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Engineering and Fabrication of TiO_2 Photocatalyst: review

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ABSTRACT

The photocatalytic reactions occurring on the surface of TiO_2 photocatalysts are crucial factors determining the kinetics and mechanisms of photocatalytic reactions. Photocatalyst engineering, especially of TiO_2, is important due to various applications in photocatalytic processes. This review paper presents the engineering of materials and fabrication processes for TiO_2 photocatalysts. Material catalyst engineering includes the development of TiO_2 composites with magnetic materials, other additives, and doping. With the development of the chitosan-TiO_2 coating to create the nanocomposite film, red grapes could be effectively protected against microbial infection and have their shelf life increased. F-doping on TiO_2 can increase the amount of photocatalytic oxidative species, encourage electron separation, and improve visible light absorption. To improve the effectiveness of removing the photocatalyst from the treated liquid waste once the procedure is finished, magnetic particles are added to photocatalysts. Fabrication methods for TiO_2 modification to obtain specific crystal structures, including hydrothermal methods, anodization, and template-assisted techniques, will also be discussed. Another important factor is the duration of the hydrothermal treatment; nanotubes are generated after more than 12 hours. In contrast to diluted solutions, longer nanotubes will be produced during the Ti anodization process when concentrated electrolyte solutions, such as ethylene glycol and glycerol, are used.

Keywords: *hydrothermal, anodization, template-assisted method, TiO_2-magnetic material composite, TiO_2-additive material composite*

1. INTRODUCTION

In the past few decades, photocatalysis has emerged as an intriguing field of research. Photocatalysis can be utilized as an innovative solution to address various global environmental and energy challenges. The photocatalytic process utilizes sunlight as an energy source to convert organic pollutants into more environmentally friendly compounds and to produce renewable energy such as hydrogen.

Lately, TiO_2 has attracted considerable attention and has been extensively studied as a desired photocatalytic material due to its various appealing characteristics. (Fujishima, Zhang, and Tryk 2008). Photocatalyst TiO_2 has several advantages including stability, non-toxicity, corrosion resistance, abundant availability in nature, and relatively low cost. (Wu et al. 2017). As a photocatalyst, TiO_2 also has some disadvantages, including its small specific surface area. (Pan et al. 2013), large recombination rate, as well as a high energy band gap value (Antony et al. 2012). These weaknesses result in low photon absorption (Liu et al. 2011).

The extensive applications of photocatalysis technology are closely related to the engineering of photocatalytic materials and fabrication processes to obtain specific morphologies or crystal structures. Catalyst material engineering can be accomplished by adding various types of dopants (metal or non-metal), engineering composites between semiconductors and specific materials, and immobilizing photocatalysts in the form of thin layers. Photocatalyst fabrication processes can be conducted using hydrothermal methods, anodization methods, and template-assisted methods (Slamet., Ibadurrohman. 2023).

To enhance the effectiveness and applicability of TiO_2 in photocatalytic processes, a deep understanding of photocatalyst engineering is required. This review paper will discuss several photocatalyst engineering approaches, particularly TiO_2, to be used in various photocatalytic process applications. Besides discussing the engineering of TiO_2 using the techniques mentioned, this review paper will also cover several fabrication methods commonly employed to modify the morphology of TiO_2 to obtain specific crystal structures and sizes. This review paper is expected to provide an understanding of the concept of photocatalysis engineering as a whole, starting from material engineering with the addition of specific substances to the modification of TiO_2 morphology using certain fabrication methods.

2. SYNTHESIS OF NANOSTRUCTURED TiO_2 MATERIAL

TiO_2 consists of three crystalline phases, namely anatase (3.2 eV), rutile (3.0 eV), and brookite (3.2 eV) (Ramchiary 2020).

(a) Anatase is a polymorph of TiO_2 that is more stable at low temperatures. The transformation from amorphous to anatase can occur at temperatures around 400 - 650°C. The band gap of the Anatase crystal structure is 3.2 eV, equivalent to the energy of UV light with a wavelength of 388 nm. The anatase phase of TiO_2 can generate a larger photon current compared to the rutile and brookite phases, as the anatase phase possesses high photoactive capability (Halme 2002).

