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Improvement of the Efficiency of TiO_2 Photocatalysts with Natural Dye Sensitizers Anthocyanin for the Degradation of Methylene Blue: Review

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Abstract

One of the potential method utilizing for dye degradation is photocatalitic, with to its low cost, highly effective, and environmentally friendly. Effectivenes of TiO_2 photocatalysts can be enhanced by adding a dye sensitizer. Dye-sensitizer material absorbs visible light to facilitate electron excitation process. Addition of dye-sensitizer makes TiO_2 photocatalyst promotes it to be more responsive to visible light. Natural anthocyanin dyes are often used as sensitizers of TiO_2 semiconductors. Anthocyanins are, usually in the purple to the red color range, a group of natural dyes found in the flowers, leaves, and fruit of plants. The essential principles of dye sensitization to TiO_2 have been explored in this review. It is feasible to reduce the band gap energy in the TiO_2 photocatalyst by modifying it using a natural dye sensitizer modification. Dye sensitizers on TiO_2 nanotubes plate have the potential to be employed in a dye degradation photocatalytic period.

Keywords: Anthocyanins, dye-sensitizer, Natural Dye, photocatalysis, TiO_2

1. Introduction

Industrial activities become a major source of dye pollutants, particularly textile, paper, and plastic (Wang & Yang, 2016). Methylene blue ($C_{16}H_{18}N_3SCl$), a heterocyclic aromatic chemical compound, is often utilized in those types of industries (Albayati et al., 2015). Methylene blue can cause several harmful effects including vomiting, increased heart rate, cyanosis, irritation of digestive tract upon inhalation, and irritation of the skin (Roosta et al., 2014; Handayani et al., 2015). At room temperature, methylene blue is a dark green powder that will produce a dark blue solution when dissolved in water.

Methylene blue waste treatment is generally carried out by physical and/or chemical processing methods covers filtration, coagulation, precipitation, adsorption, ozonation, reverse osmosis, ion exchange, and advanced oxidation processes (Jin et al., 2008; Rafatullah et al., 2010; Alsalhy et al., 2013; Al-Bayati et al., 2014). However, these quite expensive, and there are several operational problems e.g. lower removal efficiency, higher specificity for certain dye groups, and the formation of toxic intermediates (Palekani et al., 2000). To avoid the adverse effect of methylene blue, Minister of Environment of the Republic of Indonesia regulated the permissible content of methylene blue in waters is 5-10 mg / L as stated in the Decree of Permen LH No. 5 tahun 2014.

The photocatalytic method can be employed to remove methylene blue organic dyes contained in wastewater, through decolorization process, as well as degradation of methylene blue dyes (Dariani et al., 2016; Trandafilovic et al., 2017; Wu et al. 2017; Theivasanthi et al., 2018). Titanium dioxide (TiO_2) is widely used as catalyst in the photocatalytic process is. This photocatalyst has several advantages due to its stability, harmless/non-toxic, resistance to corrosion, abundant availability in nature, and a relatively cheap price (Yanmet al., 2011; Dariani et al., 2016; Wu et al., 2017). However, TiO_2 has several weaknesses including its small specific surface area (Pan et al., 2013), a large recombination rate, and a high band gap energy value (Antony et al., 2012). Those weaknesses contribute in low photon absorption (Liu et al., 2011). Some modification of TiO_2 morphology had been created, include *nanorods* (Choi et al., 2008; Shahvaranfard et al., 2020), *nanowires*

(Rahmat et al., 2019; Kustiningsih et al., 2018) dan *nanotubes* (Abu et al., 2009; Kustiningsih et al., 2020), in order to increase the surface area of TiO_2. Nanotubes becomes favorite shape of TiO_2 morphology because of it provides larger surface area compared to the other morphologies and it also has better photocatalytic effectiveness (Yan et al., 2011).

For the past several years, dye-sensitized solar cells (DSSC) have been widely researched for lowering bandgaps of photocatalysts by sensitizing them with a dye molecule (Kavitha et al., 2019; Li et al., 2013; Wongcharee et al., 2006; Ghicov et al., 2009). Using dye sensitizer TiO_2 photocatalyst, the same method has been used for photocatalytic applications (Samuel et al., 2020; Murcia et al., 2019; Watanabe et al., 2017; Zyoud et al., 2017).

The addition of dye sensitizer to TiO_2 photocatalysis can promote the effectiveness of photocatalysis (Angulo et al., 2020). Dye sensitizer material absorbs visible light to allow electrons to be excited. The addition of a dye sensitizer causes TiO_2 to be more responsive to visible light. According to Angulo (2020), dye sensitizer can easily adhere to the surface of the catalyst and reach an excited state by photon absorption in the visible light spectrum range.

