem is that the success of this method relies on multiple things: dye compatibility, adsorption and desorption, molecular interactions, as well as the semiconductor surface [20], [21-26]. Hence, a wider spectrum may result in worse performance from an optical or even photovoltaic viewpoint. Therefore, more experiments on the interactions of natural dyes are needed before a clear conclusion can be reached regarding their effect on the optical properties of TiO_2-based photoanodes.

Titanium dioxide (TiO_2) is one of the semiconductor materials that have found their way into DSSC photoanodes due to its chemical inertness, low cost, safety, and good electronic behavior. Another factor that can greatly affect the optical properties of TiO_2 is particle size or shape. It has been reported in the literature that decreasing TiO_2 crystallite size not only alters its optical performance, but also increases the surface area for dye molecule adsorption [27]. Such modifications could increase contact with the semiconductor, thereby affecting the photoanode's light output. Studies have also shown that dye sensitization changes the optical absorption and seems to alter the band gap of TiO_2 films, depending on the type of sensitizer used [28-31]. Moreover, it has been found that the changes in TiO_2 crystallite sizes can also influence to a very large extent the optical band-gap of TiO_2 films [32-33]. These results, in the main, confirm that both the dye molecules and the physical properties of the TiO2 material play important roles in the optical behavior of TiO2 photoanodes.

In our previous work [34], natural dye extracts from several plant sources were evaluated for DSSC applications. Among the investigated materials, *Citrus hystrix* and *Curcuma sp*. exhibited favorable optical absorption characteristics in the visible-light region, indicating their potential as natural sensitizers. In a separate study [27], micro and nano-TiO_2 powders were successfully prepared and characterized, revealing differences in crystallite size and optical properties. These previous studies independently demonstrated the optical potential of the selected natural dyes and the influence of TiO_2 crystallite size on semiconductor properties. However, the optical response of dye-incorporated TiO_2 films, in which both the sensitizer characteristics and TiO_2 crystallite size simultaneously determine photoanode behavior, has received comparatively limited attention.

Despite these previous investigations, the optical characteristics of films prepared by combining *Citrus hystrix* and *Curcuma sp.* sensitizers with micro- and nano-TiO_2 have not yet been systematically evaluated. In particular, the combined influence of sensitizer type, co-sensitization, and TiO_2 crystallite size on the optical absorption behavior and apparent optical band-gap energies of the resulting films remains unclear. Although co-sensitization is widely employed to broaden the spectral absorption range of DSSC photoanodes, it remains unclear whether broader light absorption necessarily corresponds to a more favorable optical response or to a lower apparent optical band gap than that observed with single-dye sensitizers. Clarifying this relationship is important for determining whether spectral broadening alone can serve as an indicator of improved optical performance in natural-dye-sensitized TiO_2 photoanodes.

Therefore, this study investigates the optical absorption characteristics and apparent optical band gap energies of micro- and nano-TiO_2 films sensitized with extracts of *Citrus hystrix*, *Curcuma sp.*, and their mixture. Particular attention is given to the combined effects of sensitizer type, co-sensitization, and TiO_2 crystallite size on the optical response of the films. Rather than simply evaluating combinations of natural dyes, this work seeks to determine whether co-sensitization produces distinct optical behavior and apparent optical band-gap trends compared with single-dye systems. The results are expected to provide a better understanding of the relationship among dye selection, TiO_2 crystallite size, and the optical behavior of dye-incorporated TiO_2 films used as DSSC photoanodes.

Experimental Method

Materials

Commercial anatase TiO_2 powder (Merck) was used as the semiconductor material. Natural dyes were extracted from *Citrus hystrix* leaves and *Curcuma sp*. rhizomes. Ethanol was used as the extraction solvent. Indium tin oxide (ITO) glass substrates measuring 2.5 × 2.5 cm^2 were used as conductive substrates for film deposition.

Preparation of Natural Dye Extracts

Natural dye extracts were prepared following the procedure reported in our previous work [34]. Briefly, the plant materials were washed, dried, and ground into powder. The powders were then extracted by maceration in ethanol using a solid-to-solvent ratio of 2 g:30 ml for two consecutive 24-hour periods (48 h in total), followed by filtration. The resulting filtrates were used as natural dye sensitizers. Detailed extraction procedures and optical characterization of the extracts have been reported elsewhere [34].

