Recent Development and Application of TiO$_2$ Nanotubes Photocatalytic Activity for Degradation Synthetic Dyes – A Review

Euis Uswatun Hasanah$^1$, Indar Kustiningsih$^{1,2,*}$, Slamet$^3$, Maughal Ahmed Ali Baig$^4$

$^1$ Master's Program in Chemical Engineering, Postgraduate Program, Universitas Sultan Ageng Tirtayasa, Cilegon, Banten, Indonesia
$^2$ Department of Chemical Engineering, Faculty of Engineering, Universitas Sultan Ageng Tirtayasa, Cilegon, Indonesia
$^3$ Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Depok, Jawa Barat, Indonesia
$^4$ Department of Mechanical, CMR Technical Campus Kandlakoya, Medchal Road, Hyderabad 501401, India

*E-mail: indar.kustiningsih@untirta.ac.id

Article History
Received: 16 April 2021; Received in Revision: 12 Agustus 2021; Accepted: 19 September 2021

Abstract

Synthetic dyes waste from textile industries, produce of the problematic pollutants in wastewater. TiO$_2$ based photocatalysis are materials that exhibit excellent absorption behavior for organic compounds in wastewater due properties including nontoxicity, high photocatalysis degradation ability, and chemical stabilities. However, several challenges exist regarding TiO$_2$ nanotubes pure applications for dyes degradation such as poor affinity, high band gap energy, and difficulty of recovery and easy to recombination so it would decrease effectiveness of the photocatalysis process. Therefore, more design and optimization testing need to be conducted on the treatment conditions in order to reach higher removal efficiencies with lower costs. The modified physical properties by adding metal dopant, nonmetal, and sensitizer significantly enhanced photocatalysis activity. These parameters, which affect photocatalysis activity on degrade dyes waste pollutants, are discussed in the current review. As a result, the photocatalysis becomes more expected, and encourages to further research development.

Keywords: Degradation, dyes, Photocatalytic, synthetic, TiO$_2$

1. Introduction

Waste processing is a critical technology for both human life and the environment. Liquid waste is considered a problem, especially waste from the textile industry. The textile industry wastewater contains organic and inorganic materials with a high concentration in every process unit (Kustiningsih et al., 2020). Many textile industries use synthetic dyes because synthetic dyes have advantages such as being more economical, has many variations of colors, and being durable (Wildan et al., 2018). Organic compounds in water will reduce dissolved oxygen levels for aquatic organisms because this oxygen is used as an oxidizer for organic compounds (Widyo et al, 2018).

Synthetic dyes are categorized as azo dyes. It has high toxicity, easily absorbed into the skin, and can be carcinogenic (Da et al., 2015). Various synthetic dyes are available, such as methyl orange, rhodamine B, remadzol red, and methylene blue. About 60%-70% of the dyes used in textile dyeing are synthetic dyes of the azo group (Bethi et al., 2016). Azo dyes are widely used in dyeing fabrics, especially for made of cellulose, rayon, and wool fibers. Azo dyes are difficult to degrade because it will be environmental pollution. And then, dye pollutants have a more serious environmental impact because it were contain mutagenic harmful chemicals and contained more metal components, such as Cu, Ni, Cr, High, and Co (Haryono et al., 2018).

Various conventional wastewater treatment options are proposed, such as biological (Pavithra et al., 2019), chemical oxidation (Hartanto et al., 2019), adsorption methods (Thahir et al., 2019), and membrane filtration (Kiswanto., 2019). However, this method has some weaknesses, such as pollutants that are not always feasible and effective. Table 1 shows a list of weaknesses and strengths of different methods. The biological measures implemented by the bacterial strain are referred to as biodegradation methods (Sari et al., 2019).
Waste treatment using microorganisms is in demand by industrialists and environmental practitioners because it is easy and inexpensive to operate and invest. In additionally, waste treatment using microorganisms has high resistance to various types of pollutants in the waste, but the drawback is that it requires a long adaptation time (Chen et al., 2020). Chemical oxidation processes are used to reduce contaminants from various types of wastewater (Hsu et al., 2013). Chemical oxidation has several disadvantages, such as the consumption of chemicals are high, the pH needs to be controlled, produces much sludge, and it can cause the secondary pollution problem (Sanford et al., 2019).

Membrane filtration is another alternative for the removal of wastewater (Mózo, 2017). The separation mechanism depends on the size of the particle, its solubility, and effective action. It has the advantages of being simple, efficient, and quick to vanish even in high contaminants (Seifhosseini et al., 2018), but membrane membranes are easily brittle and the operating costs are expensive the process is expensive (Wildan et al., 2018).