Table 1. Comparison between synthetic and natural dye sensitizer

	Synthetic Dye	**Natural Dye**	**Ref.**
Type	Ru (II) polypyridine complex, cis-$(Ru(dcbH_2)_2(NCS)_2)$(N3)	Anthocyanin, carotenoid, chlorophyll, flavonoid	(Chowdhury et al., 2013; Ludin et al., 2014)
Source	Made up of complex materials that are made through different chemical reactions.	The materials are available in nature and is the result of extracts from flowers, fruits and leaves.	(Geetam et al., 2017; Ludin et al., 2014)
Availability	Its availability is not in the long term because it is a precious metal.	Natural dye 100% always available.	(Li et al., 2014; Mehmood et al., 2014; Chien et al., 2013)
Synthesis process	Requires a complex procedure, which requires a wide variety of solvents and requires a lot of time for the purification process.	The synthesis procedure is simple.	(Sharma et al., 2014; Polo et al., 2004)
Cost	Synthetic cost is expensive.	Synthetic cost is cheap.	(Ludin et al., 2014; Chowdhury et al., 2013; Kumar et al., 2004)
Effects on the environment	Provides an adverse effect on the environment because of its chemical hazard properties.	Has very little impact on the environment because it comes from nature.	(Shalini et al., 2015; Chowdhury et al., 2013)
Stability	Degraded slowly by sunlight, therefore the DSSC process is slow.	The degradation of natural dyes by sunlight results in stability problems on the DSSC.	(Mehmood et al., 2014; Gong et al., 2012)
Solar absorption spectrum	The absorption of N_3 dye is above 800 nm	Natural Dye shows absorption in the range 400-700 nm.	(Ludin et al., 2014; Kumar er al., 2004)
Eficiency	Higher efficiency	The efficiency of NDSSC is lower, this is because of the degradation of the natural dye.	(Geetam et al., 2017; Gong et al., 2012)

Campbell et al., (2004) reported ruthenium (II) polypyridyl complex successfully induced photo-electron transfer. However, ruthenium compounds are complex, expensive and the rarely availability of these precious metals, thus finding a cheaper, simpler, and safer sensitizer is a scientific challenge. The purpose of a simpler sensitizer is a sensitizer that is easy to synthesize.

Table 1 summarizes comparison between synthetic and natural dye sensitizer. Although the efficiency of natural dye sensitizer is lower than synthetic one, its impact on the environment, availability, simpler synthesis processes, and lower prices can be sufficient reasons to continue to develop the use of natural dye-sensitizers for waste degradation. This review paper focuses on discussing the use of anthocyanin dye-sensitizers. The major goal of this study, according to the scenario above, was to see how effective natural dye sensitizer anthocyanin was at increasing TiO_2 photoactivity.

2. Photocatalytic Process Mechanism

Photocatalysis is widely used to accelerate the reaction process. During the process, a semiconductor interacts with light provided by an energy source to produce Reactive Oxidizing Species (ROS). This species is employed to direct the photocatalytic transformation process of a pollutant (Pelaez et al., 2012). Semiconductors with capability to adsorp photons can be used as photocatalysts. A semiconductor material has an electrical band structure in which the highest occupied energy band, known to as the valence band (VB), and the lowest-occupied energy band, called to as the conduction band (CB), are separated by some band gap energies. Furthermore, positive hole will be established in valence band (h_{VB}^{+}). The electrons in the conduction band (e_{CB}-) that reach the surface of the particle will reduce the surrounding oxygen (O_2) to form superoxide anions ($O_2^{\bullet\,-}$). Meanwhile, the holes in the valence band (h_{VB}^{+}) will oxidize adsorbed organic compounds either directly or indirectly through the formation of hydroxyl radicals ($OH^{\bullet}$) (Ramchiary et al., 2020). The radical compounds $OH^{\bullet}$ and $O_2^{\bullet\,-}$ act as strong oxidizers to degrade dye waste into CO_2 and H_2O (Shaban et al., 2019). On the other hand, electrons (e_{CB}^{-}) will reduce hydrogen ions (H^{+}) to form hydrogen gas.

Photocatalysis refers to the generation of catalytically active species with the help of photons rather than the use of light as a catalyst in a reaction. The process is called a "catalyzed photoreaction" when the first photoexcitation occurs in an adsorbate molecule, which subsequently interacts with the ground state of the catalyst substrate. The process is a "sensitized photoreaction" if the first photoexcitation occurs in the catalyst substrate and the photoexcited catalyst then interacts with the ground state adsorbate molecule (Testino, et al., 2007).

The mechanism of reduction and oxidation in the photocatalytic process is illustrated in Figure 1. It should be emphasized that at least two processes occur during the photocatalytic reaction. For the manufacturing to be successful, all of these things must happen at the same time. There will be a lot of reactive oxidizing species. The first reaction involves photogenerated holes oxidizing dissociatively bound H_2O, while the second involves photoexcited electrons reducing an electron acceptor (often dissolved oxygen) to produce a hydroxyl and superoxide radical anion, respectively (Mills et al., 1997).

