Development of inorganic composite material based TiO$_2$ for environmental application

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Abstract. Syntheses of various materials, for green energy nanotechnology applications have special attention to develop emerging areas, such as environmental as well as energy materials. Various approaches for preparing nanostructured photocatalysts, such as titanium dioxide, nickel oxide, lead oxide and their composites, was introduced. The use of nanomaterials as photocatalysts water detoxification by visible light photocatalyst of an inorganic composite as well as dye-sensitized photoreduction was also discussed. The enhancement of selective photocatalyst system was gain by the use of photocatalyst composite materials and applied potential bias on the system. The photoelectrocatalytic degradation of rhodamine B (RB) and Remazol Yellow FG (RY) as water contaminant using the thin film of modified TiO$_2$ as the electrode was investigated via a series of potentials, and various pH. The result showed that the anodic potential bias influence the degradation rate of water contaminant and exhibited better performance by the positive anodic bias was applied. The pH conditions influence the active dye structure whereas it will interact with inorganic semiconductor photocatalyst. Using dye-sensitized TiO$_2$ system (DSTs), we have applied this system to build water decolorization as a novelty environmental remediation system.

1. Introduction

Environmental pollution has become a serious problem for developing and developed countries in the world. Therefore, there is a need for techniques to remediate the polluted environment. Photocatalyst oxidation using a semiconductor as a catalyst has become an attractive candidate as a green technology for environmental application such as water cleaning [1], air purification [2] and soil remediation [3]. Photocatalyst has been intensively studied over the last two decades as a clean and green process to decompose pollutants in the environment. Recently, nanomaterial has received significant attention for environmental and energy applications because their shape, crystallinity, and the surface can provide unique physical and chemical properties, such as high surface area, well-defined structure, high dispersibility, and high reactivity [4-5].

Intensive research efforts have been focused on the development of novel nanostructured materials. Many nanostructure materials, such as titanium dioxide, zinc oxide, iron oxide metal sulfide have been synthesized with difference techniques, including sol-gel method, hydrothermal method, and mechanochemical method [6-9]. Green nanotechnology has the potential to help us to obtain desirable materials with low cost, low toxicity, high chemical and thermal stability, and high degradation activity for environmental detoxification.
Interest in application of titanium dioxide in photocatalytic processes has increased significantly in recent years [10, 11, 12, 13]. The use of titanium dioxide as a photocatalyst was first reported in 1972 [14]. Since then, TiO$_2$ nanoparticles have been used as photocatalysts in many fields as environmental applications of various pollutants [15, 16, 17, 18, 19, 20, 21]. Recently, dye sensitization technique has found its application in solar cells [22]. Dye sensitization can further be applied for water treatment and sacrificial hydrogen generation using photocatalysis [23, 24]. The success of the process depends on the choice of suitable dye, semiconductor material, electron donor, and light sources. The sensitized-anatase TiO$_2$ has also been shown to be a good photocatalyst under visible light irradiation. Hence, there has been much research into the photoelectrocatalytic properties of the sensitized TiO$_2$ thin film to investigate its activity in the photodegradation of dye and study the related mechanism under visible radiation [25, 26]. Attachment of dye molecule on photocatalyst surface leads to subsequent electron transfer into the conduction band of semiconductor, therefore strongly bound anchoring groups are preferred. Fixation of dye molecule on semiconductor surface also improves the electron transfer process. Incorporation of noble metals on semiconductor surface enhances their photocatalytic activity by reducing the electron/hole recombination rate. Ruthenium-based dyes in solar cells and dye-sensitized photocatalysis are the best reported so far, however, researchers are gradually switching towards inexpensive and environment-friendly organic dyes and/or natural dyes from vegetable sources [27].

2. Methodology

2.1. Chemicals
Titanium isopropoxide (TTIP, Ti(OiPr)$_4$) (Aldrich, Singapore), Sodium Chloride (NaCl) and acetic acid (HAc) (Merck, Indonesia) were used in the titania nanocrystals synthesis procedure. The sensitizer dyes for DSTs preparation use $N_3$ (di(thiocyanate)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II)) (Dye Sol)) and anthocyanin. Anthocyanin were extracted by alcoholic solution from Mangoeted rind (Garcinia mangostana L.). Whereas the rhodamine B (RB) and Remazol Yellow FG (RY) used in this study is a local material. All glassware was washed with soap, rinsed with nitric acid, and then washed with deionized water prior to use.