Preparation of Micro- and Nano-TiO_2 Powders

Micro- and nano-TiO_2 powders were prepared according to our previously reported method [27]. The micro-TiO_2 powder was obtained from commercial anatase TiO_2 and sieved through a 325-mesh screen. Nano-TiO_2 powder was produced by planetary ball milling using a Pulverisette 5 mill for 20 h at a rotational speed of 150 rpm. Zirconia balls with a diameter of

5 mm were used as the milling media, and ethanol was added during milling at a TiO_2-to-ethanol ratio of 10 g:15 ml. The milled powder was subsequently annealed at 90 °C for 3 h to remove residual ethanol. Detailed structural and optical characterization of the micro- and nano-TiO_2 powders has been reported previously [27].

Fabrication of Dye-Incorporated TiO_2 Films

Dye-incorporated TiO_2 films were fabricated on ITO glass substrates using a spin-coating technique. Prior to deposition, the ITO substrates were cleaned with ethanol and dried under ambient conditions. For the single-dye films, 0.5 g of micro- or nano-TiO_2 powder was mixed with 2 mL of either *Citrus hystrix* or *Curcuma sp.* extract and magnetically stirred for 10 min to obtain a homogeneous suspension. Approximately 170 µL of the suspension was deposited onto the ITO substrate and spin-coated for 60 s using a three-step program consisting of 500 rpm for 5 s, 1000 rpm for 10 s, and 2500 rpm for 45 s. The gradual increase in rotational speed was employed to improve film uniformity and control film thickness. For the co-sensitized films, 0.5 g of TiO_2 powder was mixed with *Citrus hystrix* and *Curcuma sp*. extracts at a 1:1 (v/v) ratio (1 mL each). The suspension preparation, deposition procedure, and spin-coating conditions were identical to those used for the single-dye films. Following deposition, all films were heated on a hot plate at 100 °C for 10 min to remove residual solvent and improve film adhesion to the substrate. Six film configurations were prepared: micro-TiO_2/*Citrus hystrix*, micro-TiO_2/*Curcuma sp*., micro-TiO_2/*Citrus hystrix–Curcuma sp.,* nano-TiO_2/*Citrus hystrix,* nano-TiO_2/*Curcuma sp.,* and nano-TiO_2/*Citrus hystrix–Curcuma sp.*

UV–Vis Characterization and Apparent Optical Band Gap Analysis

The optical absorption characteristics of the fabricated films were investigated using a UV–Vis spectrophotometer (Analytik Jena Specord 200 Plus) in the wavelength range of 200–700 nm. The absorption spectra were used to evaluate the optical response of the dye-incorporated TiO_2 films. The apparent optical band-gap energies of the films were estimated using the Tauc method. Since anatase TiO_2 is commonly treated as an indirect-transition semiconductor, the optical band-gap energy was determined using Equation 1.

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

where α is the absorption coefficient, $h\upsilon$ is the photon energy, A is a proportionality constant, and E_g is the apparent optical band-gap energy. The apparent optical band-gap energy was obtained by extrapolating the linear region of the Tauc plot to the photon-energy axis ($h\nu$). The intercept of the fitted line with the horizontal axis corresponds to the apparent optical band-gap value. For each sample, the linear fitting region was selected from the dominant rising absorption edge in the Tauc plot, avoiding regions with pronounced non-linear curvature or weak absorption tails. The absorption contributions from the dye and TiO_2 were not mathematically separated because the objective was to determine the apparent optical band gap of the combined dye–TiO_2 system. Therefore, the resulting intercept represents an effective optical transition energy of the sensitized film rather than the intrinsic band gap of TiO_2. Data processing, linear fitting, and graphical analysis were performed using Origin software. Each film composition was prepared once under identical fabrication conditions and characterized using a single UV–Vis measurement. Accordingly, the apparent optical band-gap values reported in this study were determined from individual Tauc plot analyses for each sample. Because each film composition was fabricated and measured only once, statistical uncertainty and sample-to-sample variation could not be estimated. Therefore, no standard deviation or experimental uncertainty derived from replicate measurements is reported for the apparent optical band-gap values.