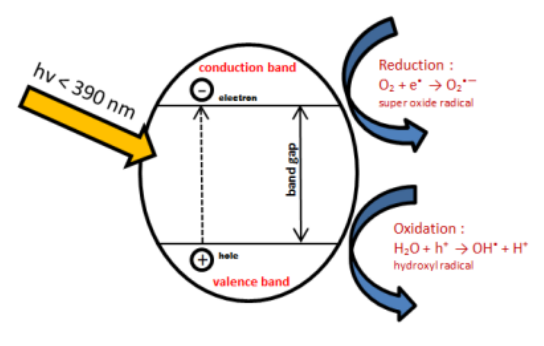

Figure 1. Schematic of photocatalytic

The photocatalytic reactions follows these equations:

$$TiO_2 + hv\ (\geq Eg) \longrightarrow TiO_2^{*} + e_{CB}^{-} + h_{VB}^{+}$$

$$O_2\ (ads) + e_{CB}^{-} \longrightarrow O_2^{\bullet -}$$

$$H_2O + h_{VB}^{+} \longrightarrow OH^{\bullet} + H^{+}$$

$$H^{+} + e_{CB}^{-} \longrightarrow H_2$$

$$OH^{\bullet}/O_2^{\bullet -} + \text{organic} \longrightarrow CO_2 + H_2O$$

(Slamet et al., 2018)

Semiconductor material can be utilized as photocatalyst due to its energy band gap between conduction band and valence band. Illumination by photon on it with equal or higher energy than its energy band gap will trigger electron excitation from valence band to conduction band (e_{CB}^{-}).

Furthermore, the excited electrons will enter the linked metal, causing the protected metal's potential to shift to a more negative state than in the oxide state. The total number of electrons on the metal surface protects the metal from oxidation and anode dissolution events (Kustiningsih et al., 2015).

3. Titanium dioxide (TiO_2) Photocatalyst

A photocatalyst is a semiconductor material with capability in adsorbing photons. Metal oxides are stable semiconductors those are easy to synthesize. Some examples of metal oxides that can be potential metal oxides to be employed in the photocatalytic process are WO_3, $BiVO_4$, SnO_2, CuO, ZnO, TiO_2. Notice the photocatalytic process is under the influence of visible light. WO_3 and $BiVO_4$ have band gaps of 2.8 eV (440 nm) and 2.4 eV (517 nm), respectively; however, due to their deep conduction band (CB) levels at potentials more significant than 0 V vs NHE (pH = 0), they could not be employed for hydrogen production (Watanabe, 2017)

TiO_2 is one of the greatest effective photocatalysts for both pollutants in water might be organic or inorganic. Organic materials can be degraded and mineralized to CO_2 and water when exposed to ultraviolet radiation (Abdullah et al., 2017)**.** Some of the advantages that TiO_2 such as, have good optical properties, does not toxic, cheap, has good activity photocatalyst a semiconductor with a wide bandgap, no soluble in water, has a wide surface area, high mechanical and thermal stability (Sun et al., 2019).

3.1 Structure and Morphology of TiO_2

Nanomaterials morphology starts to develop in line with the progression of nanotechnology. The crystal structure of anatase is more stable than that of rutile, according to a thermodynamic assessment. Anatase crystals have a 3.2 eV bandgap energy (380 nm) and are stable at low temperatures, whereas rutile crystals are stable at high temperatures and have bandgap energy of 3.0 eV (415 nm), and brookite crystals are difficult to view because they are not durable (Tian et al., 2018).

The crystal structure of TiO_2 can be described as follows:

(a) Anatase, is a polymorph form of TiO_2 that is more stable at low temperatures. The formation of anatase from amorphous may occurs at temperature range of 400 - 650 °C. The band gap of the anatase crystal structure is 3.2 eV, equivalent to the UV wave energy with a wavelength of 388 nm.
(b) Brookite, this polymorph is unstable, thus it is difficult to observe.
(c) Rutile, this polymorph is more stable at high temperatures. The formation of rutile from amorphous occurs from a temperature of 700 °C. The band gap of the rutile structure is 3.0 eV, equivalent to light energy at a wavelength of 413 nm.

According to Halme (2002), the anatase phase of TiO_2 can provide a greater photon flow compare to the rutile and brookite phases. It may be caused by high photoactive ability of anatase phase. The larger surface area of the anatase structure provides higher reduction ability. Moreover, the anatase structure also has a surface that can absorb much water to react with holes than that of rutile (Liu et al., 2009).

The morphology of TiO_2 can be established in various form of nanoparticles (Safajou et al., 2017; Giadhi et al., 2019), nanorods (Kang et al., 2008; Shahvaranfard et al., 2020), nanowires (Rahmat et al., 2019; Kustiningsih et al., 2018) and nanotubes (Ghicou et al., 2009; Kustiningsih et al., 2020). TiO_2 nanotubes can increase a lot of visible light scattering and absorption due to the ratio of length to large diameter, as well as large surface area, that can facilitate the transport of electrons to the electrodes (Gopal et al., 2012). The average diameter and tube thickness of the nanotubes is 166 nm and 52 nm, respectively (Pelawi et al., 2019). Meanwhile, according to Slamet & Kurniawan (2018), the average diameter of nanotubes is 174 nm.