2.2. Preparation of nanostructured TiO$_2$ photocatalyst
Preparation of TiO$_2$ nanostructure by sol-gel method refers to Wahyuningsih et al. methods [28]. A 10 mL solution of TTIP was hydrolyzed in the 100 mL acetic acid glacial solution and mixed under vigorous stirring in an ice water bath (10–15 °C) until a clear yellow solution of TiO$_2$ nanocrystals was formed. The solution was heated at 90 °C for 2 h when it became a gel, which was then placed in an oven at 150 °C for 24 h to undergo an aging process. Next, the TiO$_2$ xerogel was ground and pulverized into a fine powder and annealed in a muffle furnace at 400 °C for 2 h at a heating rate of 10 °C.min$^{-1}$. Characterization of the TiO$_2$ nanoparticle obtained was carried out using X-ray diffraction.

2.3. Preparation of nanostructured based TiO$_2$ composite electrodes
Preparation of Ti/TiO$_2$ electrode was done by mixing TiO$_2$ powder into ethanol then it was stirred and sonicated for 60 minutes. TiO$_2$ suspension then was sprayed onto titanium plate and heated at a temperature of 200 °C for 15 minutes. While preparation of Ti/TiO$_2$-PbO electrode was done by mixing TiO$_2$-PbO composite (12.5 g) in ethanol (50 mL) then it was stirred and sonicated for 60 minutes. The TiO$_2$-PbO solution was then sprayed onto titanium plate and heated at a temperature of 200 °C for 15 minutes. The Ti/TiO$_2$-NiO electrode has been synthesized by procedures that have been published previously [29], 1.145 grams of synthesized xerogel TiO$_2$ was added in 0.81 grams of NiNO$_3$·6H$_2$O that has dissolved in 25 mL of distilled water. The mixed solution was stirred. Then, the uniform mixture was dried at 110 °C for 3 h. To improve the crystalline TiO$_2$-NiO after the green suspension was formed, it was calcinated at 400 °C for 4 hours at 10 °C/min. The crystalline TiO$_2$-NiO
composite was superimposed onto a Ti plate electrode and was dried at 110°C for 3 h. The coating and drying treatments were repeated three times.

The working electrode of sensitized TiO$_2$ thin film was prepared in three steps including (1) thin films FTO/TiO$_2$ preparation, (2) dye sensitizer synthesis of anthocyanin and N$_3$ complexes and (3) sensitization process of the TiO$_2$ thin film. Sensitized TiO$_2$ thin films on FTO glass were prepared from the anatase TiO$_2$ powder prepared previously [28]. A certain amount of TiO$_2$ powder (3.5 g) was added to 15 mL of ethanol in the beaker under continuous magnetic stirring. The colloidal TiO$_2$ was then transferred to a sonicator for 10 min until the gel was fully formed. The gel was applied onto FTO plate (2\times2 cm$^2$, sheet resistance, 15 Ohm per square; Dye Sol Australia). The glass plates were dried at 200°C in an oven to evaporate the ethanol. The TiO$_2$ thin film was dipped into dye sensitizer solution for 12 h to obtain the sensitized TiO$_2$ thin film (DSTs).

2.4. The use of nanostructure based-TiO$_2$ as photocatalysts water decolorization

The photoelectrocatalytic degradation of RY was conducted by Ti/TiO$_2$-PbO as working electrode, and Ti/TiO$_2$ plate as the counter electrode. The photoelectrocatalytic process of RY (10 ppm) has been carried out at various pH (pH = 3, 5, 7, and 10). The process was arranged under 7.5 volts positive potential bias for 10 minutes. Meanwhile, the photoelectrocatalytic degradation of RB were conducted by Ti/TiO$_2$-NiO as working electrode, and Ti/TiO$_2$ plate as the counter electrode. 10 ppm of RB solution at optimum pH (pH = 2, 7, 8, and 9) was performed by the batch method under 6 volts positive potential bias for 10 min. The front of the working electrode was irradiated with a 300 W visible light lamp (Halogen lamp, Osram) and the progress of the photoelectrocatalytic degradation was recorded at defined intervals time by ultraviolet – visible spectroscopy.

2.5. The use nanostructure based-TiO$_2$ as a dye-sensitized photocatalytic oxidation

In order to investigate the photoelectrocatalytic (PEC) activity of the prepared sensitized TiO$_2$ thin film (DSTs), a series of degradation experiments of RB in aqueous solutions were performed. The initial concentration of RB was 5 mg.L$^{-1}$, with 0.05 mol.L$^{-1}$ of NaCl used as the supporting electrolyte. A copper wire was used as the counter electrode. The PEC degradation of RB was performed at voltages of +1.0 V and +2.0 V under 300 watts visible light irradiation. The progress of the photoelectrocatalytic degradation was recorded at defined intervals time by Ultra violet-Visible spectroscopy.

