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A review of TiO_2 nanotubes/Co_3O_4/M (M: Au, Ag) photoelectrode for degradation of methyl orange and methylene blue

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ABSTRACT

Background: Wastewater containing dyes occurs due to the discharge of wastewater into rivers without undergoing proper treatment procedures as it should. This waste generally comes from the textile industry. Wastewater containing dyes increases the concentration of organic pollutants in wastewater, which can cause water pollution. Textile dyes are generally made from compounds containing aromatic rings, such as methyl orange and methylene blue. Methyl orange and methylene blue are organic pollutants that cannot be biologically degraded because they contain aromatic rings that are difficult to break down, thus posing a risk of environmental pollution and disrupting aquatic ecosystems. Several conventional wastewater treatment methods for dye degradation, such as coagulation, flotation, sedimentation, and filtration, have been applied, but these methods still have limitations. **Methods:** This review examines recent progress in the development of TiO_2 nanotube-based photoelectrodes modified with Co_3O_4 and noble metals (Ag, Au) for the degradation of methyl orange and methylene blue from wastewater. The use of electrochemical methods has advantages over conventional methods, namely more efficient, environmentally friendly, and flexible for the degradation of dyes in wastewater. The synthesis techniques used are anodization, impregnation-deposition-decomposition, and photodeposition methods. **Findings:** The development of TiO_2/Co_3O_4/Ag and TiO_2/Co_3O_4/Au nanotube-based photoelectrodes shows better performance in the degradation of organic dyes compared to unmodified TiO_2 photoelectrodes, as they can improve photocatalytic efficiency by expanding visible light absorption and increasing surface reactivity. **Conclusion:** The use of TiO_2/Co_3O_4/Ag and TiO_2/Co_3O_4/Au materials has great potential as an environmentally friendly and efficient solution in addressing pollution from persistent textile dye wastewater. The implementation of this technology in industrial wastewater treatment systems promotes advances in the fields of photocatalysis and renewable energy. **Novelty/Originality of this article:** This review is the first to evaluate TiO_2 nanotube/Co_3O_4 photoelectrodes modified with Ag and Au for the degradation of methyl orange and methylene blue.

KEYWORDS: organic pollutants; methyl orange; methylene blue; dye degradation.

1. Introduction

The textile industry in Indonesia has shown quite significant development from year to year. From 2011 to 2017, the number of companies in the textile sector increased, with the upstream and middle sectors (yarn and fabric) increasing from 2.251 companies in 2011 to 2.738 companies in 2017. The clothing sector also recorded an increase, from 2.222 companies in 2011 to 3.595 companies in 2016. However, in 2019, the number of companies in the upstream and middle sectors decreased to 2.512, while the clothing sector decreased to 2.387 companies. Although domestic consumption increased, textile imports

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experienced a spike, with imports increasing by 0.5% per year in the 2011-2015 period, but increasing rapidly to 5.5% per year in 2015-2019, reflecting increasing competitive pressure on the domestic textile industry (Ningsih et al., 2024).

Along with the growth of the textile industry, the amount of waste it generates also increases. During the dyeing process in wet processing, some dyes are adsorbed while others are not and remain in the wastewater. If this wastewater, which still contains high levels of dye, is discharged directly into rivers, it can lead to water pollution. Textile dyes are typically composed of compounds that include aromatic structures, such as methylene blue. Methylene blue is one of the organic pollutants that is non-biodegradable due to its aromatic structure, which is difficult to break down. Even if degradation is possible, it takes a long time. Compounds with aromatic groups are carcinogenic and mutagenic, so the wastewater must be treated beforehand. Methyl orange is a type of dye belonging to the anionic azo group (Sha et al., 2016). Methyl orange has a strong coloring capacity and forms a vivid orange solution when dissolved in water, which is attributed to its molecular structure containing aromatic rings and an -N=N- azo linkage. Consequently, azo dyes such as methyl orange are highly toxic, carcinogenic (Wu et al., 2021), and relatively difficult to degrade (Sha et al., 2016).