The morphology of TiO_2 nanotubes can be synthesized by the hydrothermal method (Kustiningsih et al., 2015; Canbay et al., 2020), anodization (Li et al., 2019; Roy et al., 2011; Regonini et al., 2013; Kustiningsih et.al., 2020; Yanyue et al., 2020) and template methods (Wang et al., 2020). The hydrothermal method produces non-array nanotubes morphology, while the anodization and template methods produce array nanotubes morphology.

The hydrothermal method is a method that was used for the synthesis of inorganic materials several years ago. Hydrothermal is a methode of synthesis of materials using a one-step reaction in an aqueous medium at a temperature of low and high pressure (P > 100 kPa) (Viana et al., 2009).

Hydrothermal method has advantages: easy to obtain the morphology of the nanotubes, flexible process procedure and easy to modify, feasible for wide applications, and suitable for production with large capacities (Ou and Lo, 2007). However, this method has some drawbacks related to the high temperature and pressure of synthesis process, the synthesis duration is relatively long, and difficulties in obtaining a uniform size (Li et al., 2009). Meanwhile, the scale of the nanotubes produced by the template method can be controlled by the template used, but this is unpractical and has high difficulty level. To form nanotubes independently, neat, upright, and have uniform size/morphology, anodization method can be chosen as proper method.

The electrochemical anodization process made titanium dioxide (TiO_2) nanotubes from titanium plates with various electrolyte concentrations, voltage, and anodization time parameters. In the electrochemical process, a titanium plate is used as an anode and a Pt plate as a cathode. The electrolyte solution used is ammonium fluoride (NH_4F), water in glycerol or ethylene glycol. The use of viscous electrolyte solutions such as ethylene glycol and glycerol in the Ti anodization process will produce nanotubes with a more extended size compared to aqueous solutions, but the time required is longer, so stirring is needed to increase mass transfer through the surface of the nanotubes so that can achieve the speed of formation of nanotubes (Macak & Schmuki, 2006).

3.2. Synthesis of TiO_2 nanotubes by anodizing method

Parameters that influence the anodization process are the composition and concentration of the electrolyte solution, anodization potential, time, and pH (Bai et al., 2008; Sun et al., 2014). TiO_2 nanotubes the results of the anodization process are always amorphous, which is inactive when used in the photocatalytic process. Therefore, annealing process should be carried out to increase the crystallinity of the photocatalyst (Feng et al., 2020).
The electrolyte solution used is a solution based on acids and organic substances containing fluoride ions or chloride ions. The formation of smooth and flat nanotubes with smaller diameters can be obtained from fluoride solutions containing viscous organic electrolytes such as ethylene glycol and glycerol (Macak et al., 2008). If the fluoride content is too low (≤0.05% wt) or too high (> 1% w), it can interfere with the formation of the TiO_2 nanotubes layer. Too low fluoride content may cause the formation of the TiO_2 layer to be denser than the TiO_2 nanotubes array, while higher fluoride content may lead to the breakdown of the TiO_2 layer. The fluoride ion concentration used is usually within the range of 0.1 – 1 wt% (Roy et al., 2011).

Employment of a thick electrolyte solution e.g. ethylene glycol in the anodization process may produce nanotubes with a longer size than a dilute solution, however, it may require longer duration of the process. Therefore, stirring may be applied to enhance mass transfer through the nanotubes surface in order to accelerate nanotubes formation (Macak & Schmuki, 2006). The length and diameter of the nanotubes produced are also influenced by the value of the anodization potential (voltage). The greater the anodization value until certain conditions, the longer the tube will be.

Lai and Sreekantan (2011) reported that the voltage during anodization process affected the morphology, length and diameter of Titania nanotubes. At 10 V, a nanoporous surface morphology with length of 275 nm was obtained. Meanwhile, at 30 V a uniform nanotubes surface morphology was achieved with average aspect ratio (L/D) was 11,8. At voltages of 20, 40, and 50 volts, non-uniform nanotubes surface morphology structure was obtained with an average aspect ratio (L / D) ≤10. Kavitha S., R.S (2019) performed anodization process by employing solution of ammonium fluoride (NH_4F) in ethylene glycol as electrolyte. The NH_4F concentration used was 0.7% wt, and anodizing voltage of 30 volts. A uniform nanotubes structure was obtained at 6 h anodizing time. Usage of lower concentration indicated formation of porous structure.

Effect of pH on nanotubes morphology was investigated. At a pH lower than one, the high dissolution rate and growth rate of nanotubes in a dilute electrolyte solution will produce short nanotubes between 500 - 600 nm (Roy, P., et al., 2011). The nanotubes formation rate of 23 nm / min can be obtained at pH = 3 (Sreekantan, S., et al., 2009). At high pH the oxidation reaction and chemical dissolution have decreased and lead to the morphology of the nanotubes produced was imperfect (Ratnawati, R., & Slamet, 2012).

Furthermore, nanotubes are not formed at pH = 6 (Zhang, Y., et al., 2009).

3.3. Strategies to increase the activity of TiO_2

Several strategies have been carried out to increase the efficiency of TiO_2 in the photocatalytic process. They aimed to make TiO_2 provides better response to visible light (45% of sunlight) at wavelength 400-800 nm. This can be done by modifying morphology, such as increasing the surface area and porosity, as well as chemical modification by adding components in the TiO_2 structure.

