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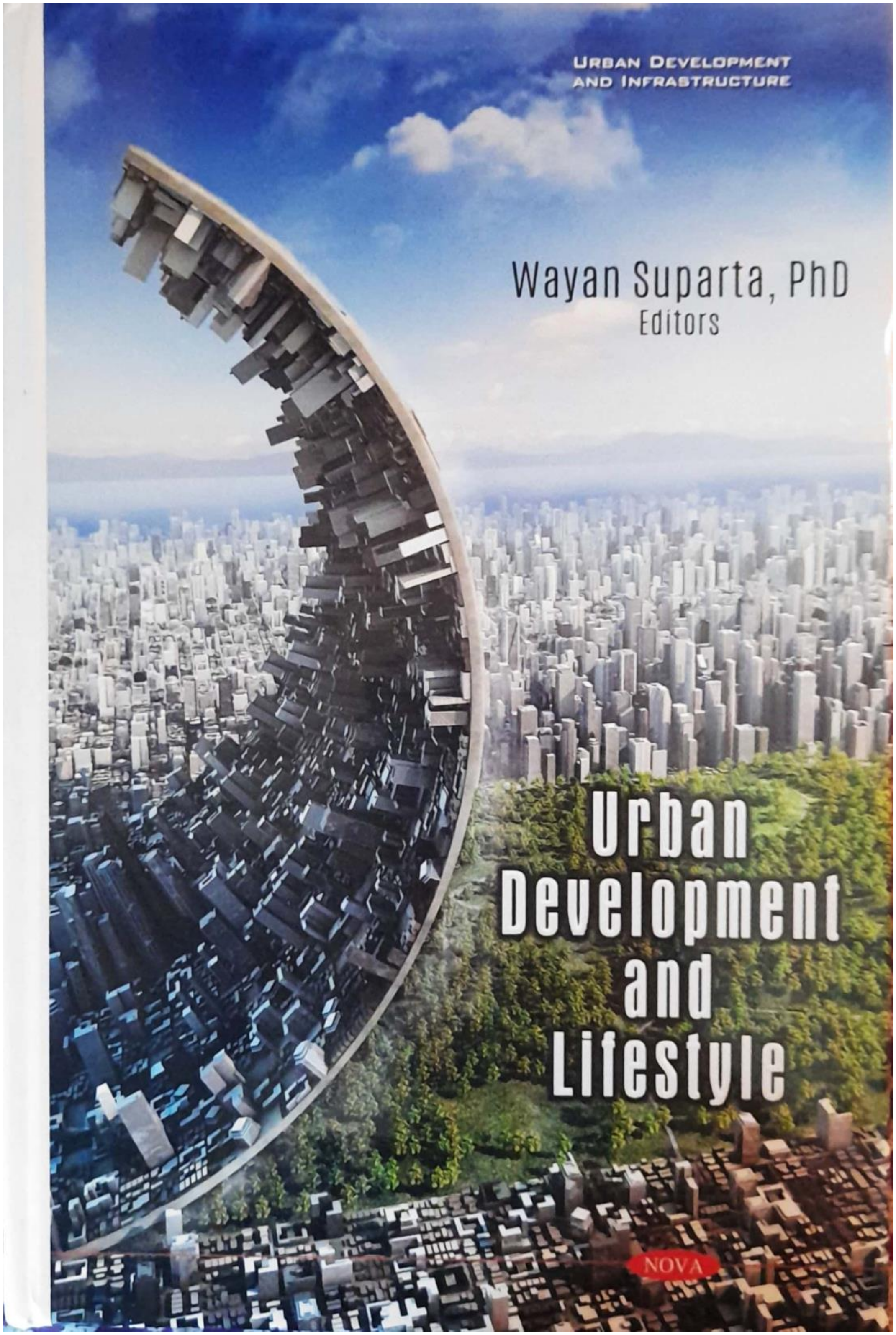