<table>
<thead>
<tr>
<th>Methods</th>
<th>Weakness</th>
<th>Strength</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biological treatment</td>
<td>1. The procedure is difficult to control.</td>
<td>1. Low cost</td>
<td>(Sarayu et al., 2012)</td>
</tr>
<tr>
<td></td>
<td>2. Unable to remove the high concentration of waste. It has no effect on the quantity of chemical energy demand.</td>
<td>2. High performance for decoloration dye waste</td>
<td></td>
</tr>
<tr>
<td>Chemical oxidation</td>
<td>1. Chemical supply is high</td>
<td>1. Capable of energy conservation</td>
<td>(Devi et al., 2016)</td>
</tr>
<tr>
<td></td>
<td>2. pH control is required</td>
<td>2. This simple method and compact</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. Make a lot of sludge</td>
<td>3. Connectivity to the material is sensible</td>
<td></td>
</tr>
<tr>
<td>Membrane filtration</td>
<td>1. Requires high maintenance costs</td>
<td>1. Effective and fast handling</td>
<td>(Ghazanfari et al., 2017)</td>
</tr>
<tr>
<td></td>
<td>2. Does not apply to wastewaters with a high concentration.</td>
<td>2. Environment friendly</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. A fast method of dye removal</td>
<td></td>
</tr>
<tr>
<td>Hydrothermal treatment</td>
<td>1. Requires a high temperature and pressure</td>
<td>1. The waste decolorization process is incredibly successful</td>
<td>(Zhang et al., 2016)</td>
</tr>
<tr>
<td></td>
<td>2. The operating costs are expensive because it requires much energy</td>
<td>2. It produces no additional pollution.</td>
<td></td>
</tr>
<tr>
<td>Conventional photocatalysis</td>
<td>1. The recovery and renewal of materials are difficult.</td>
<td>1. Low cost of production, significant energy savings</td>
<td>(Guo et al., 2019)</td>
</tr>
<tr>
<td></td>
<td>2. It is possible for recombination to occur.</td>
<td>2. Environmentally critical</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1. It is only active in the presence of UV light.</td>
<td>3. Adjustment of the catalyst loading would be simple</td>
<td></td>
</tr>
</tbody>
</table>
As mentioned previously, additional treatment of sludge methods is still not economical and unable to treat textile wastewater because dyes used in the textile industry are biopersistent. Each outflow of this inefficient wastewater treatment has serious environmental consequences. The water pollution concerns are caused by a lack of biodegradation. Photocatalysis can be used to change the potential solution in established methods for wastewater processes. To enhance photocatalyst performance, modification uses different doping materials applied to TiO₂ nanoparticles (Kustiningsih et al., 2019). Incorporating the methodology developed into the conventional treatment plan is the best way to improve the treatment process's efficiency. Therefore, the photocatalyst has high performance in the removal of organic compounds.

TiO₂ is a semiconductor material widely used to degrade organic waste (Slamet et al. 2018). TiO₂ material has many advantages such as nontoxic, more economical, non-corrosive, and more stable compared to other materials (Shayegans et al., 2018). Then, extensive studies were conducted to improve the performance of TiO₂ photocatalyst, so it would be effective in degrading synthetic dyestuffs compounds in wastewater.

2. TiO₂ Photocatalyst

Photocatalysis is a combination process of photochemical processes and catalysts, which is a chemical synthesis process involving light as a catalyst and a trigger as an accelerator of the transformation process. Semiconductors can function as photocatalysts due to the existence of an empty energy region called the energy band (Eg), it remains of the conduction band edge and the valence band, then when enabled by photons via higher energy than Eg, it strengthens the valence band to a conduction band (eCB⁺) and gives a substantial hole (h⁺) inside the valence band (hvB⁺) (Ge et al., 2016).

Titanium dioxide (TiO₂) was observed in 1972 through photolysis processes. It has many functions, such as photocatalytic pollution elimination, air separation, sensor systems, inorganic agents, and self-functioning substances (Yoo et al., 2018). TiO₂ photocatalyst has a good ability to interact with the visible region. The TiO₂ photocatalyst attached to the metal will act as a photoanode to prevent corrosion of the metal. This protection system is called photocathode protection or commonly known as cathode protection. In the photocathode system, activation of electrons from the valence band to the TiO₂ conduction band occurs when a metal is coated with TiO₂ and exposed to ultraviolet light (Hu et al., 2016).

Furthermore, the excited electrons will enter the connected metal and cause a shift in the potential of the protected metal to be more negative than in the oxide form. The total electrons on the metal surface cause the metal to be protected and protected from oxidation or anode dissolution events (Kustiningsih et al., 2015). Even so, the prevention of metal corrosion or cathode protection can be achieved (Wahab et al., 2015).

TiO₂ has different categories of crystal structures, such as anatase (tетragonal), brookite (orthohombic), and rutile (tetragonal). Based on these three crystal structures, anatase and rutile have the same structure, namely, tetragonal (Panigrahi et al., 2017). According to thermodynamic review, the crystal structure of anatase is more stable than rutile. The crystal structure of anatase is at low temperatures and it has 3.2 eV bandgap energy (380 nm), whereas rutile crystals are stable at high temperatures and have bandgap energy of 3.0 eV (415 nm), while brookite crystals are difficult to observe because they are unstable (Tian et al., 2018).