Dyes that are difficult to degrade will eventually cause environmental damage. Researchers continue to explore effective methods for dye degradation. Wastewater from the batik production process has been treated using various conventional methods, such as adsorption, ion exchange, ozonation, Fenton, and membrane filtration. These conventional methods have several shortcomings, including high cost, difficulty in managing by-products, long process time, and limited efficiency for certain types of dyes (Sahu & Poler, 2024).

Electrochemical techniques provide an efficient, eco-friendly, and adaptable approach to breaking down dyes in wastewater. Electrochemical methods compared to conventional methods, especially those based on advanced oxidation processes that are superior in decomposing complex dye structures and achieving higher degradation rates. One of the commonly used electrochemical technologies is the photoelectrochemical cell (PEC), which utilizes solar energy for the dye degradation process, reducing operational costs, dependence on chemicals, and environmental impacts, making it more economical and sustainable in the long term (Fu et al., 2017; Mansha et al., 2023; Odling & Robertson, 2016; Riaz et al., 2012; Veziroglu et al., 2020). PEC employs semiconductor materials as the photoanode (Al Jitan et al., 2020; Mohammadi et al., 2017; Tong et al., 2017) and photocathode (Wang et al., 2016).

Titanium dioxide (TiO_2) is frequently used as a photoanode in PEC applications. TiO_2 exists in two main phases, anatase and rutile, which differ in their band gap energies. The band gap of rutile is around 3.0 eV, whereas anatase possesses a marginally wider band gap of approximately 3.2 eV. TiO_2 is widely utilized as a photoanode due to its bandgap, which allows electron excitation under UV light exposure, as well as its high chemical and thermal stability, excellent photocatalytic properties, biocompatibility, and environmental friendliness. However, TiO_2 as a photoanode also has several limitations. Its photoresponse is limited to UV light only, as its wide bandgap restricts absorption occurs in the UV region, which represents merely around 5% of the entire solar spectrum. Additionally, TiO_2 exhibits limited electron mobility and significant charge recombination. High charge recombination occurs when electrons migrate from the photoanode, reducing energy conversion efficiency, as trapped electrons cannot contribute to generating an electric current. Furthermore, TiO_2 as a photoanode also faces challenges related to thick film formation, fabrication constraints, and high production costs (Celebi et al., 2021).

Given the limitations of TiO_2 as a photoanode, particularly the rapid recombination rate of electron-hole pairs, which hinders its application, effective solutions must be developed to enhance charge separation efficiency. One approach is to form a p–n heterojunction between TiO_2 and other p-type semiconductors, such as NiO, Cu_2O, and ZnO_2. Co_3O_4 is an important p-type semiconductor due to its bandgap values of 1.48 eV and 2.19 eV, which have been found to be active in the photocatalytic degradation of organic pollutants. Therefore, the formation of a p–n heterojunction between Co_3O_4 and TiO_2 is also expected

to enhance photocatalytic activity. However, the TiO_2/Co_3O_4 heterojunction also has certain drawbacks, particularly in terms of its suboptimal bandgap alignment. Although Co_3O_4 enables visible light absorption, its bandgap may sometimes be insufficient to achieve high photoelectrochemical efficiency compared to other, more optimal materials (Dai et al., 2013).