3. Result and discussion

3.1. Preparation and Characterization of nanostructure based TiO$_2$ photocatalyst

In a typical sol-gel process, a colloidal suspension, or sol, is formed from the hydrolysis and polymerization reactions of the precursors, which are usually inorganic metal salts or metal organic compounds such as metal alkoxides. Complete polymerization and loss of solvent lead to the transition from a liquid sol into a solid gel phase. Titanium dioxide has been reported synthesized by sol-gel method using titanium tetrachloride, titanium alkoxide, and titanyl sulfate as well as titanyl chloride precursors [28, 29, 30]. If TiO$_2$ is reacted with a strong base it will hydrolyze, this is splitting the polymer chains of TiO$_2$ (depolymerization) by the presence of OH- groups. Depolymerization occurs because the strength of OH- ions that break the Ti-O-Ti in polymeric structure. A result of subsequent alkaline hydrolysis is neutralized by the addition of HCl. At pH 7, it will obtain the most optimal condensation process.

The synthesized anatase TiO$_2$ from titanium tetra isopropoxide precursor was already obtained after an annealing process at 400 °C (annealing rate of 10 °C min). The fully anatase type of TiO$_2$ was obtained by synthesis using acetic acid solution media (Figure 1). Nanostructure-based TiO$_2$ photocatalyst was carried out to prepare TiO$_2$-based electrode.
The XRD pattern of Ti/TiO$_2$ electrode shows the diffraction pattern of anatase TiO$_2$ (Figure 1). The diffractogram peaks represented of TiO$_2$ content were shown at $2\theta = 25.37^\circ$ (d101 = 3.5165 Å), $2\theta = 36.95^\circ$ (d103 = 2.4307 Å), $2\theta = 48.04^\circ$ (d200 = 1.8922 Å), $2\theta = 53.88^\circ$ (d105 = 1.7000 Å), and $2\theta = 55.07^\circ$ (d211 = 1.6663 Å). The diffractogram characteristics of anatase TiO$_2$ were according to the standard JCPDS No. 78-2486.

The XRD pattern of Ti/TiO$_2$-PbO electrode (Figure 2) also shows the diffraction pattern of anatase TiO$_2$ at $2\theta = 25.18^\circ$ (d101 = 3.5334 Å), $2\theta = 37.71^\circ$ (d004 = 2.3848 Å), $2\theta = 40.1^\circ$ (d112 = 2.2457 Å), $2\theta = 53.71^\circ$ (d105 = 1.7042 Å), $2\theta = 62.61^\circ$ (d110 = 1.4842 Å), according to the standard JCPDS No. 78-2486. Whereas, the diffractogram pattern at $2\theta = 28.73^\circ$ (d111 = 3.1060 Å), $2\theta = 48.06^\circ$ (d022 = 1.8926 Å), and $2\theta = 54.73^\circ$ (d311 = 1.6782 Å) were characteristic diffractograms of PbO according to the standard JCPDS (No. 78-1666).

**Figure 1.** XRD pattern of (a) TiO$_2$ Powder and (b) Ti/TiO$_2$ electrode.

**Figure 2.** XRD pattern of electrode materials (a) Ti/TiO$_2$ (b)TiO$_2$-PbO (c)Ti/TiO$_2$-PbO.
Figure 3. XRD pattern of Ti/TiO$_2$-NiO electrode materials (a) Ti/TiO$_2$ (b) TiO$_2$-NiO (c) TiO$_2$-PbO.

The composite of TiO$_2$-NiO separately, has been obtained after an annealing process at 700 °C (annealing rate of 10 °C min) (Figure 3). Furthermore, The XRD pattern of Ti/TiO$_2$-NiO electrode also shows the diffraction pattern of anatase TiO$_2$ at $2\theta = 25.18^\circ$ (d101 = 3.5334 Å), $2\theta = 37.71^\circ$ (d004 = 2.3848 Å), $2\theta = 40.1^\circ$ (d112 = 2.2457 Å), $2\theta = 53.71^\circ$ (d105 = 1.7042 Å), $2\theta = 62.61^\circ$ (d110 = 1.4842 Å), according to the standard JCPDS No. 78-2486. The characteristic diffractograms of NiO in electrode were appear at $2\theta = 24^\circ$ (d012 = 3.6584 Å), $2\theta = 33^\circ$ (d110 = 2.6911 Å), $2\theta = 49^\circ$ (d024 = 1.8356 Å), and $2\theta = 57^\circ$ (d018 = 1.5969 Å) (Figure 3) All peaks are in good agreement with the standard spectrums JCPDS No. 753-75.

Modification of TiO$_2$ by sensitization using dye adsorption does not change the crystal structure indicated there are not differences in diffractogram X-ray result.

