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Article

Immobilization of Dibenzalacetone on TiO_2 Surface and its Potential as Anti-UV Material

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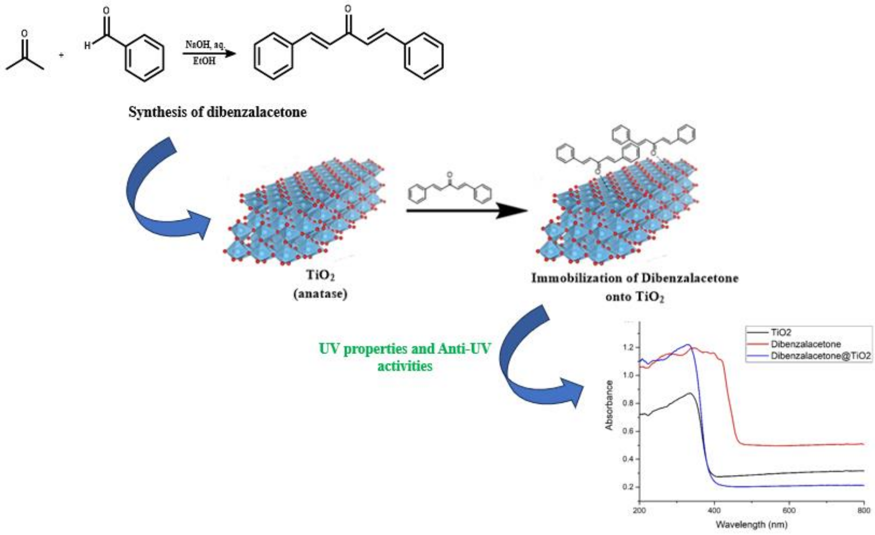
Abstract

Sunlight has been known to provide many benefits to human life. However, behind these benefits, there are some negative effects along with the destruction of the ozone layer and the environment on earth. One of them is exposure to ultraviolet (UV) rays which can cause several diseases such as skin cancer. One way to overcome this is by using sunscreen substances. In this study, dibenzalacetone immobilization on TiO_2 has been carried out for anti-UV applications. Based on the test results using UV-Vis spectrometry, TiO_2, and dibenzalacetone both have anti-UV properties with maximum peaks at wavelengths of 335 nm and 346 nm with absorbance values of 0.871 and 1.197. Immobilization of TiO_2 with dibenzalacetone gives an absorbance with a value of 1.221 at a wavelength of 329. These results indicate that TiO_2 immobilization with dibenzalacetone provides better anti-UV A properties than TiO_2 because of the higher absorbance value.

Keywords: *dibenzalacetone, TiO_2, immobilization, anti-UV*

Graphical Abstract



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Introduction

Sunlight has been utilized for a long time by humans in various fields such as for health, drying food ingredients, or just drying clothes. Over time and technological developments, the use of sunlight has also increased, such as the use of sunlight as an energy source or the use of solar cells [1]. However, behind these benefits, along with the times, environmental damage has resulted in the depletion of the ozone layer in the atmosphere [2]. The destruction of the ozone layer in the atmosphere causes the intensity of UV rays entering the earth to become more. The effects of UV light were first reported in 1983 which showed the effects of hyperpigmentation [3]. This finding was supported by research conducted by the group of Mahmoud, et al, in 2010 which proved that hyperpigmentation would occur due to UV exposure [4].

UV light found in sunlight has a wavelength between 100-400 nm. Based on its low wavelength, UV light has great energy. UV light can be divided into several types based on its wavelength, namely UV-A at 320-400 nm, UV-B at 280-320 nm, and UV-C at 100-280 nm. Rays with wavelengths below 200 nm are effectively absorbed and can be eliminated by oxygen in the Earth's atmosphere. UV-C has a wavelength below 280 nm and will be absorbed in the stratospheric layer [5]. However, environmental damage has resulted in the inhibition of UV rays in the atmosphere layer becoming ineffective [6]. Exposure to UV rays with high intensity to the skin for a long time will cause several losses such as skin redness (erythema), sunburn, or if it gets longer, it will cause skin cancer [7].

The association between prolonged sun exposure and skin cancer has been widely studied. Epidemiologically, non-melanoma skin cancer is the most diagnosed type of skin cancer in geographical populations with high sun exposure [8]. However, it is not uncommon for melanoma skin cancer cases to occur due to high sun exposure [9]. DNA damage or mutation is one of the causes of skin cancer due to high sun exposure. This DNA damage can occur due to direct or indirect radiation. Direct DNA damage can occur due to the dimerization process of pyrimidine bases predominantly. The formation of UV-induced pyrimidine dimers (Figure 1) occurs because the skin is exposed to UV-B and UV-C rays [10].