In recent developments, incorporating noble metal nanoparticles, such as silver (Ag), platinum (Pt), and gold (Au), onto TiO_2 surfaces has emerged as an effective approach to improve the efficiency of photoelectrochemical (PEC) photocatalysis (Bhardwaj & Pal, 2018; Carabineiro et al., 2010; Di et al., 2020; Fu et al., 2017; Zhang et al., 2018). These nanoparticles, known for their plasmonic enhancement properties, significantly boost photocatalytic reactions such as water splitting, CO_2 reduction in the presence of H_2O to generate hydrocarbon fuels, and the breakdown of organic pollutants (Zhang et al., 2018). For example, depositing Ag via photodeposition on Ti/Co_3O_4 nanowire (NW) layers leads to a notable improvement in photocatalytic performance. PEC tests revealed that Ag-modified Ti/Co_3O_4 NWs achieved a 91.7% decolorization rate for Reactive Brilliant Blue KN-R dye, a significant increase compared to the 68.3% efficiency of unmodified Ti/Co_3O_4 NWs. This enhancement is credited to improved charge carrier mobility, reduced resistance, higher oxygen evolution potential, broader active surface area, and more efficient electron transfer offered by the Ag-modified structures. In addition to Ag, gold (Au) has also proven to be an effective noble metal for enhancing TiO_2/Co_3O_4 photoanodes. Chen et al. (2012) demonstrated the application of Au/Co_3O_4-TiO_2 in CO oxidation, showing superior catalytic activity in hydrogen-rich conditions. Various Au-modified TiO_2 structures, including core-shell composites, nanohybrids, and Au-loaded g-C_3N_4/TiO_2 systems, have also shown promising results in dye degradation, glycerol oxidation, and CO_2 reduction (Celebi et al., 2021).

2. Methods

This review examines recent progress in the development of TiO_2 nanotube-based photoelectrodes modified with Co_3O_4 and noble metals (Ag, Au) for the degradation of methyl orange and methylene blue from wastewater. The synthesis techniques used are anodization, impregnation-deposition-decomposition, and photodeposition methods. The anodization method was used to produce TiO_2 nanotubes.

The impregnation-deposition-decomposition method was used to modify TiO_2 nanotubes with Co_3O_4. The photodeposition method was used to deposit noble metal nanoparticles (M: Au, Ag) to TiO_2 nanotubes/Co_3O_4. The use of photoelectrochemical (PEC) system has advantages over conventional methods, namely, more efficient, environmentally friendly, and flexible for the degradation of dyes in wastewater.

3. Results and Discussion

3.1 Photoelectrochemical cell

A photoelectrochemical cell (PEC) consists of two electrodes immersed in an electrolyte solution, where one or both electrodes exhibit photoactive properties. The photoelectrochemical process refers to the integration of electrochemical oxidation with heterogeneous photocatalytic degradation. This process involves the interaction between a photoactive photocatalyst and photocatalytic molecules (Umukoro et al., 2016). Electrochemical oxidation is crucial because it does not require the use of chemical reagents in the process. This oxidation method involves the direct oxidation of pollutants on the electrode surface through the formation of highly oxidative oxygen species from water itself (Equations 1–4). Additionally, when chloride ions are present in the solution, electrochemical oxidation can occur in combination with substances that generate electrochemically produced active chlorine compounds (Equations 5–7) (Valica & Hostin, 2016).

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad \text{(Eq.1)}$$

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \quad \text{(Eq. 2)}$$

$$3H_2O \rightarrow O_3 + 6e^- + 6H^+ \quad \text{(Eq. 3)}$$

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \quad \text{(Eq. 4)}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad \text{(Eq. 5)}$$

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \quad \text{(Eq. 6)}$$

$$HOCl \rightarrow H^+ + OCl^- \quad \text{(Eq. 7)}$$

3.2 Dyes

3.2.1 Methyl orange

Methyl Orange (MO) with the IUPAC name sodium; 4-[[4-(dimethylamino)phenyl]diazenyl]benzenesulfonate is an anionic azo dye, which is a synthetic organic dye that is soluble in water. When Methyl Orange (MO) dissolves in water, it will show a bright orange color. Methyl Orange (MO) has solvatochromic properties, which means that its color changes can be influenced by the type of solvent used (Alves et al., 2025). In addition to being used as a pH indicator, this dye is widely utilized in various industries, including paper manufacturing, printing, and textiles.

Methyl orange contains –N=N– azo bonds and aromatic rings in its molecular structure, which contribute to its high toxicity, carcinogenicity, teratogenic effects, and detrimental impact on both the environment and living beings (Wu et al., 2021). Due to its hazardous nature to both the environment and living organisms, proper treatment is required before disposal. One effective approach is through the photocatalytic degradation process.