Result and Discussion

Optical Absorption Characteristics of Sensitized TiO_2 Photoanodes

Figure 1 presents the UV–Vis absorption spectra of micro- and nano-TiO_2 films sensitized with *Citrus hystrix* extract, *Curcuma sp*. extract, and a combination of both extracts. All films exhibit strong absorption in the ultraviolet region below 400 nm, with weaker absorption bands in the visible region. The predominance of ultraviolet absorption may indicate that the films' optical response is still largely governed by TiO_2's intrinsic electronic transition. Previous characterization of the TiO_2 powders used in this work [27] showed UV absorption maxima and band-gap energies typical of anatase TiO_2. Therefore, the absorption bands below 400 nm can be mainly attributed to electron excitation from the valence band to the conduction band of TiO_2, whereas the absorption observed in the visible region originates from the adsorbed dye molecules.

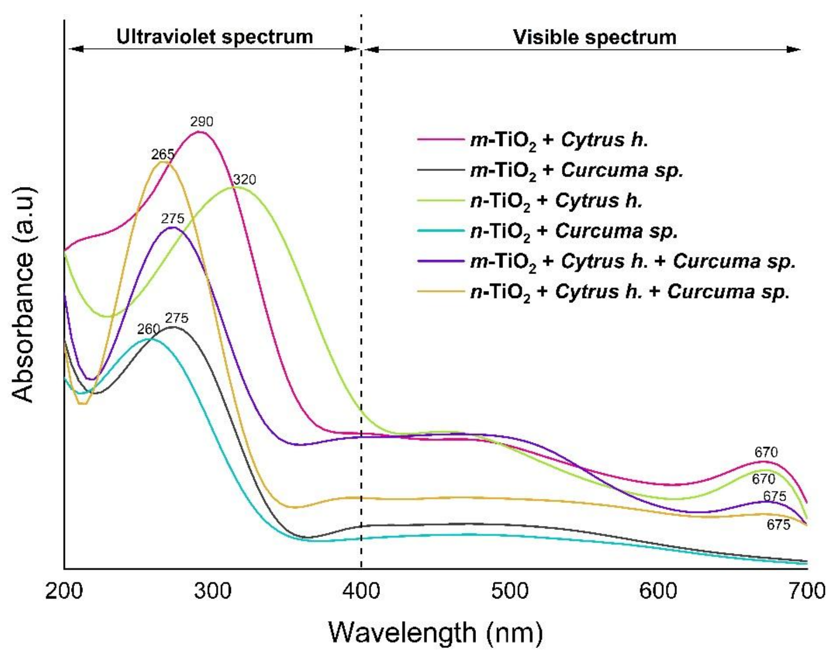

Figure 1. UV-Vis absorption spectra of micro- and nano-TiO_2 films co-sensitized with single and double natural dye extracts.

Sensitization of TiO_2 films with different natural dyes significantly influences their absorption properties. Both micro- and nano-TiO_2 systems, films sensitized with *Citrus hystrix*, show generally more intense absorption than those sensitized with *Curcuma sp*. The micro-TiO_2 film sensitized with *Citrus hystrix* exhibits the most prominent absorption peak at around 290 nm, whereas the *Curcuma*-sensitized film has a lower one at about 275 nm. Nano-TiO_2 films also show this difference. *Citrus hystrix* yields a wide absorption band peaking near 320 nm, whereas *Curcuma sp*. barely reaches an absorption maximum at around 260 nm.

The greater absorption intensity of the *Citrus hystrix*-sensitized films coincides with the intrinsic optical features of the neat extracts documented in our earlier work [34]. The UV-visible spectra of the extracts showed that *Citrus hystrix* exhibits broader absorption and greater absorption in the visible region than *Curcuma sp.* Even after adsorption on the TiO2 surface, this difference remains noticeable in the sensitized films, indicating that the pigments in *Citrus hystrix* remain capable of harvesting light and thus remain a major factor in the photoanode's optical response. This result suggests a relationship between the optical properties of the pristine dye extract and the resulting absorption behavior of the sensitized TiO_2 film. Similar correlations have been reported for natural-dye-sensitized [19] photoanodes, where extracts with stronger visible-light absorption generally produce more optically active photoanodes, could be related to enhanced photon harvesting and more efficient electronic coupling with the semiconductor surface.