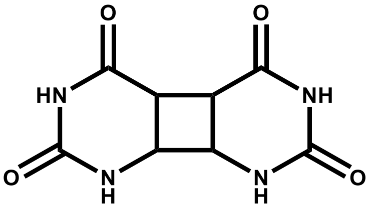

Figure 1. Dimer of pyridine

Based on the dangers of mutations due to UV exposure, one form of prevention is the use of sunscreen. Sunscreen is one of the skincare products that can protect the skin from sun exposure, especially from UV rays. This product works by absorbing or reflecting UV rays that hit the protected part [11]. In addition, the use of sunscreen is an effective way to prevent skin damage that occurs due to sun exposure such as preventing sunburn, skin aging, collagen degradation, and pigmentation of the skin [12,13].

Sunscreens are grouped into several types such as inorganic sunscreens, organic sunscreens, and plant-based sunscreens. Inorganic sunscreens are categorized as physical filters because the active ingredients contained in them are minerals, such as TiO_2 [12,13]. Besides minerals, more than 50 types of organic material-based sunscreens have been developed to date. P-aminobenzoic acid (PABA) was the first anti-UV compound to be characterized as a UV-B absorber [12]. However, further research indicates that the use of PABA can cause skin irritation. Based on this, several alternative organic compounds such as cinnamates, salicylates, benzophenones, benzimidazoles, and other chromophores were developed. One of the chromophores with an aromatic ring arrangement connected to a carbonyl group is chalcone. Several studies have reported that chalcone-derived compounds can absorb light in the UV area. In chalcone, there are two important absorptions, namely absorption at wavelengths of 220-270 nm and 340-390 nm [14]. This absorption occurs due to electronic transitions in n → π* and π → π*. This electronic transition shows the potential of chalcone as an anti-UV material. Based on research on chalcone as anti-

UV, analog compounds of chalcone are thought to have the same properties and potential. One of the analog compounds of chalcone is dibenzalacetone. Dibenzalacetone is an analog of chalcone with a conjugated π bond extension, with two aromatic rings and carbonyl groups [15,16].

Dibenzalacetone is an analog compound of chalcone which has the addition of π conjugation so that it will form a system of electron donors (D) and electron acceptors (A) with a π bridge connecting D and A [16]. Apart from using conventional methods, chalcone synthesis can also be carried out using irradiation assistance from microwave (Microwave Assisted Organic Synthesis, MAOS) [17].

In previous experimental studies, the use of TiO_2 as anti-UV has been used separately without being combined with other anti-UV materials. In addition, the use of chalcones as anti-UV derived from organic compounds has been done, but the compound has not been done. Therefore, in this research, the study of the anti-UV properties of dibenzalacetone and the effect of dibenzalacetone immobilization on TiO_2 as anti-UV will be conducted.

Experimental Section

Materials

The materials used in this experiment were sodium hydroxide (NaOH), ethanol (C_2H_6O) 98% from Merck, distilled water, titanium oxide (TiO_2), acetone (C_3H_6O) from Merck, and benzaldehyde (C_7H_6O, purity 99%) from Merck.

Instrumentation

Intruments used in this experiment is UV-Vis Spectrophotometer Jasco V760, Fourier Trnsform Infrared (FTIR) ATR-S Serial No. A224158/Shimadzu, Hotplate stirrer IKA C-MAG HS7 I.

Procedure

Dibenzalacetone synthesis

The synthesis procedure of dibenzalacetone derivatives followed the procedure performed by Conard and Morris with slight modifications. A total of 2 g of sodium hydroxide was dissolved in 20 mL of water and 16 mL of ethanol. The solution was stirred rapidly for 15 minutes at room temperature. Then 25 mmol of acetone and 25 mmol of benzaldehyde are added to the mixture. After a few minutes, 25 mmol of benzaldehyde derivative was added and the mixture was left to react for a while. After that, the precipitate produced in the reaction was filtered using a Buchner funnel and washed using water. The precipitate obtained was then purified by recrystallization or separation by column chromatography.

Immobilization dibenzalacetone on TiO_2 surface

Immobilization of dibenzalacetone is based on the principle of adsorption on the surface of TiO_2. This immobilization begins with weighing dibenzalacetone and TiO_2 in mol ratio of 2: 5. Dibenzalacetone dissolved in ethanol and placed in a closed container. In the closed container was inserted TiO_2 solids and stirred for 48 hours. After 48 hours, the solution was left for 12 hours to undergo decantation. Filtrate and solids are separated with filter paper where the solids will be dried under closed conditions from light to dry. The immobilized solid will be used in the next stage.