Compared with other nanostructures, TiO_2 nanotubes can significantly enhance the scattering and absorption of visible light due to the sizeable length-to-diameter ratio, large surface area and facilitate electron transport to the electrode (Gopal et al., 2012). The use of a dye sensitizer can affect the spectrum of light that can absorb on the surface of the semiconductor, and the ability of the dye-sensitizer to stick to the surface of the semiconductor can affect the efficiency of the photocatalytic process. The nanoporous structure of the oxide semiconductor can increase the amount of dye that is adsorbed more and more (Handini, 2008).

4. Dye Sensitizer to Increase Visible Light Active (VLA) TiO_2 Photocatalyst

Dye photosensitized is an effective way to expand the photoresponse of TiO_2 to visible light (Pelaez, M., et al., 2012). Reducing the band gap in TiO_2 photocatalysts by sensitizing with dye molecules is a technology that has been widely used in Dye Sensitized Solar cells (DSSC) (Ghosh, M. Et al., 2020). Similar technology is also applied to the photocatalytic process to produce hydrogen gas using dye-sensitized TiO_2 / Pt photocatalysts (Yuan, Y., Et al., 2015). Therefore, it is possible to use dye-sensitized technology in the photocatalytic process for the degradation process of organic waste (Zyoud, A., et al., 2013, Chowdhury, P., Et al., 2013).

The use of dye sensitizers can affect the spectrum of light that can be absorbed on the semiconductor surface. Moreover, the ability of the dye sensitizer to adhere to the semiconductor surface can affect the efficiency of the photocatalytic process. The mechanism from dye photosensitized to pollutant degradation is based on the absorption of visible light in exciting electrons from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO) of the dye. The excited dye molecule then transfers electrons to TiO_2's conduction band, converting the dye to its cationic radical in the process. The TiO_2 surface only serves as an electron acceptor for transporting electrons from the sensitizer to the substrate, and the valence band of TiO_2 is unaffected. The dye molecules' LUMO should be more negative than TiO_2's conduction band in this process. The injected electrons soon make their way to the titania surface, where they are scavenged by molecular oxygen, resulting in the formation of superoxide radical $O_2\bullet$ and hydrogen peroxide radical •OOH. These reactive species can also produce hydroxyl radicals in a disproportionate amount. Dye-sensitizer material absorbs visible light and allows electrons to be excited.

Addition of this dye-sensitizer on TiO_2 may promote it more responsive to visible light. According to Angulo (2020) dyes can easily adhere to the surface of the catalyst and reach an excited state by photon absorption in the visible light spectrum range. When the electrons in the dyes are in an excited state, the electrons from the Highest Occupied Molecular Orbital (HOMO) will be transferred to the Lowest Unoccupied Molecular Orbital (LUMO) of the dyes. Furthermore, they will be transferred to the conduction band in the TiO_2 semiconductor. The injection of electrons into the conduction band on TiO_2 increases concentration of Reactive Oxygen Species (ROS), such as superoxide anion radical (O_2^-). It leads increasing of degradation rate of pollutants compared to the photocatalytic process without TiO_2 modification (Pelaez et al., 2012; Chowdhury et al., 2013; Watanabe et al., 2017; Angulo et al., 2020).

This approach employs sunlight as the source of natural energy to provide driving force of entire photocatalytic process. The conduction band in the semiconductor must be more positive than the LUMO of the dye molecule used to certify that the sensitization process is occured successfully. Need to know that electron injection can only occurs at suitable anchoring group surface, energy level, and redox potential of the dye molecule (Chowdhury et al., 2013; Ismail et al., 2018).

The nanopore structure of the oxide semiconductor can increase the amount of dye adsorbed (Handini et al., 2008). Several studies have shown that the transition of dye metals with the anchoring group of carboxylates and phosphates shows an effective electron transfer process (Chowdhury et al., 2013). Transition metal sensitizers such as Ru (II), Fe (II), and Os (II) show a great ability to absorb the entire visible spectrum. This is due to the formation of the d6 complex (Chowdhury et al., 2013). Currently, most of the dye sensitization process has been investigated using different dyes, such as ruthenium, rhodamine B, eosin, erythrosine, and cyanin (Chowdhury et al., 2013; Ghosh, M., et al., 2020). Ruthenium complex is a dye-sensitizer with the highest efficiency up to around 11-12% (Aswaniet al., 2011; Chiba et al., 2016).

The synthesis process of ruthenium complex compounds is very complicated and expensive. Moreover, it contains heavy metals that can be polluting the environment. In contrary, natural dye-sensitized is environmental friendly with a simple and inexpensive synthesis process. Therefore, it can be an alternative to dye-sensitizers et al., 2003). (Wongcharee et al., 2007). The types of natural dye sensitizers that are often used to sensitize photocatalysts are summarized in Table 2. Although natural dye sensitizers have been widely used in solar cell applications, their utilization in water treatment is still new (Zyoud et al., 2018).