3.2. Photoelectrodegradation of dyes on TiO$_2$ based photocatalyst nanostructure

The optimum degradation occurs in the pH 3 RY, about 72.756%. The result in Fig. 4 shows that the pH of RY solution influence degradation yield. This is due to, acidic RY solution already protonated to make a positive charge, thus affinity to the reaction of hydroxyl radicals (OH$^-$) and superoxide anion radicals (O$^{2-}$) is higher. The addition of HCl also affects the degradation RY. The Cl can be oxidized to generate the ClO$_3^-$ species. These species turn out to be powerful oxidizing agents, which together with the hydroxyl radicals can degrade the dye thus at pH 3 the degradation RY becomes higher. When the potential was 3.0 V, the rate of photoelectron transport process was lower and controlled the overall PEC oxidation. Thus, the photocurrent increased within the potential of 3.0–5.0 V. Once the applied bias exceeded 5.0 V, the interfacial oxidation, which was slower than the photoelectron transport, became the rate-determining step of the overall process. Under this condition, the photocurrent saturated gradually.
Photoelectrodegradation of RY with applied bias potential 7.5 V for 10 min at various pH (a) RY initial (at pH 6.8); (b) RY at pH 3; (c) RY at pH 7; and (d) RY at pH 10.

![Figure 4](image)

**Figure 4.** Photoelectrodegradation of RY with applied bias potential 7.5 V for 10 min at various pH (a) RY initial (at pH 6.8); (b) RY at pH 3; (c) RY at pH 7; and (d) RY at pH 10.

Photoelectrodegradation of RB with applied bias potential 6 V for 10 min at various pH (a) RB neutral (at pH 6.5); (b) RB at pH 2; (c) RB at pH 8; and (d) RB at pH 9.

![Figure 5](image)

**Figure 5.** Photoelectrodegradation of RB with applied bias potential 6 V for 10 min at various pH (a) RB neutral (at pH 6.5); (b) RB at pH 2; (c) RB at pH 8; and (d) RB at pH 9.

Figure 5 showed optimum photoelectrodegradation activity under acidic conditions (pH 2) of RB with percentage degradation of RB reached 90.76%. This is due to the cationic structure of RB capable of interacting with OH• and O2•- formed by photoanode. The zwitter ionic structure of RB less degraded than the cationic form [28].

The anodic potential was an important parameter in the process of photoelectrocatalytic degradation of RB. The effect of applied potential has been determined by a series of potentials bias. To study the key factors affecting the photodegradation of RB, a series of tests were executed under different experimental conditions in which the deduction of visible absorbance was estimated. After 5 min degradation (batch system), about 96.3% of RB was removed. PEC under halogen lamp irradiation using the Ti/TiO2-NiO photoelectrode with a potential voltage of +10.0V do the electrode surface damage rapidly. Furthermore, the continuous systems were done with applied potential bias of 4, 5, and 6 volts [29].

We also have been investigated water detoxification system using dye sensitized TiO2 photocatalyst. Sensitisation of titanium dioxide was performed using a dye, i.e., anthocyanin and N3 complexes. The photoelectrocatalytic degradation of rhodamine B (RB) using ITO/TiO2/dye as
The electrode was investigated at +1.0 V to +2.0 V. The decreasing in the absorbance of RB with various potentials applied indicated that the RB concentration decreased with increasing anodic potential bias. The degradation cell exhibited better performance when the enough positive anodic bias was applied. The pH values of RB in solution systems also influence the photoelectrodegradation process because of the different RB species present. NaCl concentration also affects the activity of RB photoelectrocatalytic degradation due to changes in the ionic strength character of the electrolyte [28]. Using dye-sensitized TiO$_2$ system, we have applied that system to build green energy production as a novelty environmental remediation system.

4. Conclusion
Photocatalysis based TiO$_2$ nanomaterial can be used for water purification. The decolorization of RB and RY by photoelectrocatalytic degradation system highly was affected by the structure of each RB and RY, hydroxyl radicals (OH$^\cdot$) and superoxide anion radicals (O$_2$)$^{\cdot-}$ formed by photoanode. Decolorization of RB by photoelectrocatalytic degradation has optimum activity at RB initial pH 2, this is due to cationic structure of RB that formed by acidic condition and able to interact with OH$^\cdot$ and O$_2$)$^{\cdot-}$. Whereas the decolorization of RY by photoelectrocatalytic degradation has optimum activity at RY initial pH 3, this is due to acid solution RY already protonated form a positive charge, thus affinity to the reaction of OH$^\cdot$ and O$_2$)$^{\cdot-}$ is higher. The RB concentration decreased rapidly in the dye-sensitized TiO$_2$ photoanode system by anodic potential bias applied.

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