(b) Brookite is a polymorph of TiO_2 that is unstable, making it difficult to observe.

(c) Rutile is a polymorph of TiO_2 that is more stable at high temperatures. The transformation from amorphous to rutile occurs at a temperature of 700°C. The band gap of the rutile structure is 3.0 eV, equivalent to the energy of light with a wavelength of 413 nm.

The use of TiO_2 as a photocatalyst can be in the form of powder or film, or both forms. The morphology of TiO_2 can be in the form of nanoparticles (Giahi et al. 2019), nanorods (Shahvaranfard et al. 2020), and nanotubes (Kustiningsih et al. 2020). Nanoparticles are particles that have a size of less than 100 nm. The advantage of nano-sized particles is their high surface area, allowing more particles to interact, thus increasing their binding strength and mechanical properties (Slamet and Ratnawati 2012). The morphology of TiO_2 nanomaterials such as nanotube arrays or non-array nanotubes has been extensively studied due to their significant potential for various photocatalytic process applications. The fabrication methods of photocatalysts to produce specific morphologies can be achieved through hydrothermal methods, anodization methods, and template-assisted methods (Slamet., Ibadurrohman. 2023).

2.1 Hydrothermal Methods

The fabrication of TiO_2 nanotubes using the alkaline hydrothermal method in a tightly sealed vessel demonstrates pure structure and good crystal formation. After the hydrothermal process in an autoclave vessel, the resulting solution is washed with a strong acid such as HCl solution. According to Slamet., Ibadurrohman, (2023) hydrothermal temperature influences the morphology of the formed catalyst. At temperatures ranging from 100 °C to 160 °C, there is a transformation from anatase/rutile to TiO_2 nanotubes. The concentration of alkali solution used also affects the morphology of the resulting photocatalyst. TiO_2 nanotubes form at NaOH concentrations between 5 and 20 M. The duration of hydrothermal treatment also plays a crucial role, nanotubes are formed after a hydrothermal duration exceeding 12 hours. The calcination temperature during post-treatment to obtain nanotube morphology in the anatase crystal structure ranges between 350°C and 500°C.

Kustiningsih, Slamet, and Purwanto (2015) conducted the synthesis of TiO_2 nanotubes using the hydrothermal method and a combination of sonication and hydrothermal treatment. In a stainless steel autoclave with a Teflon lining, the hydrothermal treatment was carried out for 12 and 24 hours at 130°C. The first step involved dispersing 2 grams of TiO_2 DegussaP25 in 100 milliliters of NaOH 10M. This was followed by sonication for 5, 10, and 15 minutes in an ultrasonic processor (CT ChromTech, 800 watts). The sonicated solution was then transferred to a Teflon-lined stainless steel autoclave to undergo hydrothermal treatment at 130 ^{0}C for 12 hours. Following hydrothermal treatment, the precipitate was thoroughly washed with distilled water, then further washed with HCl and distilled water repeatedly until the pH of the washing solution was below 7. Centrifugation was used to obtain the final products, which were subsequently dried at 150°C in an air furnace and finally calcined at 500°C. In this study, using high-power sonication (800W), nanotube morphology was achieved with sonication treatment for 10 minutes followed by 12 hours of hydrothermal treatment. Without the sonication process, after 12 hours of hydrothermal treatment, nanotube morphology had not yet formed.

El Saeed et al.(2015) synthesized TiO_2 nanotubes by dispersing 3 grams of TiO_2 powder in 100 ml of 10 N NaOH, followed by hydrothermal treatment at 140°C for 24 hours in a Teflon-lined autoclave. Several times, distilled water is used to wash the final product to get rid of sodium hydroxide. To neutralize the solution during sonication, 0.1 M HCl aqueous solution is then added. After that, the TNT product is filtered and dried for five hours at 100 °C. The material structure obtained was analyzed using Transmission Electron Microscopy (TEM), revealing TiO_2 nanotubes with nearly uniform sizes around 10-20 nm, with lengths varying from several tens to several hundreds to two hundred nanometers.