The anatase phase of TiO₂ semiconductor shows the highest photocatalytic activity to its energetic separation capability between the conduction and valence bands exposed to UV radiation (Jang et al., 2017). TiO₂ semiconductor receives an absorption spectrum from UV light in the ultraviolet spectrum, enabling light absorption and reactivity at the molecular level (Nasirian et al., 2018). To improve its performance as a photocatalyst, TiO₂ is changing the catalyst’s size to a nanosize. To improve the visible light active photocatalyst appearance of TiO₂, chemical treatment must support semiconductor morphology.

2.1. The Synthesis of Photocatalyst Methods

Many studies have been optimized TiO₂ performance as a photocatalyst by changing the catalyst to nanostructures. Nanoparticles TiO₂ have been used in photocatalysis for many years (Sun et al., 2018). In the
development of photocatalyst technology, researchers have developed many semiconductor morphologies for TiO$_2$ nanomaterials such as nanowires (Kustiningsih et al., 2018), nanotubes (Tian et al., 2018), and nanofibers (Yin & Jia, 2015).

TiO$_2$ nanowires have been synthesized in significant quantities recently. The formation of TiO$_2$ nanowires from layered titanate particles involves three steps, such as the removal of the layer Na$_2$Ti$_3$O$_7$, formation of nanosheets, and the formation of nanowires. Electrophoretic deposition of TiO$_2$ colloidal suspensions with a template followed by template removal can be used to fabricate highly ordered TiO$_2$ nanowires. Additionally, solvothermal, physical vapor deposition and electrodeposition methods for preparing TiO$_2$ nanowires have been reported (Safajou et al., 2017).

The effect of the relative nanowire ratio on the efficiency of the photocatalyst was discussed elaborately. While nanowires counted for less than 20% of the composites, the internal surface of the composite is equivalent to that of a pure nanoparticle film (Wu et al., 2012). The composite cells containing 5% and 20% nanowires showed higher activity than pure nanoparticle cells (Maheswari et al., 2015). Those other results indicated that carefully evaluating the nanowire composites has benefit from the particle size of nanoparticles combined and the extended electron light absorption of nanowires. A nanowire is a nanostructure with a diameter of approximately between 9 and 10 nm (Sun et al., 2018). The relatively homogenous hydrolysis of metal alkoxide and the subsequent oxidation with sodium hydroxide made an interesting method for preparing TiO$_2$ nanofibers.

Nanofibers are a type of nanoscale material in nanotechnology. Nanofibers TiO$_2$ can form using hydrothermal (Wu et al., 2018) and electrospinning processes (Ismaya et al., 2017). Electrospinning is a process of producing TiO$_2$ nanofibers. The parameter process such as calcination temperature, applied voltage, and syringes collector distance. The final phase of TiO$_2$ was identified by calcination at a temperature of 500 °C (Kim et al., 2019). Their dimensions range between 1 and 200 nm. It is constructed using metals or semiconductors materials. Aspect ratios (width divided by length) are common in both 3-5 nm (Khan et al., 2017). Direct chemical synthesis is needed to produce nanofibers. Integration of binding acts as a structure control agent and forms strong bonds with various aspects of nanofibers.

TiO$_2$ nanotubes are attracted interest and intensive studies due to their activity of the high specific surface area, ion-changeable, and photocatalytic ability. TiO$_2$ nanotubes are achieving popularity, resulting in high photoactivity for different kinds of dyes removal. According to the particular geometry, nanotubes have an organized structure and surface volume ratio, show special features, and the specific surface area. TiO$_2$ nanotubes have tube diameters ranging from 10 to 500 nm, thickness of layers ranging from a few hundred nanometers to 1000 μm (Fu et al., 2018).

Nanotubes were produced using the Ti and Pt sheet as substrates on process electrochemical containing an electrolyte solution. TiO$_2$ can be used in the application as a powder or as a film. TiO$_2$ powder has many disadvantages, such as being dispersible, quickly emulsions are too complex to handle, has a low illumination reaction, and causes pollution when used incorrectly (Mo et al., 2018). TiO$_2$ film has high stability and a larger surface area to further increase the photocatalyst activity compared to TiO$_2$ powder (Chun Chen et al., 2017).

Nanofibers and nanowires are two quasi-one-dimensional (Q1D) structures with a specific growth and a diameter of less than 250 nm direction. In contrast, nanowires and nanofibers have a similar structure shorter in length. Nanotubes have a hollow internal system similar to that of nanowires, even with excellently structured surfaces. In table 2 summarized, nanotubes have the largest surface area of any TiO$_2$ structure based on BET examination for enabling light and reaction conditions to diffuse across the tube length. Holes, ions, and electrons formed by photocatalysis are being transferred to the boundary layer's wide area.
Table 2. Examination of BET specific surface areas and bandgap value systems for TiO$_2$, nanotubes, nanowires, nanofibers, and nanoparticles

<table>
<thead>
<tr>
<th>Nanostructure</th>
<th>Average Pore Size (Å)</th>
<th>Surface Area (m$^2$/g)</th>
<th>Bandgap (E$_g$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanotubes</td>
<td>45</td>
<td>354</td>
<td>3.00</td>
<td>(Pelawi et al., 2020)</td>
</tr>
<tr>
<td>Nanowires</td>
<td>60</td>
<td>189</td>
<td>3.09</td>
<td>(Cho et al., 2015)</td>
</tr>
<tr>
<td>Nanofibers</td>
<td>67</td>
<td>219</td>
<td>3.10</td>
<td>(Truppi et al., 2017)</td>
</tr>
<tr>
<td>Nanoparticles</td>
<td>44</td>
<td>228</td>
<td>3.18</td>
<td>(Xiao et al., 2020)</td>
</tr>
</tbody>
</table>