Upon exposure to light with energy exceeding the photocatalyst's band gap, electrons in the valence band are excited to the conduction band, resulting in the formation of electron-hole pairs. The holes remaining in the valence band react with water molecules to produce hydroxyl (•OH) radicals, which then interact with methyl orange (MO), breaking it down into simpler organic compounds as the end products of degradation (Kaur & Singhal, 2014).

3.2.2 Methylene blue

Methylene blue is an organic chloride salt with the IUPAC name [7-(dimethylamino)phenothiazin-3-ylidene]-dimethylazanium; chloride and has 3,7-bis(dimethylamino)phenothiazin-5-ium as its counterion. Methylene blue is a formal derivative of phenothiazine with the chemical formula $C_{16}H_{18}ClN_3S$ or $C_{16}H_{18}N_3S.Cl$ and is also referred to as methylthioninium chloride or swiss blue. In its physical form, it is a dark green powder that yields a blue-colored solution upon dissolving in water. One of the primary applications of methylene blue is as a synthetic dye. Methylene blue poses hazardous effects on human health as it is synthesized from azo compounds containing the chromophore group –N=N– within its molecular structure. The presence of Methylene Blue (MB) in liquid waste can cause various health problems in humans, such as nausea, dizziness, poisoning, and even liver damage. In plants, MB can reduce protein and chlorophyll content and inhibit growth (Mishra et al., 2025).

Photodegradation is one of the methods within Advanced Oxidation Processes (AOPs). The main characteristic of AOPs is their ability to generate highly reactive free radicals, particularly hydroxyl radicals (•OH) (Malato et al., 2003). The material used in photodegradation is a semiconductor capable of absorbing photons. Houas et al. (2001)

investigated the degradation of methylene blue using a TiO_2 photocatalyst, resulting in environmentally friendly compounds, cations, and anions as the final products.

3.3 Preparation methods

3.3.1 Anodization

The anodization method is one method to produce TiO_2 nanotubes. The working principle of the anodization method is oxidation on the anode using a Ti plate as a precursor and matrix (Santos et al., 2023). One of the benefits of this method is its ability to tailor the nanotube's shape and size according to specific requirements. Parameters to control the formation of nanotubes include electrolyte, pH, fluoride concentration, anodizing voltage, temperature, and distance between electrodes. In previous studies, the treatment that produced the best TiO_2 nanotubes, namely by using a 0.3% NH_4F electrolyte solution and 2% H_2O at 50 V for 20 minutes with a distance between electrodes of 4 cm and a calcination temperature of 450°C for 2 hours (H. Li et al., 2019).

3.3.2 Impregnation-deposition-decomposition

The impregnation method is a method used to forcefully insert metal catalysts into the pores of the material. The material used must provide a large surface so that the spread of active sites becomes easier, so that the contact surface is wider and more efficient. The impregnation method is often used because the synthesis process is more practical, the success of the process is greater, and it produces little waste. The advantage of the wet impregnation method is that researchers can regulate how much metal they want to impregnate (Munnik et al., 2015).

The deposition method is a method used to disperse active metals on materials. The results of metal deposition on the surface of the material can improve thermal efficiency and stability. The combination of the impregnation method and the deposition method proved effective to increase the surface area of the catalyst, resulting in more active sites on the catalyst (Li et al., 2023).

The decomposition method is a method used to break down chemical compounds into simpler substances (Ishii & Kita, 2000). After impregnation and deposition methods, the active metal added to the material must be decomposed to obtain the desired compound. The decomposition process can be through reactions with other chemical compounds (Ishii & Kita, 2000) or through heating at high temperatures (Di et al., 2020). The decomposition process is the last step performed in the impregnation-deposition-decomposition method.