Comparing micro- and nano-TiO_2 films shows that reducing the TiO_2 crystallite size does not always increase absorption intensity. The effect of crystallite size is actually manifested by changes in the absorption pattern and peak positions. In *Citrus hystrix* -film, the absorption peak moves from about 290 nm in micro-TiO_2 to approximately 320 nm in nano-TiO_2. On the other hand, *Curcuma* -film absorption peaks are found at around 275 nm and 260 nm for the micro- and nano-TiO_2 samples, respectively. These spectral differences imply that crystallite size affects the dye molecule–semiconductor surface interaction. Nanostructured TiO_2 usually offers more adsorption sites and a larger specific surface area than larger crystallites. However, the results presented here suggest that the effect of crystallite size is much more complicated than a mere increase in dye loading. Alterations in surface energy, adsorption configuration, intermolecular spacing, and electronic coupling of dye molecules and TiO_2 may change the optical response of the sensitized films [35-39]. Finally, crystallite size primarily affects the absorption characteristics and therefore should not be regarded as uniformly enhancing absorbance at all spectral regions.

The co-sensitized films comprising both *Citrus hystrix* and *Curcuma sp*. exhibit absorption features that are distinctly different from those of single-dye systems. The absorption peak of the micro-TiO_2 co-sensitized film is located at around 275 nm, whereas the peak of the nano-TiO_2 co-sensitized film is situated near 265 nm. The co-sensitization undoubtedly changes the absorption spectrum and expands the spectral response, but it does not attain the maximum absorption among all the samples studied. This finding implies that the optical characteristics of co-sensitized materials are not a mere sum of the individual dye absorption spectra. In fact, during co-sensitization, the different dye molecules mutually limit the adsorption sites on the TiO_2 surface [40]. On top of that, the final spatial layout of the dye molecules on the semiconductor surface could be dictated by intermolecular interactions, steric constraints, aggregation effects, and differences in adsorption affinity that, in turn, may lead to different surface coverages of the individual dyes [41-43]. Therefore, broader spectral coverage does not necessarily translate into stronger absorbance. Complementing such experimental results, previous co-sensitization studies have reported similar observations, i.e., combining two dyes was very effective in broadening the absorption spectrum, but the optical response was not always proportionally improved, which may be associated with competitive adsorption and molecular interaction effects [19], [44].

A significant feature of Figure 1 is the emergence of rather weak, though quite distinct absorption peaks in the visible region centered at approximately 670–675 nm. Pure TiO_2 does not exhibit such absorption; hence, the absorption is due to adsorbed natural dyes. Interestingly, the UV–Vis spectrum of the *Citrus hystrix* extract also showed an absorption feature in this wavelength region. The persistence of this feature after sensitization indicates that the pigments responsible for the absorption remain optically active after incorporation into the TiO_2 film. The absorption feature around 670–675 nm is typically associated with chlorophyll-containing pigments and has been frequently reported in natural-dye-based DSSC studies [39]. In the present study, this feature is more evident in the *Citrus hystrix*-containing films, whereas it is not clearly resolved in the *Curcuma sp*.-only films. This difference is consistent with the distinct pigment compositions of the two plant extracts and their previously reported optical absorption characteristics [28]. Therefore, the absence of a pronounced peak around 670–675 nm in the *Curcuma sp*.-sensitized films does not necessarily indicate the absence of visible-light absorption, but rather reflects the weaker and less distinct absorption response in this wavelength region.

In summary, Figure 1 reveals that the sensitized films' optical absorption behavior is mostly determined by the sensitizer's nature and, to a lesser extent, by TiO_2 crystallite size. *Citrus hystrix* induced stronger optical absorption than *Curcuma sp.*, consistent with the pristine extract's better absorption properties.

Apparent Optical Band Gap Analysis

The apparent optical band-gap energies of the sensitized TiO_2 photoanodes were estimated using the Tauc relation, as shown in Figures 2 and 3. The corresponding values obtained by extrapolating the linear absorption edge are summarized in Table 1. It should be noted that the calculated values represent the apparent optical band gaps of the dye–TiO_2 systems rather than the intrinsic band gap of TiO_2. Following sensitization, the optical response arises from the combined contribution of the semiconductor, the adsorbed dye molecules, and their interfacial interactions. Therefore, the estimated values should be interpreted as effective optical transition energies of the sensitized photoanodes.