The review of TiO$_2$ nanotubes synthesis the would be discussed shortly here. The disadvantages of TiO$_2$ nanotubes have bandgap of 3.0 eV, low in terms of light energy, and recombination is relatively easy. TiO$_2$ nanotubes can be formed by three methods such as hydrothermal, template, and anodization. The hydrothermal method uses a liquid material’s chemical reactivity at a high temperature in an insulated pressure vessel (Ranjitha et al., 2015). The nanotube surface morphology is controlled by the hydrothermal method, such as the type of alkaline, the concentration of alkaline, reaction temperature, and time (Kustiningsih et al., 2020). And then, the most commonly used technique for preparing nanotube systems is the template method.

The precursor nanotubes are formed within tubular structures. The nanotubes physical dimensions will be identical to those of the template (Sun et al., 2020). The nanotubes physical size would also match those of the template accurately. The template has controllable pore sizes of up to 250 nm, and a film thickness ranges from 0.1 to 100 µm (He et al., 2019). The electrochemical anodization ensured be the most valuable processes to receive the titania nanotubes as reasonably easy techniques and it could be automated effectively. Moreover, anodization is a cheap method and can also be acceptable for other transition metals. The anodic oxidation of titanium substrates in a fluoride solution containing electrolytes in the formation of TiO$_2$ nanotubes and highlighting the critical element of fluoride ions. Titanium film anodizing is a common technique for producing high surface area TiO$_2$ nanotubes (Elysabeth et al., 2020).

However, all of the Ti plates are used in application areas. In an electrochemical anodization TiO$_2$ nanotube synthesis process, a titanium substrate is anodized containing fluoride in the electrolyte solution at a constant anodic voltage. A good composition of fluoride is contained in the electrolyte (0.5 wt%). Too much fluoride in the electrolyte composition (more than 1 wt%) will damage the formation of TiO$_2$ nanotube layers (Yanyuefeng et al., 2020).

Table 3. The method of forming TiO$_2$ nanotubes

<table>
<thead>
<tr>
<th>Methode</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodizing</td>
<td>1. Easy to apply 2. Can form smooth nanotubes 3. High aspect ratio.</td>
<td>Difficult to make suitable nanotubes if produced in large quantities</td>
<td>(Elysabeth et al., 2019)</td>
</tr>
<tr>
<td>Template</td>
<td>1. Cheap 2. Easy to modify</td>
<td>1. Unstable 2. Need more time for the operation</td>
<td>(Hsu et al., 2019)</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>1. Does not require several chemicals 2. The equipment is easy to use</td>
<td>1. Operates at high temperatures and pressures 2. unstable</td>
<td>(Kustiningsih et al., 2015)</td>
</tr>
</tbody>
</table>
According to the explanation from table 3 of the three different methods, anodization is considered the best method because anodization is the best method for produce TiO₂ nanotubes because it is more efficient and effective than other methods. For decades, the anodization of titanium to form oxide layers has been studied. It is necessary to determine the efficiency for controlling anodizing processes such as potential, electrolyte, fluorine concentration, and time. When the optimum anodization is in suitable condition, it would be produced a large diameter and length of the tube. Usually, the anodizing process will occur in 30 minutes to 2 hours to allow the structure to modify and enhance itself.

Almost all electrolyte conditions (salt solutions, organic solvents, and most acids) form a compact oxide layer with a uniformly increasing thickness with a potential range (Pasi khani et al., 2016). The other variation is when determining the solubility of Ti₄⁺ (perchloric acid, electrolytes with a high fluoride concentration). The anodization process enables a wide variety of tube structures and morphologies to be formed. A few approaches have been explained to form more complex nanotube structures and morphologies. These approaches are based on modifying the electrochemical conditions during the anodization.

The first step of the anodization process is dissolving the TiO₂ film layer in an electrolyte solution containing many F⁻ ions, and then small holes can be formed in the pore formation process. After that, a pore appears on the surface of the TiO₂ layer, and a high level of acidity at the bottom of the tube can scratch the pore into a tube structure (Pelawi et al., 2020). The reaction mechanism for the formation of TiO₂ nanotubes is shown in equations 1 through 5 (Slamet et al., 2018).

\[
\begin{align*}
\text{Ti} & \quad \rightarrow \quad \text{Ti}^4+ + 4e^- \\
2\text{H}_2\text{O} & \quad \rightarrow \quad 2[\text{O}] + 4e^- + 4\text{H}^+ \\
\text{Ti} + 2[\text{O}] & \quad \rightarrow \quad \text{TiO}_2 \\
\text{Ti} + 2\text{H}_2\text{O} & \quad \rightarrow \quad \text{TiO}_2 + 4\text{H}^+ + 4e^- \\
4\text{H}^+ + 4e^- & \quad \rightarrow \quad 2\text{H}_2
\end{align*}
\]