Visible light irradiation will cause excited dyes and transfer of electrons to the conduction band in semiconductors. It improves the performance of the photocatalytic water splitting reaction for hydrogen production (Singh & Dutta, 2018; Angulo et al., 2020). Electrons are injected from the excited state of the oxidation potential of the dye onto the conduction band in inorganic semiconductors on a time scale of several hundred femtoseconds. The injected electrons move to the surface inorganic semiconductors and react with protons to produce hydrogen (Ga'bor et al., 2001; Akihiro et al., 2018). Natural pigments, including chlorophyll, anthocyanins, nasunins, and carotenoids, can meet these requirements. Previous research on TiO_2 sensitization has been carried out by natural pigments (Nerine et al., 1997; Calogero et al., 2008; Zyoud et al., 2018; Ghosh et al., 2020). The manufacture of natural dye solutions is the process of extracting color pigments found in fruit, flowers, seeds, leaves, stems, and roots of plants (Fitrihana et al., 2007). The type of compound, texture, and water content of the plant material to be extracted obviously influence the determination of the extract method.

Table 2. Natural Dye Sensitizer

Natural Dye Sensitizer	Source	Ref
Anthocyanin	Rosella (Hibiscus Sabdariffa), blue pea (Clitoria Ternatea)	(Wongcharee et al., 2007; Khwanchit et al., 2006)
Betalain	Red Beet Roots	(Zhang et al., 2008)
Anthocyanin	Red Cabbage, Red Onion	(Dumbrava et al., 2008)
Betalain	Bougainvillea, red turnip	(Calogaron et al., 2010)
Anthocyanin	Colombian Caribbean Species (Sysygium Cumini)	(Carloz Diaz-Uribe et al., 2017)
Anthocyanin	Mangosteen peel (Garcinia Mangostana)	(Ghosh et al., 2020)
Chlorophyll	Leaves of spinach	(Samuel & Yam, 2020)
Carotene	Pelthophorum Pterocarpum	(Samuel & Yam, 2020)

Extraction methods that can be used to extract dry plant tissue powder are maceration, reflux, and soxhletation using solvents with a certain degree of polarity. Maceration method is conducted by immersing the sample in a suitable solvent to withdraw the desired component at low temperature discontinuously. The advantage of the maceration method is that it require less solvents, no heating, and is more practical. However, this method requires longer processing time. The reflux method is carried out at high-temperature conditions discontinuously, while the soxhletation method is carried out at high temperatures continuously. Reflux method consumes less solvent than soxhletation method, and requires shorter time compare to maceration method (Kristianti et al., 2008).

Natural dyes extracted from leaves, flowers, and fruits have advantages over complex precious metal compounds and other organic dyes. Natural dyes are readily available in nature, easy to extract, cheaper, and environmentally friendly. Anthocyanin natural dyes are used to sensitize semiconductor TiO_2 nanotubes made by chemical anodization techniques (Pelaez et al., 2012). Anthocyanins are polar pigments that dissolve well in polar solvents (Hanum et al., 2000). Anthocyanin is a pigment that can be extracted from natural sources. Anthocyanins are included in a class of flavonoid compounds. It play a role in the emergence of red to blue colors on fruit, leaves, and flowers (Ghosh et al., 2020). Anthocyanins can also be extracted from other plant parts such as tubers, stems, and roots (Patrocinio et al., 2009; Rajan et al., 2019). Anthocyanins generally contain hydroxyl, methoxyl, carboxyl groups along with the core structure of the flavylium cation. Natural anthocyanins always have one or more sugar components such as β-D-Glucose, β-D-Galactose, and α-L-Rhamnose (Calogero et al., 2009; Pinto et al., 2015).

Anthocyanin has potential to be used as natural dye sensitizers, due to its availability of in nature is abundant, cheap and has no harm for the environment. Furthermore, it has an α-hydroxyl carbonyl group that may bond to the surface of the TiO_2 semiconductor. The electrons are excited from the sensitizer (*anthocyanin*) leading to the conduction band in the TiO_2 semiconductor (Hao et al., 2006; Zyoud et al., 2018; Atli et al., 2019). Anthocyanins contain hydroxyl groups (OH), which maintain the surface of the catalyst hydrophilic. It makes the organic waste molecules present in the water closer to the surface of the catalyst. It simultaneously reduce the surface tension between the catalyst surface and organic waste (Zyoud et al., 2018). Mangosteen rind contains anthocyanins such as cyanidin-3-sophoroside, and cyanidin-3-glucoside which play a role in mangosteen peel coloring (Qosim & Ali, 2007; Chaovanalikit et al., 2012).

The LUMO level of the sensitizer is required to be higher than the conduction band in semiconductors (for example for TiO_2, -4 to -4.3 eV). Meanwhile, the HOMO level of the sensitizer must be lower than the redox potential of the semiconductor (for example, TiO_2 has a redox potential range of -4.6 to -5 eV). Anthocyanin dyes from mangosteen peel have E (LUMO) and E (HOMO) of -2.27 eV and -4.81 eV, respectively. Both of them meet the criteria to be able to transfer electrons to the conduction band in the semiconductor TiO_2 efficiently under visible light (Ismail et al., 2018; Ghosh et al., 2020).