Based on the above explanation, according to research by Slamet., Ibadurrohman, (2023) and El Saeed et al.(2015), it takes more than 12 hours to prepare TiO_2 nanotubes using the hydrothermal method. Kustiningsih, Slamet, and Purwanto (2015) conducted TiO_2 nanotube preparation using the hydrothermal method combined with sonication treatment, which only requires 12 hours to achieve the nanotube morphology.

2.2 Anodization Methods

Titanium dioxide (TiO_2) nanotubes are produced through the electrochemical anodization process of titanium plates, with variations in electrolyte concentration, voltage, and anodization time. In the electrochemical process, titanium plates are used as the anode and Pt plates as the cathode. The electrolyte solution used consists of ammonium fluoride (NH_4F), water in glycerol, or ethylene glycol.

The use of concentrated electrolyte solutions such as ethylene glycol and glycerol in the Ti anodization process will result in nanotubes with longer lengths compared to dilute solutions. However, it requires a longer processing time, necessitating agitation to enhance mass transfer across the nanotube surface, thereby increasing nanotube formation rates. (Roy, Berger, and Schmuki 2011).

The percentage of water in the anodization process affects the morphology of the resulting nanotubes. Chemical dissolution can be further reduced by using glycerol or ethylene glycol solutions in the anodization process. The water content in the electrolyte solution during anodization affects both the formation rate and the chemical dissolution rate of the nanotubes. In other words, the water content in the electrolyte solution is necessary for the formation of the oxide layer on the tube base, but water can also accelerate the dissolution of the nanotube layer (Roy et al. 2011). The water content in the electrolyte solution affects the morphology and size of the tubes (inner diameter, thickness, and length of the tubes). The higher the water content in the electrolyte solution, the longer the tubes formed, while the thickness of the tubes remains relatively constant (Slamet., Ibadurrohman. 2023).

The Ti^{4+} ions formed from the Ti plate in the electrolyte solution will bond with F ions to form stable titanium hexafluoride complexes $[TiF_6]^{2-}$. Anions such as O^{2-} and OH^- resulting from the dissociation process of water and F^- ions migrate to the anode. The presence of F^- ions can dissolve some of the oxide layer that has formed on the surface of the Ti plate, believed to be the cause of pore formation and the initial step in tube formation. Fluoride ions in aqueous media are more aggressive than in organic media, causing TiO_2 nanotube growth to be shorter (Regonini et al. 2013).

According to Bai et al. (2008), the mechanism of TiO_2 formation in a solution containing F- ions begins with the formation of an oxide layer from Ti covering the metal surface, thus forming a TiO_2 layer. Hydrofluoric acid (HF) in the electrolyte solution causes the oxide layer to dissolve, initiating the formation of a layer consisting of small pores. Adjacent small pores merge to form larger pores. The formation of larger pores is the initial step in tube formation. Low acidity levels at the base of the pores and narrow pores facilitate pore etching to form tube structures. The formation of a perfectly arrayed nanotube structure occurs over time, accompanied by an increase in tube length.

2.3 Template Assisted Method

The template-assisted method is used to produce complex materials by employing a template as a guide for the growth and arrangement of the resulting material structures. Templates are used as molds to selectively shape the desired structures.

Porous alumina membranes or track-etched polycarbonate membranes with channels serve as template membranes that can be utilized for producing nanostructures through the sol-gel process. Nanostructures of TiO_2, either fibrous or tubular, can form within each channel of the porous template membrane. Templates that already possess structures like vanadium oxide nanobelts and polymer fibers processed through electrospinning have also been used in fabricating TiO_2 nanotube structures (Slamet., Ibadurrohman. 2023).