Zhang et al (2017), argued that the use of TiO₂ nanotubes prevents charge recombination when randomly packed TiO₂ nanoparticles and TiO₂ nanotubes have the same electron diffusion coefficient. TiO₂ nanotubes with a greater diffusion layer and a bigger electron would show superior electron transport. Consequently, TiO₂ nanotubes demonstrate a greater light absorption impact, which improves the light-harvesting properties. Special features of the internal and external surface area are available for the adsorption and chemical reactions of organic pollutant molecules (Yoo et al., 2018). TiO₂ nanotubes can increase efficiency due to the fast electron transport and 1D structure with minimum charge recombination sites (Wahab et al., 2015). This step would also lead to an adverse increase in the total density. Combined oxidation and dissolution increase the length of nanosized holes and establish a morphology, decreasing the current of this method here again. The width and length of nanotubes can continue to grow as long because their rate of increase affects the separation value and will continue to grow until the dissolution value equals the growth rate. A pretreatment, both chemical or physical, must raise the oxide film on the Ti foil to increase nanotube growth. However, nanotubes show a great potential as heterogeneous catalysts for accelerating the degradation of azo dyes in a water solution via photocatalysis. So that, the following sections discuss the advancement of research on TiO₂ nanotube enhancement using various synthesis techniques.

2.2. Modification of TiO₂ Nanotubes as Photocatalyst

The major limitation of TiO₂ is the widest bandgap, which causes a series of factors, most significantly, by reducing the amount of solar energy modified to UV light, which also reports only for 4% of solar irradiance (Yoo et al., 2018). Consequently, electrons and holes obtained by photons quickly recombine due to low effectiveness. Several methods were applied to enhance the photocatalytic quality of TiO₂ nanotubes for further effectiveness for waste degradation. The processes can be defined in three ways: a surface-active area for optimum catalytic performance, band structure for charge exchange, and effective absorption across the total visible spectrum (Sa et al., 2019).

It is important to understand about photocatalytic operation of TiO₂. Enhanced TiO₂ nanotubes have been developed for electron separation and catalytic performance. TiO₂ nanotubes can customize in various ways, such as the relation of a sensitizer and the deposition of metal nanoparticles. The TiO₂ nanotube rearrangement has been discussed using various methods.
**Doping Metal and Non-Metal TiO$_2$ Nanotubes**

Doping is a widely used technique for modifying the electrical and optical properties of substances where certain one or even more components or molecules are doped into the substrate to form required electrical and optical properties. Recent studies have reported that doping TiO$_2$ with carbon, nitrogen, fluorine, iron, and iodine results in the required narrow bandgap leading to a more significant reaction to visible light while also increasing the overall photocatalytic activity (Wang et al., 2019). Conversely, Metal ion doping has been researched to optimize photocatalytic performance. Metal doping would get a more significant effect on the TiO$_2$ conduction band, because Ti contributes to the conduction band while adding value even a small amount to the valence band.

Specified metals, for example, Cu and Fe can take titanium molecule area, resulting in new energy sizes in TiO$_2$ conduction and valence bands. (Hejazi et al., 2019). It is discovered that while reducing the bandgap, energy is procured through various metal groups. The study mainly contains different metals to doping TiO$_2$, such as a noble metal, a rare earth metal, and a transition metal. Transition metals including Fe, Zn, Mn, Cr, and Co have been analyzed as dopants for TiO$_2$ to increase its photocatalytic activity and change the spectrum of TiO$_2$ absorption spectra into a visible range (Zhang et al., 2019). Finally, transition metals act as photogenerated charge carriers and enhance photocatalytic activity by lowering the energy required to generate photons.

As demonstrated recently, researchers have shown the ability of TiO$_2$ photocatalyst with nonmetals doping. Several other nonmetal doping agents such as C, N, S, F, and Cl are mainly used to improve the photocatalysis of TiO$_2$ (Basavarajappa et al., 2020). Under ultraviolet irradiation, the quantum supply of nonmetal doping with TiO$_2$ would be greater than visible irradiation. (Joseph et al., 2018). Nonmetal nitrogen doping of TiO$_2$ photocatalysts has attracted attention based on their electrical structures, these included good sensitivity, low ionization, and an atomic width similar to that of oxygen compared to conventional TiO$_2$ (Bjelajaj et al., 2017). It is commonly integrated as interstitials and replace in nanocomposite structures. Moh Hasmizam et al (2017), discussed based on the fact that nonmetal fluorine does not only change the TiO$_2$ bandgap, but also it can increase the surface acidity and lead to the formation of oxidized Ti$^{4+}$ ions. Additionally, the charge separation would be enhanced and promoted in photogenerated methods.