URBAN DEVELOPMENT AND INFRASTRUCTURE

URBAN DEVELOPMENT AND LIFESTYLE

WAYAN SUPARTA
EDITOR

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As Professor at the Universitas Pembangunan Jaya, with daily activities in lecturing, doing research, as well as water resources development planning, I really praise the Nova Science Publishers for publishing selected papers from "2020 International Conference on Urban Sustainability, Environment, and Engineering (CUSME 2020)". Hence, this publication would be useful for professionals, reseachers, scholar, policymakers, and NGO. I believe that currently, many professionals would like to give more attention on development of sustainable urban. In addition, this publication could be used as reference for City authorities to make appropriate policy choices to protect the provision of equitable housing, health, and transportation services.

Prof. Ir. Frederik Josep Putuhena M.Sc., Ph.D
Center for Urban Studies – Universitas Pembangunan Jaya

Urban Development and Lifestyle are trend issues for the cities around the world. Learning from experiences is the most effective way to support the cities to be sustainable developed. This book offers the knowledge sharing among countries which covers variety of cities' issues. It also provides the great lessons for researchers, officers and policy makers on coping with several urban problems.

Associate Professor Sarintip Tantanee, Ph.D.
Director
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CONTENTS

PREFACE

One of the issues of urban development and urban lifestyle, which can be studied from the sea to space, has posed important challenges for humanities, environmental management of cities and urban areas, and the economy. This field is one of the pillars of sustainable development from urban studies towards sustainability welfare. Research and development (R & D) in this part plays a crucial role where urban problems are always alive and increasing every year because of changing customer preferences and needs. City authorities must make appropriate policy choices to protect the provision of equitable housing, health, and transportation services in the future. The megatrends 2030 triggered by the Industrial Revolution 4.0 estimates urbanization will increase sharply, massive move from rural to urban areas, and the land is getting narrower, especially in Asia. New directions and developments in this field and discussion of future priorities must be well anticipated, meticulous, dignified, and innovative.

This book highlights the latest views and solutions to technological innovations adapted to achieve prosperity in urban sustainability. For instance, adapting new buildings for urban needs with low-cost and modern design materials, the housing environment and the layout of city space, weather changes to disaster, and smart transportation systems are also taken into account. It also involves electricity, environmental management, and ways to use agricultural land to increase income. The ease of technology produced will change the business model.

This contributed volume presents solicit selected papers of the 2020 International Conference on Urban Sustainability, Environment, and Engineering (*CUSME 2020*) with the theme "Urban Life and Technology". The book covers the point of view in urban architectures with green technology, sustainable environmental, management, agrotechnology, and smart transportation systems. The impact of urban development such as psychological and cultural influences, communication and social complexity, information systems and technology is also discussed with various solutions offered. The outcomes of the conference will certainly support government policy, stakeholders, policymakers, scientists, and engineers by bringing together their latest findings towards achieving a sustainable economy, improved quality of life, and protecting the environment. The findings of this study will create opportunities for further collaboration and are expected to improve the welfare of humanity.

The conference committee and all our contributors wish to pleasantly thank for their efforts and cooperation in finalizing this volume. We wish to acknowledge and gratitude

Nova Science Publishers Team for supporting our book proposal and for granting the opportunity to publish these conference proceedings and for their cooperation and support.