3. MATERIAL CATALYSIS ENGINEERING

To enhance its photocatalytic efficiency and broaden the range of light absorption, material engineering of TiO_2 photocatalysts is necessary. This review paper will discuss the material engineering of catalysts by adding various types of dopants (both metallic and non-metallic), engineering composites between TiO_2 and magnetic materials, TiO_2 composite with additive materials, and the addition of dopants.

3.1 TiO_2 Composite with Additive Materials

One type of TiO_2 composite material is the TiO_2-Chitosan composite. Chitosan is a biopolymer derived from chitin commonly found in the main components of cell walls in fungi and arthropods, and it has various applications in several industries. (Morin-Crini et al. 2019). Chitosan (poly(D-glucosamine)) is a derivative compound of chitin, utilized in various applications such as the food industry, cosmetics, biomedicine, and pharmaceuticals. Chitosan is commonly employed in the production of hydrogels, films, fibers, or sponges, with most of these materials applied in the biomedical field, where biocompatibility is crucial (Rinaudo 2006).

The use of TiO_2-chitosan composite film has been shown to exhibit efficient antimicrobial activity for red wine to prevent microbial infection and extend its shelf life (Zhang et al. 2017). TiO_2-chitosan composite packaging is believed to possess photocatalytic degradation properties of ethylene and antibacterial activities against various types of bacteria (such as Staphylococcus aureus, Escherichia coli, Salmonella Typhimurium, and Pseudomonas aeruginosa) as well as fungi (Aspergillus and Penicillium) (Siripatrawan and Kaewklin 2018).

Zhang et al (2017) synthesized chitosan and chitosan-TiO_2 film, after adding 0.5 g of chitosan and 0.05 g of TiO_2 nanopowder to 20 mL of acetic acid (2.5%, v/v), the mixture was homogenized for 10 minutes using a 120 W ultrasonic treatment. The cross-linking reaction was then carried out by adding 0.1 mL of epichlorohydrin and agitating the mixture for 4 hours at room temperature using a magnetic stirrer until a homogenous emulsion was achieved. Next, the emulsion was applied to a 15 cm x 15 cm square glass plate that had been covered with plastic film and let air dry for the entire night. The resulting chitosan-TiO_2 coating was easily peeled off the plate and immersed for two hours in a solution containing one mol/L of NaOH. Ultimately, the film was repeatedly cleaned with deionized water until it reached a neutral pH and allowed to air dry at nighttime temperature. The same method outlined above was used to make the pure chitosan film; however, TiO_2 nanopowder was not added. The produced chitosan-TiO_2 films exhibit enhanced whiteness and decreased transparency, which is comparable with the earlier work of Zhang et al. (2016). The pure chitosan films are transparent.

A chitosan-TiO_2 composite film was produced after the introduction of TiO_2 nanopowder into the chitosan matrix with good dispersion. TiO_2 nanopowder was added to the composite film to improve its mechanical and wettability characteristics. Under ambient conditions, the chitosan-TiO_2 film's photocatalytic antimicrobial effect was assisted by its lower transmittance in the visible light band. The effective antibacterial activity of the chitosan-TiO_2 coating against bacteria, fungus, and molds was demonstrated by the complete sterilization of all tested strains in 12 hours. The membrane integrity was harmed by the chitosan-TiO_2 film's antibacterial action causing the cellular materials to seep out. Red grapes could be successfully shielded from microbial infection and have their shelf life extended by the developed chitosan-TiO_2 coating (Zhang et al. 2017).