3.3.3 Photodeposition

The photodeposition method involves the incorporation of noble metals such as gold (Au) and silver (Ag) onto TiO_2 nanotubes/Co_3O_4, functioning as photoelectrodes within electrochemical cells. Ag-modified TiO_2 nanotubes/Co_3O_4 offer several advantages, including low electrical resistance, high oxygen evolution overpotential, an extensive active surface area, and efficient electron transport, all of which contribute to improved photoelectrochemical (PEC) performance (Di et al., 2020). his method operates based on the photocatalytic characteristics of semiconductor materials, which are governed by their bandgap energy. To initiate photodeposition, several criteria must be met: (1) the energy of incident photons must exceed the semiconductor's bandgap energy to promote electron excitation from the valence to the conduction band; (2) the reduction potential of the metal ions must be more positive than the conduction band level of the semiconductor; (3) efficient charge carrier separation and migration are critical to minimize recombination of electron-hole pairs; and (4) the semiconductor must act as a support structure with sufficient active sites and surface area for metal deposition. Photodeposition is considered

a straightforward and eco-friendly approach, as it does not require additional chemical agents or complex conditions beyond exposure to light (Lee et al., 2018).

3.4. Titanium-based photoelectrodes

3.4.1 TiO_2 nanotubes

TiO_2 is an n-type semiconductor material that is widely used as a photoanode in PEC because it has the advantages of high stability, easy manufacture, low cost, and non-toxicity (Wang et al., 2019). The photocatalytic performance of TiO_2 is influenced, in part, by its morphology and structural characteristics. TiO2 with nanoscale, such as nanotubes, has a large surface area, so it can increase photocatalytic activity (Li et al., 2015). One method for making TiO_2 nanotubes is the anodization method. The results of TiO_2 nanotubes are very suitable for application as electrodes in PEC.

Li et al. (2019) reported that TiO_2 nanotubes synthesized at anodization voltage of 50 V exhibited complete hydrophilicity and high photocatalytic degradation efficiency. It was also observed that when the anodization voltage is below the optimal level, increasing the voltage results in a reduced contact angle; however, when the voltage exceeds the optimum, further increases lead to a larger contact angle. A contact angle of 0° indicates full contact between the sample surface and foreign substances, resulting in the most effective photocatalytic degradation.

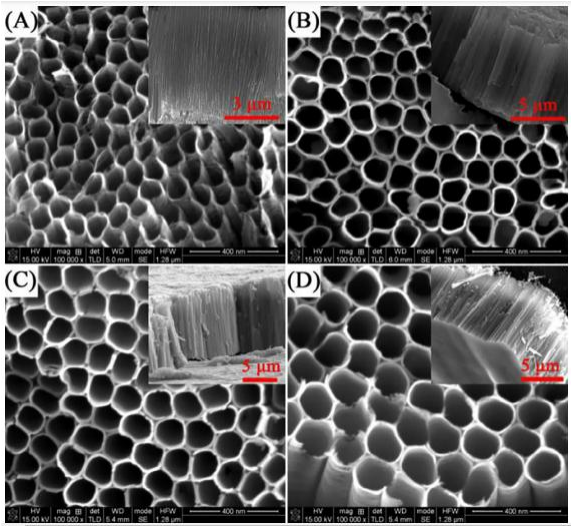

Fig. 1. SEM results of TiO_2 nanotubes in various voltages, reprinted by permission (Li et al., 2019)

3.4.2 TiO_2 nanotubes/Co_3O_4

Co_3O_4 is a spinel-type metal oxide characterized by a unit cell length of 0.8084 nm. Within this structure, oxygen ions are densely arranged in a cubic configuration, with Co^{2+} ions occupying one-eighth of the tetrahedral sites and Co^{3+} ions filling half of the octahedral sites (Liang et al., 2020). The material naturally adopts a truncated octahedral shape bounded by the (001) and (111) crystal facets, both of which are composed exclusively of Co^{2+} ions. The (110) facet displays two possible surface terminations: type A, which includes two tetrahedral Co^{2+} ions, two octahedral Co^{3+} ions, and four O^{2-} ions; and type B, which features two octahedral Co^{3+} ions and four O^{2-} ions. The catalytic behavior of Co_3O_4 is closely linked to the specific crystal facet exposed, indicating that the surface concentration of Co^{3+} can be modulated by tailoring the orientation of the crystal planes (Sheng et al., 2017).