Wayan Suparta
Chairperson of CUSME 2020
The Editor-in-Chief

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Chapter 44

SYNTHESIS CDS/PT-TIO$_2$ WITH ENHANCED ITS PERFORMANCE FOR PHOTOCATALYTIC DEGRADATION OF PALM WASTEWATER TREATMENT

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ABSTRACT

In this work, CdS/Pt-TiO$_2$ were produced by incorporating Pt/CdS on TiO$_2$ nanoparticles with chemical reduction and hydrothermal method using chloroplatinic acid (H_2PtCl_6) and $CdCl_2$/CH_4N_2S as precursors, respectively. The Field Emission Electron Microscopy (FESEM), UV-Vis Diffuse Reflectance Spectroscopy (Uv-Vis DRS), X-Ray Diffraction (XRD) were applied to characterize the photocatalyst samples. Results indicated by EDX spectra and elemental mapping depicted the decoration of Pt and CdS on TiO$_2$. Depositing Pt/CdS on TiO$_2$ enhanced the redshift in the UV-Vis DRS analysis. The photocatalytic performance 1 g of CdS/Pt-TiO$_2$ could reduce the 500 ppm COD in 1 L palm wastewater by 71.4% elimination under mostly visible light irradiation in 3 h. The increased photocatalyst efficiency was caused by synergy effects due to the capability of Pt acts as an electron trapper that can eliminate the recombination of photogenerated electron-hole pairs and decorating CdS on TiO$_2$ could result in photocatalyst which shifts towards the visible light region.

Keywords: CdS/Pt (TiO$_2$), photocatalytic, palm wastewater

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Introduction

The environmental issue is a significant problem faced in the past few decades since increasing industrial activity results in generating various waste that dangerous for human life. Efforts have been made to find the most suitable technology in treating the pollutant. Conventional treatment such as physical, chemical, and biological processes has been performed in reducing organic pollutants from wastewater [1] but still has problems. In recent years, utilizing solar energy to drive the semiconductor photocatalyst is a green technology to solve environmental pollutions [2-4], and it has interested great attention. The application of $BiVO_4$ as a promising photocatalyst is considered. However, it still has drawbacks, such as fast recombination of photoexcited electrons-holes and weak adsorption capacity, and therefore it needs $BiVO_4$ modifications [4]. On the other hand, TiO_2 is also one of the semiconductor photocatalysts widely used due to its exceptional properties such as inexpensive, outstanding oxidation ability, non-toxicity, high chemical stability, and chemical inertness [3, 5]. However, in its further applications, rutile TiO_2 has a 3.0 eV, and anatase TiO_2 has a 3.25 eV of bandgap energy that can only absorb photons in the UV light region. Moreover, the recombination rate of electron-hole pairs is high [6]. Factually, TiO_2 can be used to treat high organic carbon from industrial wastewater if the photon source utilizes the UV light [7]. However, a further application is limited due to the UV light only occupying around 5% of the solar light.

Excessively studies have been done to deposit other semiconductors that have narrower bandgap such as CdTe and CdSe onto TiO_2 for increasing the visible–light response [6, 8, 9] and to load noble metal, for instance, Au, Pt, Ni, and Pd for obstructing the fast recombination of electron-hole pairs in order greatly enhances the photocatalytic activity [1, 5, 6]. Loading of CdS (Eg = 2.4 eV) semiconductor on TiO_2 can result in enhanced extending absorption edges to visible light response, as reported by the previous researcher [6, 10]. Furthermore, the structure of the bandgap energy of CdS can also give benefit to avoiding recombination or effective separation of electron-hole pairs [6, 10]. Meanwhile, Pt nanoparticle loading on TiO_2 exhibits avoids recombination of photo-generated electron-hole pairs [1, 5]. Pt is one of the excellent electron trappers since it has the highest work function [1, 5]. When photon sources come into TiO_2, electrons will transfer from valence to conduction band [11]. Subsequently, photo-excited electrons in the conduction band migrated and captured quickly to Pt that already deposited or decorated on TiO_2 since the Schottky barriers at the interface between Pt and TiO_2 were formed. Electron anchoring by Pt necessitates the abundance of holes available for oxidation in the valence band. Hence, Pt acts as electron trapping that can decrease the recombination of photo-generated electrons-holes pairs [12, 13], and therefore dramatically increases the photocatalytic activity.