Chitosan with a deacetylation level of 85% was extracted from Thailand's Seafresh Industry Public Co., Ltd. 2% w/v chitosan film-forming solution was made utilizing a method adapted from the approach of Siripatrawan and Kaewklin (2018), in which glycerol was utilized as a plasticizer and chitosan powder was dissolved in 1% acetic acid solution. To create the chitosan-TiO_2 (CT) films, TiO_2 nanopowders with a size of 21 nanoparticles (>99.5%, Sigma-Aldrich Co., St. Louis, MO, USA) were added to the chitosan solution. The final TiO_2 concentrations of the films were 0, 0.25, 0.5, 1, and 2% w/w (designated as CS, CT0.25, CT0.5, CT1, and CT2, respectively). In a controlled-temperature water bath shaker (1083 GFL, Burgwedel, Germany), the resultant solution was shaken for six hours at 90 rpm and 90 C. A homogenizer (D-79282, Ystral GmbH, Ballrechten-Dottingen, Germany) was used to homogenize the solution, and a sonicator (Ultrasonic Processor, Cole-Parmer, Vernon Hills, Illinois, USA) was used to degas it after that. After being poured onto 30 x 12 cm^2 ceramic plates, the film-forming solution (190 mL) was dried. Prior to additional examination, the acquired films were conditioned for 48 hours at 25 C and 50% relative humidity (RH) in an environmental chamber.

TiO_2 was added to chitosan films to increase their tensile strength and water vapor barrier capabilities, but this also reduced the film's optical transmittance. The films of Chitosan-TiO_2 (CT) nanocomposite had photodegradation activity of ethylene. Nevertheless, the mechanical and ethylene photodegradation of the nanocomposites was impacted by a 2% TiO_2 agglomeration. The antimicrobial activity of the CT film containing 1% TiO2 was evaluated because it had the best mechanical, barrier, and ethylene photodegradation characteristics. The CT1 film displayed anti-bacterial action against fungi and bacteria that are both Gram-positive and Gram-negative. The CT nanocomposite film exhibits mechanical, barrier, ethylene photodegradation, and antibacterial properties that suggest its potential for usage as active packaging in postharvest applications (Siripatrawan and Kaewklin 2018).

3.2 Composite of TiO_2 with Magnetic Materials

The composite of TiO_2 with magnetic materials holds great promise, especially for photocatalysis in nanoparticle form. The addition of magnetic particles to photocatalysts aims to enhance the efficiency of separating the photocatalyst from the treated liquid waste after the process is completed.

Degusty, Rahmayeni, and Arief (2013) have synthesized TiO_2-$ZnFe_2O_4$ nanocomposites using the co-precipitation/hydrolysis method. TiO_2-$ZnFe_2O_4$ nanocomposite is created using the coprecipitation/hydrolysis method. Approximately 0.404 g $Fe(NO_3)_3.9H_2O$ dispersed in 20 milliliters of isopropanol and 0,131 grams of $Zn(NO_3)_2.4H_2O$ dispersed in 10 milliliters of isopropanol. The linear relationship between Fe and M is characterized by a molar Fe:M ratio of 2:1. This mixture is heated to 65 ^{0}C while being stirred continuously for 30 minutes. Next, 2M NH_4OH is added to the mixture to bring its pH to 6.5. After that, 20 mL of distilled water is added, and the mixture is stirred for 45 minutes. Subsequently, a 1:2 alcohol-to-TIP (Titanium isopropoxide) 97% solution is added dropwise to the mixture and agitated once more for 90 minutes at 65°C. The mixture is brought up to 120°C in temperature. Once heated, a chunky combination of metal is produced, which is subsequently ground fine and calcined for three hours at 450°C, 500°C, 550°C, and 600°C. The photocatalytic activity test of the resulting nanocomposite was conducted for the degradation of Rhodamine B with the assistance of sunlight for exposure durations of 1, 2, and 3 hours. The photocatalytic activity test shows that the TiO_2-$ZnFe_2O_4$ nanocomposite with a ratio of 1:0.1 and calcination temperature of 550°C exhibits good activity.