Co_3O_4 is classified as a p-type semiconductor, featuring two band gap energies of 1.48 eV and 2.19 eV (Zou et al., 2008). If Co_3O_4 is combined with TiO_2 nanotubes, a heterojunction

semiconductor composite will be formed. This composite has better photocatalytic activity than TiO_2 nanotubes alone (Nyathi et al., 2023; Xu et al., 2022). TiO_2 nanotubes/Co_3O_4 are often used as photoanodes for photodegradation applications of organic pollutants (Dai et al., 2013; Qiu et al., 2024).

Dai et al. (2013) reported their research on the use of TiO_2 nanotubes/Co_3O_4 for the degradation of methyl orange in a photoelectrochemical cell (PEC). The UV-Vis DRS test results indicated that the band gap of TiO_2 nanotubes/Co_3O_4 is lower than that of pure TiO_2 nanotubes. The photocatalytic activity test showed that the current density of TiO_2 nanotubes/Co_3O_4 was significantly higher than that of TiO_2 nanotubes alone. During the degradation of methyl orange in PEC for 90 minutes, the TiO_2 nanotube photoanode could only degrade 60%, whereas the TiO_2 nanotubes/Co_3O_4 photoanode was able to degrade 92%.

3.4.3 TiO_2 nanotubes/Co_3O_4/Ag

Silver (Ag) is a precious metal that is often found in nature. Usually, Ag is found in mineral form (cerussite and galena). Not infrequently, Ag is found in concentrated deposits in ores with other metals, such as Au, Cu, Zn, and Sn (Angelini et al., 2013). In the absence of oxidizing or complexing agents, Ag is stable in solution. Ag does not react significantly in dry air.

In recent developments, Ag nanoparticles have been identified as a key strategy for boosting photocatalytic performance (Di et al., 2020; Tayebi et al., 2019; Zhang et al., 2018). This enhancement is primarily attributed to the localized surface plasmon resonance (LSPR) effect exhibited by Ag nanoparticles. LSPR plays a crucial role in increasing the absorption of visible light, particularly within the 400 – 800 nm wavelength range (Rufina & Thangavelu, 2023). Additionally, the deposition of noble metals like Ag can enhance the catalytic surface properties and electron distribution, resulting in a more effective hybridization effect (Di et al., 2020).

Di et al. (2020) reported their research on the use of Ti/Co_3O_4 nanowires/Ag for the degradation of anthraquinone dye (reactive brilliant blue KN-R). The photocatalytic activity test results indicated that the electrophotoactive surface area could be increased with the addition of Ag. In this study, the researchers varied the Ag deposition time, with the maximum deposition time being 20 minutes. During the degradation process of the anthraquinone dye in PEC for 120 minutes, the Ti/Co_3O_4 nanowire photoanode could only degrade 71.1%, while the Ti/Co_3O_4 nanowires/Ag photoanode was able to degrade 91.7%.

Zhang et al. (2018) reported their research on the use of Co_3O_4/Ag/TiO_2 nanotubes for the degradation of nitrobenzene. The photocatalytic activity test results showed that the addition of Co_3O_4 could enhance the photoconversion efficiency of Ag/TiO_2 nanotubes. The photoconversion efficiency of Co_3O_4/Ag/TiO_2 nanotubes was 0.180% at 0.44 V vs. SCE, while that of Ag/TiO_2 nanotubes was only 0.016% at 0.20 V vs. SCE. The degradation results of nitrobenzene using the Co_3O_4/Ag/TiO_2 nanotube photoanode in PEC also proved capable of degrading 90% of nitrobenzene within 60 minutes.