Table 1 compares the apparent optical band-gap energies of the sensitized micro- and nano-TiO_2 films with the corresponding TiO_2 powders reported in our previous study [27]. For micro-TiO_2, sensitization with *Citrus hystrix* reduced the apparent optical band gap from 3.50 to 3.27 eV, while *Curcuma sp.* and co-sensitization resulted in values of 3.45 and 3.47 eV, respectively. For nano-TiO_2, the *Citrus hystrix*-sensitized film exhibited the lowest apparent optical band gap, decreasing from 3.20 eV for the powder to 2.82 eV after sensitization. In contrast, the *Curcuma sp.*- and co-sensitized nano-TiO_2 films exhibited higher apparent optical band-gap values than the corresponding powder. These results indicate that the effect of sensitization on the apparent optical band gap depends on both the sensitizer type and the TiO_2 system. The apparent optical band-gap energies of the micro-TiO_2 photoanodes were 3.27, 3.45, and 3.47 eV for *Citrus hystrix, Curcuma sp*., and the co-sensitized films, respectively. Among these samples, the *Citrus hystrix*-sensitized film exhibited the lowest apparent optical band gap, consistent with its stronger absorption response in Figure 1. Relationships between increased visible-light absorption and lower apparent optical transition energies have been documented in various dye-sensitized semiconductor systems [19]. This result indicates that the optical response of the sensitized films depends strongly on the type of sensitizer. For the nano-TiO_2 photoanodes, the apparent optical band-gap energies were 2.82, 3.50, and 3.68 eV for *Citrus hystrix, Curcuma sp.*, and the co-sensitized films, respectively. The nano-TiO_2/*Citrus hystrix* film, therefore, exhibited the lowest apparent optical band gap among all investigated samples, consistent with its strong optical absorption in Figure 1. This result indicates that its optical response extends to lower photon energies than that of the other sensitized films.

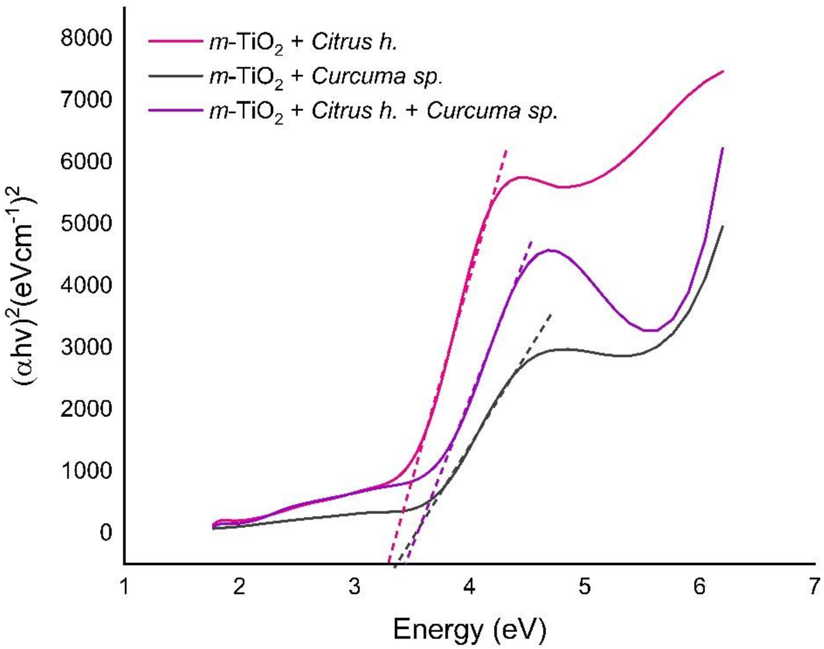

Figure 2. Apparent optical band gap energy of micro-TiO_2 films co-sensitized with single and double natural dye extracts.