Mosahab et al (2011) synthesized TiO_2-$CoFe_2O_4$ through the following procedure: Alcohol was used to dissolve $Fe(NO_3)_3.9H_2O$ and $Co(NO_3)_2.6H_2O$, yielding a 0.5 M concentration of nitrate salt solution. The molar ratio of Fe = 2:1 was used to combine the solutions of Fe nitrate and Co nitrate. After that, this mixture was heated for 30 minutes at 65°C while being continuously stirred. The mixture was then stirred for 45 minutes until the pH reached 6.5 by adding NH_4OH in alcohol, 10 mL of distilled water, and more stirring. Subsequently, a 1:2 TIP solution in alcohol was added dropwise to the mixture, and it was agitated once more for 90 minutes at 65°C. After that, the mixture was baked. TiO_2-$CoFe_2O_4$ nanoparticles had an 82% breakdown rate and photocatalytic activity in the visible light spectrum. These particles' magnetic characteristics make it possible to recycle them after using them in water for photocatalytic reactions.

3.3 The Addition of a Dopant

The energy bandgap values of TiO_2 are 3.2 eV for the anatase crystal and 3.0 eV for rutile. Therefore, TiO2 can only respond to UV light (with wavelengths < 400 nm), which accounts for only 5% of the sunlight spectrum. Hence, efforts are needed to enable TiO_2 to respond to visible light, which constitutes 45% of sunlight (wavelengths ranging from 400-800 nm).

The addition of dopants is the process of adding metal and non-metal elements or ions into photocatalytic materials. Adding metal dopants can inhibit the recombination rate of electron-hole pairs, thereby enhancing the photocatalytic activity. Adding non-metal dopants can decrease the semiconductor's energy band gap. (Slamet., Ibadurrohman. 2023)

F-doped TiO_2 is obtained by adding fluorine dopant into the TiO_2 structure through specific methods. Specifically, fluorine is commonly used as an agent to control morphology in enhancing the physical and chemical properties of TiO_2. Fluorine has been proven to be an effective anionic dopant in forming microstructural variations in the TiO_2 conduction band (Wang, Yang, and Huang 2015). F-doping treatments, such as inappropriate calcination and dissolution, lead to suboptimal fluorine absorption on the TiO_2 morphology. Therefore, F-doped TiO_2 needs to be properly prepared using methodologies that can optimize the absorption of F-doping on TiO_2 (Zhang et al. 2014). F-doping on TiO_2 can enhance visible light absorption, promote electron separation, and increase the photocatalytic oxidative species. Consequently, increased F-doping can enhance the surface acidity and drive the photocatalytic activity of TiO_2 (Yu et al. 2014).

4 CONCLUSION

TiO_2 is one of the most widely used photocatalysts in photocatalysis processes, as it offers many advantages compared to other photocatalysts. To enhance the reaction effectiveness on the surface of TiO_2 photocatalysts, material catalyst engineering and morphology modification of TiO_2 are conducted to achieve specific crystal structures and sizes. This review presents the basic principles of TiO_2 photocatalyst engineering. From the exposition provided, it is evident that material engineering and morphology modification of TiO_2 catalysts play a crucial role in enhancing the effectiveness of photocatalysis processes.

5 REFERENCES

Antony, Rajini P., Tom Mathews, C. Ramesh, N. Murugesan, Arup Dasgupta, S. Dhara, S. Dash, and A. K. Tyagi. 2012. "Efficient Photocatalytic Hydrogen Generation by Pt Modified TiO 2 Nanotubes Fabricated by Rapid Breakdown Anodization." *International Journal of Hydrogen Energy* 37(10):8268–76.

Bai, Jing, Baoxue Zhou, Longhai Li, Yanbiao Liu, Qing Zheng, Jiahui Shao, Xinyuan Zhu, Weimin Cai, Junsheng Liao, and Lexi Zou. 2008. "The Formation Mechanism of Titania Nanotube Arrays in Hydrofluoric Acid Electrolyte." *Journal of Materials Science* 43(6):1880–84.

Degusty, Dian, Rahmayeni, and Syukri Arief. 2013. "Sintesis, Karakterisasi Dan Uji Aktivitas Fotokatalitik Nanokomposit TiO2 -ZnFe2O4." *Jurnal Kimia Unand* 2(2303):98–103.