Indonesia is one producer of palm oil commodity and its annual consumption increases due to population growth. As a result, the wastewater resulted from the palm oil industry increasing year by year. It will come up with the wastewater problem if the waste does not threaten properly and effectively. Open ponding is a conventional process to treat the palm oil mill effluent (POME), which is expensive due to needs long hydraulic retention time. It is generally acidic, hot, and contains high organic matter, for instance, pectin, amino acid, lignin, and phenolics. Therefore, it has high biological oxygen demand (BOD) and chemical oxygen demand (COD) [14]. Many treatment methods have been proposed, such as anaerobic digestion, membrane technology, and biological treatment. However, all these processes are costly. Photocatalytic degradation of organic matters in oil palm wastewater with semiconductor TiO_2 is one of the technologies that can be amendable in recent years. Furthermore, depositing Pt and CdS on TiO2 nanoparticle to form the composite of CdS/Pt-TiO_2 is a promising strategy in enhancing photocatalyst performance.

Decorating CdS on TiO_2 nanotube arrays (TNTAs) and nanorod array has been used for solar hydrogen production [10, 15], degradation of rhodamine B [3] and solar cell application [16]. Meanwhile, CdS sensitized TiO_2 for methylene blue, and ofloxacin degradation has been studied [17, 18]. Moreover, some researchers also studied Pt deposited on TNTAs for H_2 reduction [19] and water splitting [20], TiO_2 nanotube/TNT for fuel cell, and H_2 production [12, 21], titania nanoparticles/TNP for the production of H_2 [22, 23]. On the other hand, the previous study has also been performed for depositing Pt, CdS or CdSe to form the composite of Pt/CdS/TNTAs for rhodamine B degradation [1], CdSe/CdS/Pt/TNTAs for immunoassay of octachlorostyrene [6] and CdS/TiO_2/Pt for hydrogen production [24]. However, a little study was paid for the degradation of palm wastewater using CdS/(Pt-TiO_2). It is urgent to study the degradation of organic matters in oil palm wastewater with photocatalyst CdS/(Pt-TiO_2) since it is one of the technologies that can be amendable in recent years and still infrequently studied.

In this study, we performed Pt/CdS deposited on TiO_2-P25 nanoparticles by chemical reduction and hydrothermal method, applying H_2PtCl_6 with $NaBH_4$ as a reducing agent and CH_4N_2S/$CdCl_2$ respectively to increase photocatalytic performance on photo-degradation of palm wastewater. The as-prepared samples are characterized by the use of FESEM-EDX, UV-Vis DRS, and XRD equipment. The degradation of palm wastewater on CdS/Pt-TiO_2, CdS-TiO_2, Pt-TiO_2, and TiO_2 based material were performed.

MATERIALS AND METHODS

Materials

TiO_2-P25 (consist of 21% rutile and 79% anatase) was purchased from Evonic Industry. Chloroplatinic acid (H_2PtCl_6 $6H_2O$), sodium borohydride ($NaBH_4$), thiourea (CH_4N_2S, 98%), cadmium chloride ($CdCl_2$, 99%), ethanol (96%), and chemicals for COD treatment were obtained from Sigma Aldrich. High purity distilled water is used for preparing all solutions.

Synthesis of CdS-TiO_2, Pt-TiO_2 and CdS/Pt-TiO_2

The making of CdS is done by dropped CH_4N_2S in the ethanol solution into the $CdCl_2$ solution at alkali condition with the addition of NH_4OH at 70°C. A precipitate of CdS formed was then washed repeatedly and dried at 110 °C. The CdS-TiO_2 sample was prepared by mixing the sol of 1 g TiO_2-P25 with 1w% of CdS via hydrothermal method under ultrasonic wave for 1 h, heated at 110°C until the paste of CdS-TiO_2 was formed, and hereafter it was dried for 2 h at 150°C. Subsequently, it underwent calcination for 30 min at 550°C in the muffle furnace. The crystalline CdS was synthesized according to the reaction as follows:

$$CdCl_2 + 6NH_4OH \rightarrow 2NH_4Cl + [Cd(NH_3)_4](OH)_2] + 4H_2O \quad (1)$$

$$[Cd(NH_3)_4](OH)_2 \rightarrow Cd^{2+} + 4NH_3 + 2OH \quad (2)$$

$$CS(NH_2)_2 + 2OH^- \rightarrow S^{2-} + CN_2H_2 + H_2O \quad (3)$$

$$Cd^{2+} + S^{2-} \rightarrow CdS \quad (4)$$

Photocatalyst Pt-TiO_2 made via chemical reduction method was started by preparing the suspension of 2 g TiO_2 in 400 ml aqueous solution that contained precursor H_2PtCl_6 (Pt = 1 w%). The loading 1 w% of Pt on TiO_2 is an optimal condition obtained from the previous study. The excess of $NaBH_4$ was added under stirring for 1 h. Subsequently, centrifugation for 20 min of the solution was performed, and the filtrate was washed twice with purified water and ethanol. The slurry was then put on the hot plate for drying at 90 °C for about 3 h, heated at 130 °C for 1 h, and finally followed by calcination for 1 h at 500 °C. The chemical reduction of Pt with chloroplatinic acid as a Pt precursor can be presented as follow:

$$NaBH_4 + H_2PtCl_6 + H_2O \rightarrow Pt + H_3BO_3 + 5\ HCl + NaCl + 2H_2 \quad (5)$$

$NaBH_4$ was added onto the H_2PtCl_6 solution that has been pre-mixed with TiO_2-P25 leading to a pH increase from 5 to 9. Besides, it undergoes color alteration from white to grey, indicating that ionic Pt has been reduced to the metallic Pt. The mixing of Pt with TiO_2-P25 resulted in Pt decorated on the photocatalyst to form Pt-TiO_2.

To prepare photocatalyst CdS/Pt-TiO_2, a certain amount of CdS (1 w%) was mixed with the solution of Pt-TiO_2 for 30 min under sonication. The mixture was then dried in the oven at 110 °C. The slurry subsequently experienced calcination in the furnace at 500 °C for 1 h. The prepared sample (CdS/Pt-TiO_2) was then used for photo-mineralization of palm wastewater and underwent characterization. The deposition of CdS on the Pt-TiO_2 method is more efficient than the deposition Pt on CdS-TiO_2 [24]. The availability of Pt and CdS on TiO_2 will be proven with FESEM/EDX analysis.

Characterization of CdS/Pt-TiO_2

EDX analyzer fitted to the FESEM (JEOL Multibeam System 4610F type) was used for elemental analysis. XRD was performed on the PANalytical Empyrean type diffractometer with Cu Kα (λ = 0.154066 nm) as the radiation source with the scan rate at 10° min-1 over the 2θ range of 10–80°. It was operated at 30 mA and 40 kV. Spectrophotometer Shimadzu 2450 type was applied to UV-Vis DRS analysis. The reflectance and absorbance of the photocatalysts were measured at room conditions in the wavelength range of 200-600 nm.

Photocatalytic Degradation of Palm Wastewater

The degradation of palm wastewater experiments was evaluated in the apparatus that consists of a 1000 ml Pyrex glass reactor that contains 500 ml of waste and is equipped with a mercury lamp of Philips HPL-N 250 W/542 E40 HG ISL. This lamp that consists of 83% of visible light (approximate the solar light), is applied as a light source to trigger the reaction. The lamp was positioned 20 cm away from the solution surface. The photoreactor system was fixed inside a reflector box, and the reactions were planned in 6 h irradiation. Before the commencement of the reaction, 1 g of the photocatalyst samples and the 1 L of palm wastewater in the reactor flask were magnetically stirred. Filtration with the fabric material is performed as pretreatment for the real palm wastewater to reduce the sludge, oil, and turbidity. The color of the waste was brown, and its initial COD and pH after filtration were around 10000 ppm and 5, respectively. Dilution was performed to get samples with the initial COD around 500 and 1000 ppm. To convince the homogeneity during photocatalytic reactions, magnetic stirring (500 rpm) was operated at the bottom of the photoreactor. To evaluate the photocatalytic performance, the COD value was measured with the reflux method every 3 hours.