Characterization of dibenzalacetone-TiO_2 using FTIR

The immobilized solid was analyzed using FT-IR Shimadzu from wave number 350 to 4000 $cm^{-}1$. The characterization process was carried out at Department of Chemistry, Brawijaya University. The immobilized solid was taken with the tip of a spatula and crushed using KBr solids. The results of mixing the solids were analyzed using FT-IR to determine the functional groups of the solids. As a comparison, FT-IR characterization was also carried out on TiO_2 and dibenzalcetone which had not been treated with immobilization.

Diffuse reflectance UV study immobilizes dibenzalacetone-TiO_2

The UV Reflectance Diffuse study was conducted at Ma Chung University Pharmacy laboratory with UV-Vis Spectrophotometer Jasco V760 instrumentation with solids mode. The wavelength used in this study was 190-900 nm. The immobilized solid was compacted in the sample container using a manual press to avoid air in the solid cavity. The solid was then inserted in the sample holder and analyzed under dark conditions. The results of the DR UV study were used in the study of the anti-UV potential of the solid results of dibenzalacetone immobilization on the TiO_2 surface.

Analysis of anti-UV potency of dibenzalacetone-TiO_2

Anti-UV potential analysis was conducted using the CSV file obtained from the DR UV study results in the previous step. The CSV file obtained was opened using Origin application to see the spectra pattern obtained. The spectra obtained were analyzed for the position of the absorption that occurred and whether it had absorption in the UV region. The absorption results are then continued by classifying them as anti-UV-A, UV-B, or UV-C.

Results and Discussions

Synthesis of dibenzalacetone and immobilized dibenzalacetone to TiO_2 surface

The dibenzalacetone synthesis reaction belongs to the category of aldol condensation reactions that can occur in either acidic or basic environments [18]. The use of several types of acid catalysts such as hydrochloric acid (HCl) or the use of bases such as sodium hydroxide or potassium hydroxide has been carried out. The synthesis reaction of dibenzalacetone is carried out through the Claisen-Schmidt condensation reaction by reacting benzaldehyde and acetone in an alkaline atmosphere. hydroxide ions from NaOH will react with alpha hydrogen from acetone to form enolate ions. The enolate ion will attack the electrophile side of benzaldehyde (carbonyl group) forming an aldol condensation product. The same reaction occurs twice to produce a yellow dibenzalacetone product. The resulting product, dibenzalacetone, was obtained with a yield of 85.12%. Based on FTIR analysis, there is an absorption at 3053 cm^{-1} and 3026 $cm-^{1}$ which shows the C-H bond in the benzyl ring, which is reinforced by the double bond C=C absorption at 1446 - 1600 cm^{-1}. Then there is a signal in the 1647 cm^{-1} region which shows the absorption of the C = O bond (carbonyl group). This absorption spectra shows the characteristic absorption of dibenzalacetone compound [19]. The FTIR spectra of dibenzalacetone is available on Figure 2.

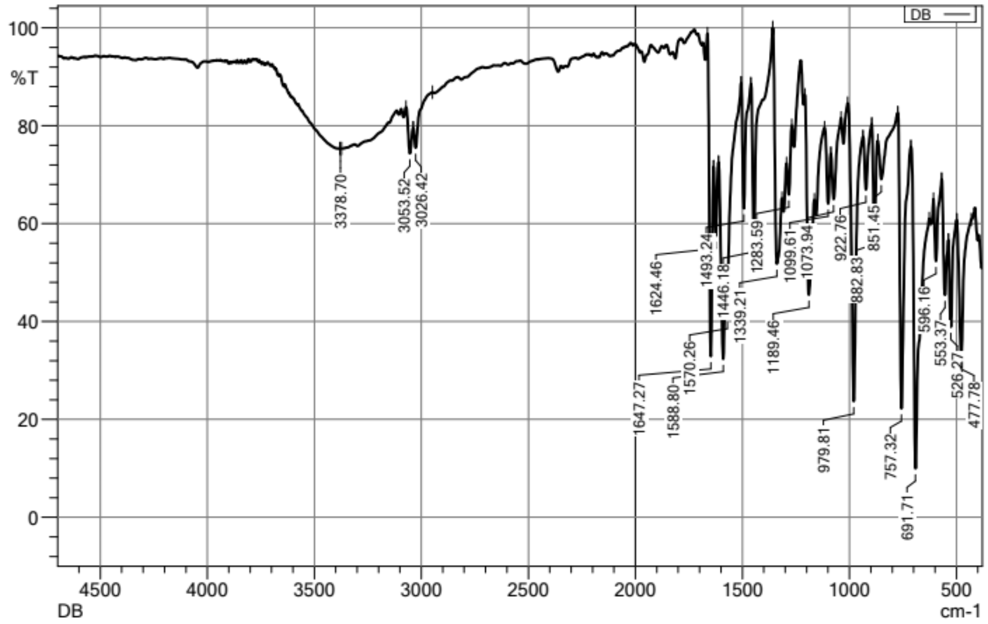

Figure 2. FTIR spectra of dibenzalacetone.