All types of flavonoids can be extracted with alcohol compounds such as ethanol, methanol, and propanol. Ethanol as an organic solvent is often employed in extracting natural dyes from various plants. As consideration, ethanol is more environmental friendly compared to methanol (Khusniati et al., 2007). Acid can denature plant cell membranes, then dissolves anthocyanin pigments leave the cells. Therefore an acidic atmosphere is recommended when extracting flavonoids.

5. Application of Dye-Sensitizer in the Photocatalytic Process of TiO_2

Ghosh et al., (2020) using natural dye-sensitized aeroxide TiO_2 sensitized by natural dyes from mangosteen rind extract. The photocatalytic process of MS-TiO_2 was studied in the degradation process of methylene blue (MB) by visible light irradiation (MS-TiO_2) (Ghosh et al., 2020). About 28 mg anthocyanin dyes was successfully extracted from 100 grams of dry mangosteen rind and then was used to sensitize TiO_2 aeroxide. It provided lower band gap of MS-TiO_2 photocatalysts than the band gap of TiO_2 aeroxide photocatalyst (Ghosh et al., 2020).

Adsorption of dye molecules on the surface of TiO_2 aeroxide causes changes in the structure of the surface molecules (Ghosh et al., 2020). UV-Vis spectrophotometry may be employed to measure band gap of MS-TiO_2. The band gap of the TiO_2 anatase is -3.2 eV. It will make the photocatalytic process controllable only by UV light when uses as photocatalyst. However, MS-TiO_2 has a band gap of -2.95 eV. This suggests that a lower band gap can be achieved by mangosteen dye-sensitizing TiO_2 (MS-TiO_2) molecules using natural anthocyanin dyes, which can make the photocatalytic process controlled by visible light (Ghosh et al., 2020).

TiO_2 aeroxide does not show photocatalytic activity for the degradation of MB by visible light. This may caused by the band gap of TiO_2, does not allow the formation of electron-hole pairs with visible light energy. Meanwhile, MS-TiO_2 can absorb a lot of energy from visible light. (Ghosh et al., 2020). The results of research conducted by Ghosh et al., (2020) with the addition of anthocyanin to TiO_2 showed a more significant MB degradation of 78% when compared to research conducted by Tang et al., (2003) which used TiO_2 without the addition of anthocyanin sensitizer resulting in degradation MB by 28%. The addition of anthocyanin can increase the absorption of photon light on the TiO_2 photocatalyst, which has an impact on increasing the degradation of dyes.

Most photocatalytic reactor systems involve the dispersion of the photocatalyst into an organic waste solution. Although this method has advantages in the photocatalytic process, it is necessary to separate TiO_2 particles from the organic waste solution at the end of the process (Samuel & Yam, 2020; Jallouli et al., 2017). Samuel & Yam, (2020) used a natural dye sensitized TiO_2 nanotubes plate to degrade methylene blue under the visible light. The size of nanotube used was 2 cm x 4 cm. Spinach leaves, dry leaves and fresh flower from Peltophorum Pterocarpum were use to siynthesize natural dye sensitizer as new chlorophyll, old chlorophyll and source of β-carotene, respectively. Synthetic dye N-719 was also used in this photocatalyst.

The anodization method was used to synthesize the TiO_2 nanotubes array by using two electrodes immersed in an electrolyte solution. A platinum metal wire was used as a cathode while Ti metal with a size of 2 cm x 4 cm was used as an anode. Natural dyes were obtained by maceration extraction method. Acetone-heptane was used as solvent. Extraction process was conducted for 24 h. Synthetic dye N-719 is dissolved in butanol to obtain concentration of 20 mg/ml prior to the dye sensitization process. The dye sensitization process on TiO_2 nanotubes was carried out by dipping the TiO_2 nanotubes plate into the dye solution. This process was carried out for 24 h to ensure maximum dye adsorption process. The plates were cleaned briefly in ethanol solution by using ultrasonicator then rapidly dried.

Methylene blue 200 ml was used to evaluate the performance of the photocatalytic process of prepared natural dye-sensitized TiO_2 nanotubes. The effectiveness of chlorophyll could degrade methylene blue dyes up to 40% of the initial methylene blue concentration (Samuel & Yam, 2020).

William et al., (2019) had successfully synthesized and characterized composites of graphene oxide (GO) and TiO_2 (GO-TiO_2). Doctor blade technique was employed to deposit film layer. This film layer was sensitized with natural dye extracted from Colombian Source (Bactris guineensis) (CO). The presence of natural dye sensitizers and GO increased the optical properties of the inner TiO photocatalyst visible light range. This prepared photocatalyst was used to degrade methylene blue solution. The kinetic of degradation was observed as pseudo-first-order model. It can be concluded that the presence of GO contribute significant synergistic effect together with natural sensitizers to achieve a yield of 35% photocatalytic reactions.