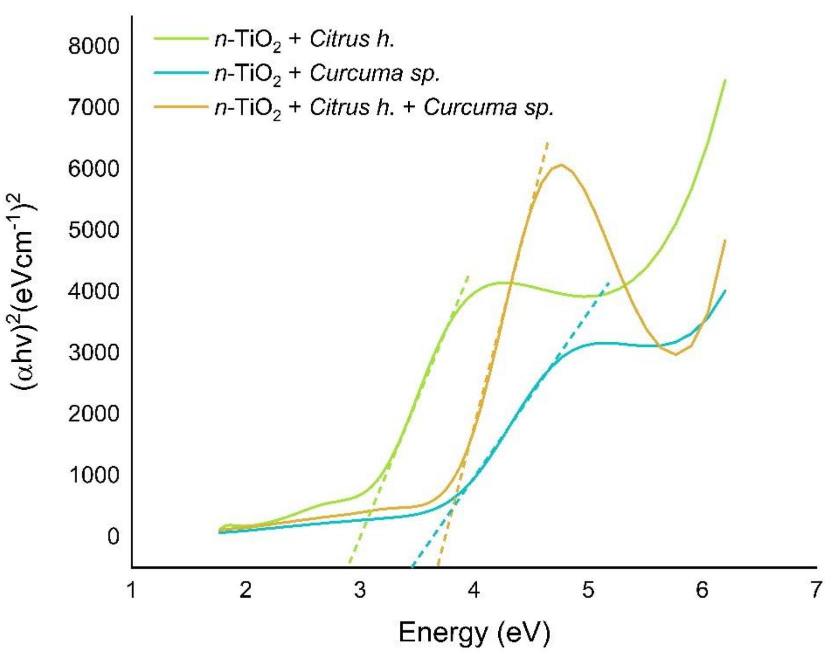

Figure 3. Apparent optical band gap energy of nano-TiO_2 films co-sensitized with single and double natural dye extracts.

Table 1. Apparent optical band gap energy of micro- and nano-TiO_2 films co-sensitized with single and double natural dye extracts and the corresponding TiO_2 powders reported in Ref. [27].

Film	**Apparent optical band gap energy (eV)**
m-TiO_2 + *Citrus h.*	3.27
m-TiO_2 + *Curcuma sp.*	3.45
m-TiO_2 + *Citrus h.* + *Curcuma sp.*	3.47
n-TiO_2 + *Citrus h.*	2.82
n-TiO_2 + *Curcuma sp.*	3.50
n-TiO_2 + *Citrus h.* + *Curcuma sp.*	3.68
m-TiO_2 powder [27]	3.50
n-TiO_2 powder [27]	3.20

A comparison of micro- and nano-TiO_2 photoanodes further demonstrates that the crystallite size can affect the apparent optical transitions of sensitized films. Characterization results [27] indicated that the nano-TiO_2 powder was prepared with a smaller crystallite size than the micro-TiO_2 powder. The smaller crystallite size of the nano-TiO_2 powder may be associated with a higher available surface area, which could potentially facilitate dye–surface interactions. However, dye loading was not measured in the present study, so this explanation remains a hypothesis rather than direct experimental evidence. Although dye loading was not directly measured in the current work, the lower apparent optical band gap of the nano-TiO2/Citrus hystrix photoanode is consistent with the typical enhancement of optical interactions reported in other dye-sensitized nanostructured TiO_2 systems. The present results do not directly reveal the underlying mechanism, and further characterization would be needed to determine the exact roles of dye adsorption and interfacial interactions.

A major finding emerges from comparing co-sensitized photoanodes with single-dye systems. Co-sensitization alters the absorption profile shown in Figure 1 and broadens the spectral response across different wavelength regions. Nevertheless, this extended spectral response is not associated with lower apparent optical band-gap energies. Actually, the co-sensitized photoanodes have larger apparent optical band gaps than the *Citrus hystrix*-sensitized photoanodes in both micro- and nano-TiO_2 systems. This observation is one of the key results of the current study because it shows that broader spectral coverage does not necessarily mean lower optical transition energies.

This discrepancy between the spectral broadening and the reduction of the apparent optical band gap may indicate that a sensitizer's efficiency should not be judged solely by the extent of its absorption spectrum. Co-sensitized DSSC studies have found that the optical properties of mixed dye systems are strongly dependent on dye compatibility, adsorption behavior, molecular aggregation, and competition for adsorption sites on the semiconductor surface [41-43]. However, these factors were not directly characterized in the present study and therefore remain possible explanations rather than demonstrated mechanisms. Sometimes, the combination of two sensitizers can result in a wider absorption range without necessarily improving the photoanode's optical transition properties. Thus, the current results imply that the use of co-sensitization with *Citrus hystrix* and *Curcuma sp*. changes the optical behavior of TiO_2 but does not result in a better apparent optical band gap than the *Citrus hystrix* one.