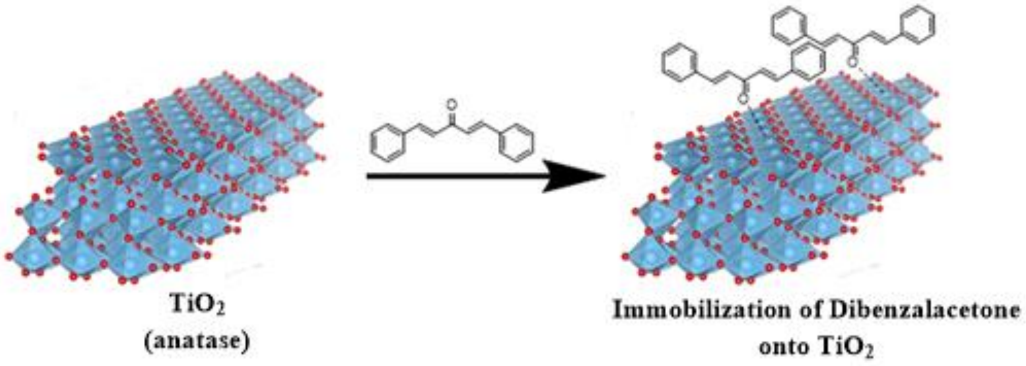

Figure 3. Proposed immobilization mechanism of dibenzalacetone on TiO_2 surface.

The successful immobilization of dibenzalacetone was inferred from the detection of a distinct functional group signal in the immobilization outcomes. The process of immobilization can be attributed to electrostatic interactions between the positively charged Ti surface and the electron-rich sites of dibenzalacetone, particularly the carbonyl groups. Figure 3 illustrates the proposed mechanism of immobilization. The manifestation of dibenzalacetone on the TiO_2 surface prompted a modification in its properties, which were subsequently investigated using a UV-Vis spectrophotometer.

UV properties and activities as anti-UV

UV-Vis analysis was performed with a wavelength of 200-800 nm. This analysis aims to know the maximum wavelength of each material associated with anti-UV properties. TiO_2 used analyzed using a UV-Vis spectrophotometer showed anti-UV properties with a peak at 335 nm with an absorbance of 0.871. This peak is in accordance with previous research where TiO2 is a material that acts as anti-UV A[20]. TiO_2 material is immobilized with dibenzalacetone which shows anti-UV-A properties with a maximum wavelength at 346 nm. Dibenzalacetone has a higher absorbance with an absorbance value of 1.197. The results of dibenzalacetone immobilization on the TiO_2 surface provide anti-UV-A properties according to Figure 4. The immobilized material has a maximum wavelength of 329 nm and absorbance of 1.221 which shows better properties than TiO_2 because it has a higher absorbance.

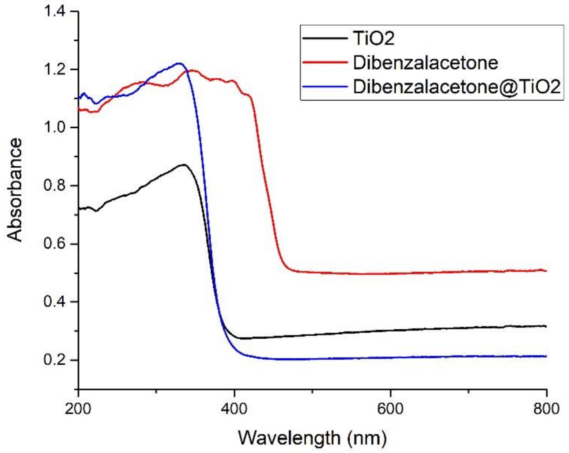

Figure 4. UV spectra of dibenzalacetone, TiO_2, and dibenzalacetone immobilized on TiO_2.

Conclusions

Dibenzalacetone immobilization on TiO_2 has been carried out for anti-UV applications. based on the test results using UV-Vis spectrometry, TiO_2, and dibenzalacetone both have anti-UV properties with maximum peaks at wavelengths of 335 nm and 346 nm with absorbance values of 0.871 and 1.197. Immobilization of TiO_2 with dibenzalacetone gives an absorbance with a value of 1.221 at a wavelength of 329. These results indicate that TiO_2 immobilization with dibenzalacetone provides better anti-UV A properties than TiO_2 because of the higher absorbance value.

Acknowledgments

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