**Sensitizer**

A further critical method for reducing the recombination rate is implementing a heterojunction band structure. The primary purpose of optimizing the adsorption electron transport of TiO$_2$ nanotubes with various materials create pairs of electrons that can be effectively divided and streamed into various directions. Nanostructured TiO$_2$ nanotubes can generate many photons during a phase transition and have higher efficiency in the visible light spectrum. This element would be measured to use various materials, including chalcogenides (binary and ternary), carbon nitride, and metal oxides. TiO$_2$ photocatalytic activity under visible light can be further increased by combining sensitizer with the TiO$_2$ surface. Sensitized TiO$_2$ has been successfully used to reduce various contaminants (Daghnir et al., 2013). This method involves several electron transfer stages. The adsorption mechanism of the sensitizer occurs due to the molecule's contact with the TiO$_2$ surface.

Tiwari et al (2018), discussed many methods that have been developed to increase the photocatalytic activity under visible light, and using a sensitizer with a semiconductor material that has a small band gap. Several researchers have researched to increase the absorption of visible light in TiO$_2$ nanotubes by adding a sensitizer using chalcogenide material. Chalcogenide material has a small band gap and is suitable because it has good absorption capacity from ultraviolet to infrared wavelength regions and has good stability (Torimoto et al., 2014).

Several chalcogenide materials can be used as sensitzers such as, Cu$_2$ZnSnS$_4$, FeS$_2$, Cu$_3$SbS$_4$, CuInS$_2$, SnS, CuS$_2$, and AgInS$_2$ (Malankowska et al., 2020). AgInS$_2$ is the best chalcogenide material (Cui et al., 2015). Recently, the AgInS$_2$-TiO$_2$ nanocomposite configuration has been applied to various solar-based energy photocatalytic (Liu et al., 2015). Combining AgInS$_2$ and TiO$_2$ nanotubes improve the photoelectrochemical performance of TiO$_2$ nanotubes in visible light (Kobosko et al., 2017). AgInS$_2$ has high absorption in the visible area, has low bandgap energy, and close to the infrared area due to the absorption coefficient and bandgap energy between 1.87 and 2.03 eV is

---

**References**

- Basavarajappa et al., 2020.
- Joseph et al., 2018.
- Hejazi et al., 2019.
- Wang et al., 2019.
- Zhang et al., 2019.
- Torimoto et al., 2014.
- Cui et al., 2015.
- Liu et al., 2015.
- Malankowska et al., 2020.
an excellent approach for photocatalytic applications.

The other techniques are available for combining sensitizer and TiO$_2$ nanotubes are chemical bath deposition. (Wang et al., 2011), hydrothermal (Liu et al., 2016), and SILAR (Successive ionic layer adsorption and reaction) (Zhang et al., 2017). SILAR method is an effective method in combined the manufacture of sensitizer and TiO$_2$ nanotubes. The advantages of the SILAR method are easy application, more economical in terms of costs, and the equipment required is easy to apply (Kalarivalappil et al., 2018). Synthesis of sensitizer and TiO$_2$ nanotubes using the SILAR method is more efficient at transferring electrons in the photocatalytic process (Z. Liu et al., 2014). Compared to other techniques, the successive ionic layer adsorption and reaction (SILAR) are simple, inexpensive, and having a faster method. Additionally, it can also use to develop sizeable thin films (Shameem et al., 2017).

The SILAR technique involves immersing the substrate in two precursor solutions sequentially and then washing it with water to remove any loosely attached species. Thus, a SILAR cycle consists of the following steps: adsorption of the cation precursor, washing with water, the adsorption of the anion precursor, reaction, and further rinse. The growth rates of thin films using the SILAR technique have been shown to range between a quarter and half of a monolayer, depending on the experimental circumstances. Additionally, the process reports that aqua receptors accept at least some of their structure after adsorption, reducing the concentration of cations and anions in a single layer. Therefore, the thin film development can be perfectly arranged in one SILAR round (Tian et al., 2019).

### 2.3. Application of TiO$_2$ Nanotubes Modification as a Photocatalyst For Dyes Wastewater Treatment

There is two processes for reducing of dyes wastewater using the photocatalysis method. First, an intermediate process the dye initiates excitation is an effect of the energy provided by visible light. The transformed into a semi-oxidized radical by electron injection into the TiO$_2$ conduction band (Cai et al., 2020). The second mechanism dyes was photodegraded process, where the dye compounds connect with the hydrogen peroxide agents formed, and with the electron-hole pairs created because of band-edge excitation, resulting in dye oxidation and reduction directly (Wazir et al., 2020).

Titanium dioxide nanotubes have been identified to become a strongly efficient agent when used on activated approval, with catalysts indicated high removal patterns of more azo dyes (Chen et al., 2020). Yang et al (2019) reported TiO$_2$ nanotubes have shown incredible performance in eliminating methyl orange. The formulation via a hydrothermal process utilizing the solvent NaOH achieved the best responses for color removal, with thermodynamic research showing that degradation occurred through a physical adsorption mechanism.