RESULTS AND DISCUSSION

FESEM Analysis

FESEM images, EDX analysis, and elemental mapping of prepared samples are depicted in Figure 1. EDX and elemental mapping results indicated the presence of Pt and CdS decorated on TiO_2. Similar results are reported by [1] and [6].

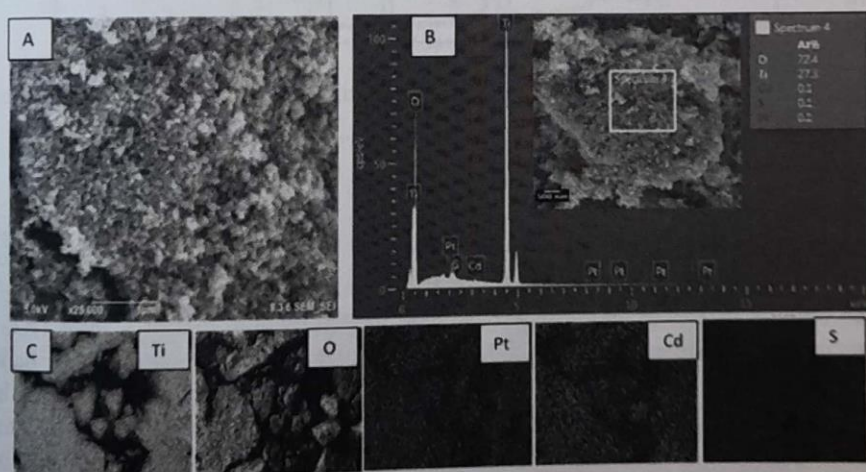

Figure 1. (A) FESEM images, (B) EDX spectra and (C) elemental mapping of synthesized catalyst $CdS/Pt\text{-}TiO_2$.

XRD Analysis

XRD patterns of photocatalyst $CdS/Pt\text{-}TiO_2$ is presented in Figure 2. The detected peaks at 2θ of 25.3°, 37.0°, 37.9°, 38.6°, 48.1°, 54.4° corresponds to (101) (103) (004) (112) (200) and (211) planes of TiO_2 anatase phase respectively (PDF2 # 84-1286), whereas the signals at 2θ of 27.4°, 36.1°, 41.3°, 44.1°, 54.1° 55.2° conform to (110) (101) (111) (210) (211) and (220) planes of TiO_2 rutile phase respectively (PDF2 # 78-1510). This result confirms that no phase transition or structure destruction of TiO_2 since the XRD pattern indicates anatase and rutile phase. However, the Pt and CdS peaks were not found since Pt and CdS concentration on TiO_2 were not enough to induce the diffraction peak. Another reason is the high Pt and CdS dispersion on TiO_2. This phenomenon is in agreement with the previous researchers [13, 17, 25]. Pt diffraction peak can be found at 2θ of 39.7° and 46.2° if the Pt loading more than 5% [5] and CdS at 2θ of 26.5°, 37°, 28°, 44°, 52° [17, 24].