3.4.4 TiO_2 nanotubes/Co_3O_4/Au

Gold (Au) is a soft, shiny transition metal. Au does not react with other chemicals but is attacked by chlorine, fluorine, and aqua regia. Au melts into a liquid state at approximately 1000°C. It is a soft, malleable metal with a hardness between 2.5 and 3 on the Mohs scale. Its specific gravity varies depending on the type and proportion of other metals it is alloyed with.

Gold nanoparticles (Au NPs) have attracted significant interest because of their capability to interact with light through surface plasmon resonance (SPR). Au NPs have been used in various applications such as chemistry, material science, physics, medicine, and life science. Generally, the use of Au NPs in combination with TiO_2 has been shown to enhance photocatalytic activity (Carabineiro et al., 2010; Cheng et al., 2022; Du et al., 2018;

Fu et al., 2017; Veziroglu et al., 2020). Basically, surface plasmons in Au nanostructures promote photochemical reactions.

Chen et al. (2012) reported their research on the use of Au/Co_3O_4-TiO_2 for carbon monoxide (CO) oxidation. The photocatalytic activity test results showed that Au/Co_3O_4-TiO_2 performed better for CO oxidation in hydrogen-rich gas. This was attributed to the presence of Au^+ species stabilized by cobalt oxide. The study found that Au/Co_3O_4-TiO_2 (5:95) exhibited higher CO conversion than other catalysts when the temperature was above 65°C.

Table 1. Modification of titanium-based photoelectrodes

Method	Modification	Performance	Results	Ref
Impregnation-Deposition-Decomposition	p–n junction Co_3O_4/TiO_2 NTs	Co_3O_4/TiO_2 NTs are capable of absorbing light across almost the entire visible spectrum.	Co_3O_4/TiO_2 NTs achieved a 92% degradation efficiency of methyl orange (MO).	(Dai et al., 2013)
Photodeposition	$Ti/Co_3O_4/Ag$	The electrode has an active surface area of 4 cm^2 and generates a current density of 30 mA/cm^2.	The photoanode achieves a 91.7% decolorization rate of KN-R after 120 minutes and demonstrates long-term cycling stability.	(Di et al., 2020)
	$Co_3O_4/Ag/TiO_2$-NTs	The photocurrent density of $Co_3O4/Ag/TiO_2$-NTs is 0.54 mA/cm^2.	The removal rate of NB and Cr(VI) reached 90% and 78% after 1 h degradation, respectively.	(Zhang et al., 2018)
	$Au/Co_3O_4–TiO_2$	The size of the Au particles remained unchanged even after 400 hours of continuous operation.	The enhanced performance of $Au/Co_3O_4–TiO_2$ in the preferential oxidation of CO within hydrogen-rich gases is attributed to the stabilization of Au^+ species by cobalt oxide.	(Chen et al., 2012)

4. Conclusions

This review comprehensively analyzed the recent advancements in titanium dioxide (TiO_2) nanotube-based photoelectrodes modified with Co_3O_4 and noble metals (Ag, Au) for the degradation of persistent organic dyes such as methyl orange and methylene blue. The integration of p-type Co_3O_4 with TiO_2 forms a heterojunction structure that enhances photocatalytic activity by improving charge separation and extending light absorption into the visible range. Further modification with noble metals like Ag and Au via photodeposition significantly boosts the photoelectrochemical (PEC) performance due to localized surface plasmon resonance (LSPR), reduced charge recombination, and increased surface area and electron mobility.

The fabrication methods, including anodization, impregnation-deposition-decomposition, and photodeposition, each offer specific advantages in optimizing the structure and function of the composite electrodes. Comparative studies show that $TiO_2/Co_3O_4/Ag$ and $TiO_2/Co_3O_4/Au$ photoelectrodes demonstrate superior dye degradation performance compared to unmodified TiO_2, achieving high decolorization rates, improved current density, and long-term stability.

These findings highlight the promising potential of TiO_2 nanotube-based heterojunctions, particularly those modified with Co_3O_4 and noble metals, as efficient,

environmentally friendly solutions for industrial wastewater treatment. The continued development of these materials supports innovation in both photocatalysis and sustainable environmental technologies.

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