Further understanding might be achieved by comparing the current data with the optical characteristics of TiO_2 powders previously reported [27]. Earlier characterization showed that the apparent optical band-gap energies of micro- and nano-TiO_2 powders were approximately 3.50 and 3.20 eV, respectively. The corresponding values after sensitization with *Citrus hystrix* dropped to 3.27 and 2.82 eV. Such a shift to lower optical transition energies correlates with the increased absorption feature observed in Figure 1 and implies that the dye molecules play an important role in the overall optical response of the photoanodes. The decrease in apparent optical band-gap energies of TiO_2 photoanodes sensitized by chlorophyll-, anthocyanin-, and carotenoid-rich natural dyes was related to the overall optical response of the dye–semiconductor system.

Another point is that the apparent optical band-gap energies determined in this work are based solely on absorption measurements in the UV–Vis region. Hence, the current study provides only information on the effective optical transition energies of the sensitized photoanodes; it does not directly reveal the details of the electronic interaction mechanism between the dyes and TiO_2. Complementary studies, including photoluminescence, electrochemical impedance spectroscopy, dye-loading analysis, or surface-sensitive spectroscopic techniques, would be the best approach to further understand the origin of the optical behavior observed here.

The present study focused on a comparative evaluation of the optical behavior of dye-incorporated TiO_2 films prepared under identical experimental conditions. Each film configuration was fabricated once and characterized by a single UV–Vis measurement. Therefore, the reported apparent optical band-gap values represent individual measurements rather than statistical averages. Although this approach enables comparison of optical responses across different sensitizer systems, it does not provide information on experimental reproducibility or sample-to-sample variation. Furthermore, the interpretation of the observed optical behavior is primarily based on UV–Vis spectroscopy and apparent optical band-gap analysis. Consequently, the proposed effects of TiO_2 crystallite size, dye–TiO_2 interaction, adsorption competition in the co-sensitized system, and possible intermolecular interactions between dye molecules should be regarded as plausible interpretations rather than direct experimental evidence. Additional characterization, such as XRD, SEM, AFM, FTIR, Raman spectroscopy, dye-loading measurements, and film-thickness analysis, would be valuable for confirming these proposed mechanisms and establishing a more direct relationship between the films' structural and optical properties. Future studies should therefore include repeated film fabrication, along with complementary structural characterization and statistical analysis, to further validate the observed optical trends.

Conclusion

The optical response of dye-incorporated TiO2 films derived from Citrus hystrix, Curcuma sp., and co-sensitizers was successfully investigated using UV–Vis absorption spectra. The spectra have shown that both the type of sensitizer and the crystallite size of TiO_2 affect the optical response of the films. Among the sensitizers, *Citrus hystrix*, the stronger single sensitizer, produced higher optical absorption than *Curcuma sp*., indicating that the system has better light-harvesting ability. The analysis of the apparent optical band-gap energies suggests that the optical transition behavior of the films was strongly influenced by the combination of the sensitizer and the TiO_2 crystallite size. The film of nano-TiO_2/*Citrus hystrix* exhibited the lowest apparent optical transition band gap of 2.82 eV, suggesting that its optical response can be extended further toward the lower photon energies as compared to other samples tested. On the other hand, although co-sensitization was able to change and broaden the absorption profile, it is not capable of producing lower apparent optical band-gap energies than the *Citrus hystrix*-sensitized films. The evidence suggests that more extensive spectral coverage does not necessarily translate to more desirable optical transition features. The effectiveness of a natural dye sensitizer is affected not only by its absorption features but also by its interaction with the TiO_2 matrix. The findings provide additional insight into natural dyes and semiconductor morphologies, support the use of green TiO2-based photoanodes, and serve as a stepping stone for further exploration of natural dye-sensitized photovoltaic materials. For DSSC photoanode design, the selection of TiO_2 crystallite size and natural dye sensitizer should therefore consider both spectral absorption characteristics and apparent optical band-gap response, rather than relying on spectral broadening alone.

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