Fujishima, Akira, Xintong Zhang, and Donald A. Tryk. 2008. "TiO2 Photocatalysis and Related Surface Phenomena." *Surface Science Reports* 63(12):515–82.

Giahi, Masoud, Deepak Pathania, Shilpi Agarwal, Gomaa A. M. Ali, Kwok Feng Chonge, and Vinod Kumar Gupta. 2019. "Preparation of Mg-Doped TiO 2 Nanoparticles for Photocatalytic Degradation of Some Organic Pollutants." *Studia Universitatis Babes-Bolyai Chemia* 64(1):7–18.

Halme, Janne. 2002. "Dye-Sensitized Nanostructured and Organic Photovoltaic Cells: Technical Review and Preliminary Tests." *Solar Cells*.

Kustiningsih, Indar, Cecep Saripudin, Siti Suwansih, Denni Kartika Sari, Jayanudin, and Slamet. 2020. "Photocatalytic Degradation of Organic Waste in Visible Light Using TiO2 Nanotubes Array." *IOP Conference Series: Materials Science and Engineering* 796(1).

Kustiningsih, Indar, S. Slamet, and Widodo Wahyu Purwanto. 2015. "Synthesis of TiO2 Nanotubes by Using Combination of Sonication and Hydrothermal Treatment and Their Photocatalytic Activity for Hydrogen Evolution." *Reaktor* 15(3):204.

Liu, Xu, Zhongqing Liu, Jian Zheng, Xin Yan, Dandan Li, Si Chen, and Wei Chu. 2011. "Characteristics of N-Doped TiO2 Nanotube Arrays by N 2-Plasma for Visible Light-Driven Photocatalysis." *Journal of Alloys and Compounds* 509(41):9970–76.

Morin-Crini, Nadia, Eric Lichtfouse, Giangiacomo Torri, and Grégorio Crini. 2019. "Applications of Chitosan in Food, Pharmaceuticals, Medicine, Cosmetics, Agriculture, Textiles, Pulp and Paper, Biotechnology, and Environmental Chemistry." *Environmental Chemistry Letters* 17(4):1667–92.

Mosahab, Rahim, Osman Mahamad, T. Ramayah, RA Nur Amalina, Fakultas Ekonomi, Universitas Diponegoro, Jaeqline Citraluki, Program Studi, Akuntansi Fakultas, Ekonomi Dan, Universitas Muhammadiyah Surakarta, Pebriani Efendi, Kastawan Mandala, عبدالله،ماهر, Sadegh Fayzollahi, Alireza Shirmohammadi, Behzad Latifian, 崔宇红, 楚恒亚, 李枫, Handriyani Timor, Udin Syaefudin Saud, Dadang Suhardan, Universitas Pendidikan Indonesia, Kinerja Guru, Mutu Sekolah, Ali Bakhit Jaafreh, Abedalfattah Z. Al-abedallat, Therese A. Joiner, Keng Boon Ooi, Binshan Lin, Boon In Tan, Alain Yee Loong Chong, TY Koh, SP Low, D. A. N. Kepuasan, Konsumen Pada, P. T. Taspen, Fajri Ziha Rahman, and Jurnal Riset Akuntansi. 2011. "No Title福島県況調査." 图书情报工作 4(3):410–19.

Pan, Xi, Qin Xie, Wu Lin Chen, Gui Lin Zhuang, Xing Zhong, and Jian Guo Wang. 2013. "Tuning the Catalytic Property of TiO2 Nanotube Arrays for Water Splitting." *International Journal of Hydrogen Energy* 38(5):2095–2105.

Ramchiary, Anjalu. 2020. *Metal-Oxide Semiconductor Photocatalysts for the Degradation of Organic Contaminants*. INC.

Regonini, D., C. R. Bowen, A. Jaroenworaluck, and R. Stevens. 2013. "A Review of Growth Mechanism, Structure and Crystallinity of Anodized TiO2 Nanotubes." *Materials Science and Engineering R: Reports* 74(12):377–406.