The catalytic reaction reported an increase in level in response to the growing temperatures. Divyasri et al (2021), discussed the qualified of TiO$_2$ nanotube doped with N and F by either anodizing a Ti material in NH$_4$F and NH$_4$Cl solutions. They realized which annealing the doped TiO$_2$ nanotube arrays in an N$_2$ atmosphere significantly decreased the problem of F atom repair, resulting in greater photocatalytic activity forward into methyl orange. While also, a degradation process using heterostructure as a bridge among photogenerated electron-hole pairs was developed, which was found to be able to degrade 99.9% of Methylene Blue and Rodhamin B solution. Photocatalytic decomposition of a large variety of dyes is sufficient. Even so, it is commonly challenging to validate photocatalyst productivity by evaluating its capability to degrade a specialized dye. The conditions affecting the photocatalytic activity depend on the type of catalyst and dye used.

An immediate comparison of different photocatalysts operating under different conditions is complicated. Additionally, it demonstrated surface research methods by using analysis based on optimization. The observational value was compared to the predicted value, indicating the optimum models consistency. The application of a response surface method can significantly improve the productivity required to obtain the maximum dye decolorization efficiency.

The composite material was produced by effectively combining TiO$_2$ nanotubes with nanomaterials of platinum class metals (Pd, Ru, and Pt). Additionally, the improvement of sample electrodes working as photoanode and cathode in a photoelectrocatalytic reaction has been investigated.

59
The effect of platinum class metal (Pt, Pd, and Ru) modification on the activity enhancement of pure TiO$_2$ nanotubes has been investigated by photocatalyst degradation of 10 ppm MO in the presence of visible light (>420 nm). After 4 hours of reaction, only 4.5% of MO was removed from the pure TiO$_2$ nanotubes, which related to the electrochemical method, and had greater efficiency for the same reaction time. TiO$_2$ nanotubes-Ru had the highest efficiency of 85.8%, which is more than the Platinum and Palladium electrode with 45% and 75% efficiency in the methyl orange degradation process (Li et al., 2019).

The combination AgInS$_2$ with TiO$_2$ nanotubes was degraded Methyl orange used the simple SILAR technique at deposition rates of 2, 3, and 4 cycles. The findings showed of distributed AgInS$_2$ nanoparticles are attached to the surface and inside of TiO$_2$ NTs. The electrodes visible light sensitivity is significantly improved when the TiO$_2$ nanotubes were sensitized with AgInS$_2$ nanoparticles. Under visible light irradiation, the TiO$_2$ nanotubes-AgInS$_2$ with 3 cycles SILAR method photoelectrode exhibits increased photocurrents and increased the photocatalytic activity. Comparable research with pure TiO$_2$ nanotubes carried, and the degradation rate of less than 10%. TiO$_2$ nanotubes-AgInS$_2$ has the greatest photocatalytic activity of these samples, with a degradation rate of 79% under the same irradiation period. According to directing electrons to the conduction band of TiO$_2$ nanotubes-AgInS$_2$ with three deposition cycles significantly improve the photon efficiency and reduce the rate of electron-hole recombination by injecting TiO$_2$ with fluorine, visible light activity enabled, and the formation of electron-hole pairs improved, and greater productivity compared to traditional photocatalysts (Razali et al., 2017). The efficiency of 38% for 2 hours in visible light irradiation.

The degradation of dye in a photocatalytic process was investigated in various cases. The photocatalytic reaction produced no hazardous substances and pursued Kinetics of a pseudo-first order. Temperature increases increased the rate of decolorization, so while increases in pH reduced the rate (Sanjaya et al., 2018). Table 4 summarizes the specific dopants and sensitzers involved with the use of TiO$_2$ as a photocatalytic activity. The enhanced visible light activation methods, the origin of visible light activity, and the electronic structure of various visible light active TiO$_2$ photocatalysts.

Additionally, it has might be effectively used to develop new photocatalysts capable of enhancing photocatalytic performance advances in UV and visible light driven dyes degradation applications. Finally, different methods for identifying suitable methods that promote light absorption and electron-hole separation to enhance photocatalytic activity are described.

**Table 4.** Modification and Best Condition of TiO$_2$ nanotubes photocatalyst using dopant metal, non-metal, and sensitizer for degradation synthetic dyes waste