Carlos et al., (2017) investigated the effect anthocyanins extracted from Caribbean species S. cumini as natural dye sensitizer of thin films of TiO_2 photocatalyst on photocatalytic reactions. The photocatalytic activity using the prepared photocatalyst increased three fold compared to the use of non modified TiO_2 thin films. The effect of pH value on the degradation process of methylene blue was investigated by Dariani et al., (2016). 0.5 grams TiO_2 photocatalyst with particle size of 200 nm was equilibrate with methylene bule at concentration of 10 mg / L for 5 h. pH of the system was varied to 3, 5, 7, 9, and 11. As conclusion, higher pH resulted more methylene blue molecules that can be degraded. Meanwhile, smaller TiO_2 particle size used, facilitated more methylene blue molecules to be degraded. Table 3 summarized the studies that have been carried out to increase the photoactivity of TiO_2 photocatalysts for dye degradation.

Table 3. Previous Research Relating to Photocatalytic Reactions

Title	Result	Reference
Photocatalytic Reaction and Degradation of Methylene Blue on TiO_2 nano-sized Particles	The effect of pH value on the photocatalytic reaction using a TiO_2 photocatalyst as much as 0.5 grams with a particle size of 200 nm. The concentration of methylene blue was 10 mg / L at various pH values of 3,5,7,9 and 11 for 5 hours. The greater the pH value, the more methylene blue molecules are degraded. The smaller the TiO_2 particle size used, the more methylene blue molecules that can be degraded.	Dariani et al., 2016
Improvement of the Photocatalytic activity of TiO_2 using Colombian Caribbean Species (Syzygium cumini) as Natural Sensitizrers:Experimental and Theoritical Studies	The results of the study showed that the photocatalytic activity using a TiO_2 photocatalyst that had been modified using natural dye sensitizer from the S.cumini extract resulted in an increase of 3 (three) times greater, when compared to the use of unmodified TiO_2 thin films.	Carloz et al., 2017
Powder and Nanotubes Titania Modified by Dye Sensitization as Photocatalysts for the Organic Pollutants Elimination	The photoactivity of TiO_2 powder and nanotubes was enhanced by modification using Quinizarin and Zinc protoporphyrin dye sensitizers and has been shown to reduce band gap energy. The rate of degradation of methyl orange has increased significantly when compared to conventional catalysts without modification.	Murcia et al., 2019
Photocatalytic activity of Graphene Oxide-TiO_2 thin films sensitized by natural dyes extracted from Bactric guineensis	The natural dye sensitizer extracted from Colombian Source (CO) and Graphene Oxide (GO) improves the optical properties of TiO_2 photocatalysts in the visible light range. Photocatalytic degradation using TiO_2-GO-CO photocatalyst in a methylene blue solution, indicates that the presence of GO has a synergistic effect in conjunction with a natural sensitizer to achieve a yield of 35%.	Vallejo et al., 2019
Photocatalytic Activity of Aeroxide TiO_2 Sensitized by Natural Dye Extracted from Mangosteen Peel	TiO_2 aeroxide which has been sensitized with natural anthocyanin dyes from mangosteen rind extract is used to degrade methylene blue, and has been proven to be successful in reducing the band gap energy of the photocatalyst to 2.95 eV, so that it can make the photocatalytic process controlled by visible light.	Ghosh et al., 2020
Photocatalytic Degradation of Methylene Blue under Visible Light by Dye Sensitized Titania	As a photocatalyst, TiO_2 nanotubes plates with a size of 2 cm x 4 cm were used which were sensitized with natural dyes to degrade methylene blue by a photocatalytic process using visible light. Methylene blue dye can be degraded up to 40% of the initial concentration.	Samuel & Yam, 2020

Efficiency of natural dye as a sensitizer in TiO_2 nanotubes is lower than that of synthetic dye. If viewed from the impact on the environment, availability, simpler synthesis processes, and lower prices can be sufficient reasons to continue to develop the use of natural dye-sensitizers for the degradation of dye waste.

To increase the efficiency of removing dye pollutants, the photocatalytic process using a natural dye-sensitizer on TiO_2 nanotubes can be combined with other processes. The combination of photocatalytic methods with other methods has been carried out by many previous researchers, including the addition of ozone (Sulaiman et al., 2017), incorporation with zeolites (Kustiningsih et al., 2020), and electrocoagulation (Ates et al., 2017; Slamet & Kurniawan, 2018; Keramati et al., 2019). The combination of electrocoagulation and photocatalysis methods with photocatalyst TiO2 nanotubes for the degradation of tartrazine dye waste and simultaneous hydrogen production has been carried out by Slamet & Kurniawan, (2018).

6. Conclusion

In this review, the basic principles of dye-sensitization to TiO_2 have been discussed.
Modifications to the TiO_2 photocatalyst using a natural dye-sensitized are possible to decreases the band gap energy in the TiO_2photocatalyst. The use of dye sensitizers on TiO_2 nanotubes plates has the potential to be used in the / photocatalytic system for dye degradation. The addition of anthocyanin can increase photon light absorption on the TiO2 photocatalyst, leading to increased dye degradation. The results of research conducted by Ghosh et al., (2020) with the addition of anthocyanin to TiO_2 showed a more significant MB degradation of 78%.

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