Rinaudo, Marguerite. 2006. "Chitin and Chitosan: Properties and Applications." *Progress in Polymer Science (Oxford)* 31(7):603–32.

Roy, Poulomi, Steffen Berger, and Patrik Schmuki. 2011. “TiO2 Nanotubes: Synthesis and Applications.” *Angewandte Chemie - International Edition* 50(13):2904–39.

El Saeed, Ashraf M., M. Abd El-Fattah, and M. M. Dardir. 2015. “Synthesis and Characterization of Titanium Oxide Nanotubes and Its Performance in Epoxy Nanocomposite Coating.” *Progress in Organic Coatings* 78:83–89.

Shahvaranfard, Fahimeh, Marco Altomare, Yi Hou, Seyedsina Hejazi, Wei Meng, Benedict Osuagwu, Ning Li, Christoph J. Brabec, and Patrik Schmuki. 2020. “Engineering of the Electron Transport Layer/Perovskite Interface in Solar Cells Designed on TiO2 Rutile Nanorods.” *Advanced Functional Materials* 30(10).

Siripatrawan, Ubonrat and Patinya Kaewklin. 2018. “Fabrication and Characterization of Chitosan-Titanium Dioxide Nanocomposite Film as Ethylene Scavenging and Antimicrobial Active Food Packaging.” *Food Hydrocolloids* 84:125–34.

Slamet., Ibadurrohman., M. 2023. *Teknologi Nano Fotokatalisis: Teori Dan Aplikasi*. Pertama. Depok: Pena Persada Kerta Utama.

Slamet and Ratnawati. 2012. “Potensi Titania Nanotube Array Dan Aplikasinya (Prospect of Titania Nanotube Array and Its Application on Hydrogen Production and Waste Treatment).” *Jurnal Kimia Kemasan* 34(2):249–62.

Wang, Junpeng, Ping Yang, and Baibiao Huang. 2015. “Self-Doped TiO 2-x Nanowires with Enhanced Photocatalytic Activity: Facile Synthesis and Effects of the Ti 3+.” *Applied Surface Science* 356:391–98.

Wu, Fangjun, Xin Li, Wei Liu, and Shuting Zhang. 2017. “Highly Enhanced Photocatalytic Degradation of Methylene Blue over the Indirect All-Solid-State Z-Scheme g-C 3 N 4 -RGO-TiO 2 Nanoheterojunctions.” *Applied Surface Science* 405:60–70.

Yu, Wei, Xinjuan Liu, Likun Pan, Jinliang Li, Junying Liu, Jing Zhang, Ping Li, Chen Chen, and Zhuo Sun. 2014. “Enhanced Visible Light Photocatalytic Degradation of Methylene Blueby F-Doped TiO 2.” *Applied Surface Science* 319(1):107–12.

Zhang, Wei, Jiwang Chen, Yue Chen, Wenshui Xia, Youling L. Xiong, and Hongxun Wang. 2016. “Enhanced Physicochemical Properties of Chitosan/Whey Protein Isolate Composite Film by Sodium Laurate-Modified TiO2 Nanoparticles.” *Carbohydrate Polymers* 138:59–65.

Zhang, Xiaodong, Gang Xiao, Yaoqiang Wang, Yan Zhao, Haijia Su, and Tianwei Tan. 2017. “Preparation of Chitosan-TiO2 Composite Film with Efficient Antimicrobial Activities under Visible Light for Food Packaging Applications.” *Carbohydrate Polymers* 169:101–7.

Zhang, Yuliang, Mingwei Shang, Yifan Mi, Ting Xia, Petra Wallenmeyer, James Murowchick, Lifeng Dong, Qiao Zhang, and Xiaobo Chen. 2014. “Influence of the Amount of Hydrogen Fluoride on the Formation of (001)-Faceted Titanium Dioxide Nanosheets and Their Photocatalytic Hydrogen Generation Performance.” *ChemPlusChem* 79(8):1159–66.