<table>
<thead>
<tr>
<th>Photoelectrode</th>
<th>Methode</th>
<th>Light source</th>
<th>Pollutant</th>
<th>Result</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ NT-Cu</td>
<td>Hydrothermal</td>
<td>Visible light</td>
<td>Methylene orange</td>
<td>The performance of the Cu doped TiO$_2$ nanotubes has been analyzed in the presence of sunlight for the degradation of 90% methyl orange.</td>
<td>(Razali et al., 2020)</td>
</tr>
<tr>
<td>TiO$_2$ NT-Ag</td>
<td>Anodization</td>
<td>UV light</td>
<td>Orange II</td>
<td>Orange II 20 ppm was successfully degraded with optimum loading of dosage 0.5% of TiO$_2$-Ag.</td>
<td>(Zulfikar et al., 2018)</td>
</tr>
<tr>
<td>TiO$_2$NT-Fe</td>
<td>Anodization</td>
<td>Visible light</td>
<td>Congo Red</td>
<td>The greatest catalytic endurance 91% for its decoloration of Congo red.</td>
<td>(Zafar et al., 2020)</td>
</tr>
<tr>
<td>Photo electrode</td>
<td>Methode</td>
<td>Light source</td>
<td>Pollutant</td>
<td>Result</td>
<td>Ref</td>
</tr>
<tr>
<td>---------------------</td>
<td>-----------------------</td>
<td>--------------</td>
<td>-------------</td>
<td>------------------------------------------------------------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>TiO$_2$ NT-6Ni/4Cr</td>
<td>Hydrothermal</td>
<td>Visible light</td>
<td>Methylene Blue</td>
<td>The co-doped TiO$_2$ with 6Ni/4Cr showed higher photocatalytic activity of 95.6% and high stability toward MB degradation.</td>
<td>(Shaban et al., 2019)</td>
</tr>
<tr>
<td>TiO$_2$ NT-CeO$_2$</td>
<td>Hydrothermal</td>
<td>Visible light</td>
<td>Methylene Blue</td>
<td>The analysis reported that the maximum degradation is 93.4% and the best parameters temperature is 160 °C.</td>
<td>(Quang et al., 2018)</td>
</tr>
<tr>
<td>TiO$_2$ NT-PbS</td>
<td>SILAR deposition</td>
<td>Visible light</td>
<td>Amido Black</td>
<td>Decoloration has been removed 75% of Amido Black after 30 SILAR deposition cycles.</td>
<td>(Hajjaji et al., 2020)</td>
</tr>
<tr>
<td>TiO$_2$ NT-Se</td>
<td>Anodization</td>
<td>Visible light</td>
<td>Rhodamine B</td>
<td>RhB successfully degrade 73.27%.</td>
<td>(Muzzakar et al., 2019)</td>
</tr>
<tr>
<td>TiO$_2$ NT-B</td>
<td>Anodization</td>
<td>Visible Light</td>
<td>Methylene Blue</td>
<td>Methylene blue successfully egraded 34% for 2 hours.</td>
<td>(Szskoda et al, 2016)</td>
</tr>
<tr>
<td>TiO$_2$ NT-NaOH</td>
<td>Template</td>
<td>UV Light</td>
<td>Rhodamine B</td>
<td>After 60 minutes of UV light irradiation, the degradation rate of RhB on TiO$_2$NT-NaOH was 69.8%</td>
<td>(He et al., 2019)</td>
</tr>
<tr>
<td>TiO$_2$ NT-Gd</td>
<td>Anodization</td>
<td>UV light</td>
<td>Methyl Orange</td>
<td>Under ideal conditions (60V 10 h) MO was degraded 95.8%.</td>
<td>(Li et al., 2020)</td>
</tr>
<tr>
<td>TiO$_2$ NT-CuInS$_2$</td>
<td>SILAR deposition</td>
<td>UV-Vis light</td>
<td>Rodhamin B</td>
<td>CuInS$_2$ successfully sensitized TiO$_2$ NT degraded of RhB 97.37%</td>
<td>(Yan et al., 2019)</td>
</tr>
<tr>
<td>TiO$_2$ NT-AgInS$_2$</td>
<td>SILAR deposition</td>
<td>Visible light</td>
<td>Methyl Orange</td>
<td>The highest photodegradation MO rate achieves 79% with 3 SILAR optimum condition</td>
<td>(Zhang et al., 2017)</td>
</tr>
</tbody>
</table>

### 3. Conclusion

This paper highlights the modifications of TiO$_2$ nanotubes, which are regarded as the most exciting and valuable photocatalyst to enhance the photocatalytic activity in dyes wastewater treatment while attached to UV-Vis radiation. Furthermore, TiO$_2$ non-modified applies only to medium concentrations of pollutants because it has low efficiency and cannot perform under the visible parts of the solar spectrum. This article gives a thorough update and research focused on several fundamental difficulties.
while also emphasizing the achievements achieved to enhance the surface-electronic structure of titania significantly. Several methods for enhancement of TiO₂ photocatalyst have been established to reduce recombination, including metal doping, nonmetal doping, and sensitizer. We have evaluated the impacts of ideal dopants on the photocatalytic efficiency of modification TiO₂ nanotubes. The removal efficiency of azo dyes using sensitizer, metal, and TiO₂ doped with nonmetal ions is incredibly attractive. Due to the increased photocatalytic activity, low toxicity, and stabilities of modified TiO₂ photocatalysis, it is expected for industrial applied in the future. This strategy effectively removes dyes from textile wastewater, thus further resolving contaminated water concerns. To improve the processing of synthetic dye waste by photocatalytic besides modified the photocatalyst, several strategies will be used to save energy and costs. It would have minimized the waste generated and reuse the waste in the production process. Then, it would have to increase the quality of the final product and reduce waste formation. Lastly, forbid the use of toxic raw materials to prevent

Acknowledgments

The authors want to thank The Ministry of Education, Culture, Research, and Technology Republik Indonesia under World Class Research Grant 2021.

References


photoelectrocatalytic application. IOP Conference Series: Materials Science and Engineering, 509(1).


Litbang Kota Pekalongan, 17.


Pelaez, M., Nolan. (2012). Applied Catalysis B: Environmental A review on the visible light active titanium dioxide photocatalysts for environmental
applications."Applied Catalysis B: Environmental," 125, 331-349.