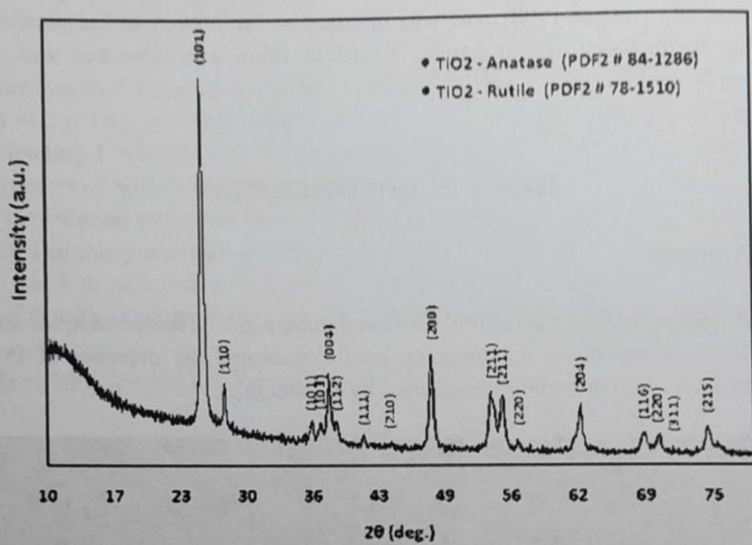

Figure 2. XRD pattern of $CdS/Pt\text{-}TiO_2$.

UV-Vis DRS Analysis

The UV-Vis spectra of photocatalyst samples are presented in Figure 3. Pure TiO_2 has a bandgap of 3.17 eV and can only respond in the UV region (<390nm). On the other hand, the deposition of CdS and Pt on TiO_2 could present strong absorptions in the wavelength of > 400nm (visible-light region) compare to the titania (TiO_2) based material. It means that decreasing the bandgap of the prepared samples occurred. It is most likely caused by the decoration of Pt and CdS on titania and could come from the electronic interaction among TiO_2, Pt, and CdS as reported by several authors [1, 5, 26].

Photocatalytic Test for Palm Waste Water Treatment and Mechanism

The reduction of COD value from the palm wastewater treatment was presented in Figure 4, with the initial concentration of approximately 500 ppm for 3 and 6 h irradiation under 87% of visible light with different photocatalyst samples. As shown in Figure 4, the best photocatalyst performance is $CdS/(Pt\text{-}TiO_2)$ since it gave the highest % COD reduction and followed by $Pt\text{-}TiO_2$, $CdS\text{-}TiO_2$, and bare TiO_2. This condition points out that there is an interaction between Pt, CdS, and TiO_2. In this study, although $CdS\text{-}TiO_2$ has stronger absorption than $Pt\text{-}TiO_2$ as previously reported (Figure 3), the % COD reduction of $Pt\text{-}TiO_2$ is higher than CdS-TiO_2. With Pt as an electron anchor, excessively of holes available undergo oxidation reaction of organic matters and therefore increase the COD elimination in the palm wastewater.

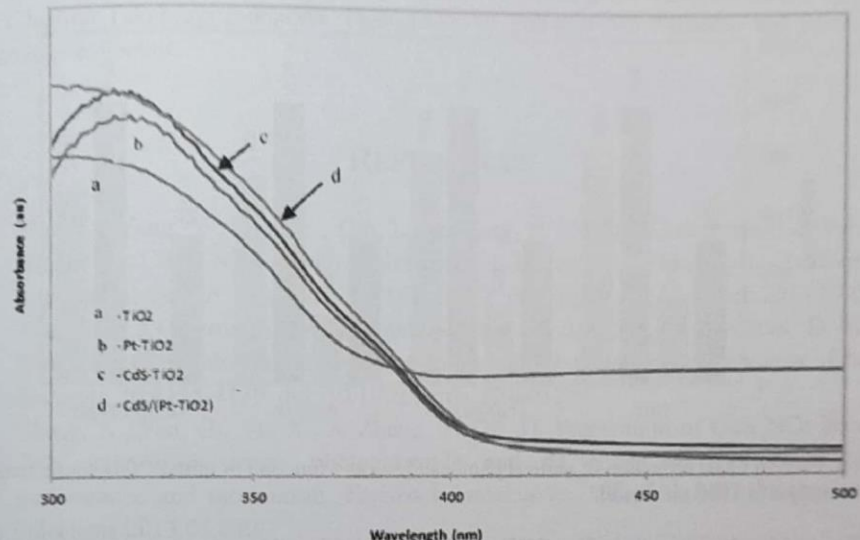

Figure 3. UV-Vis Spectra of various photocatalyst samples.

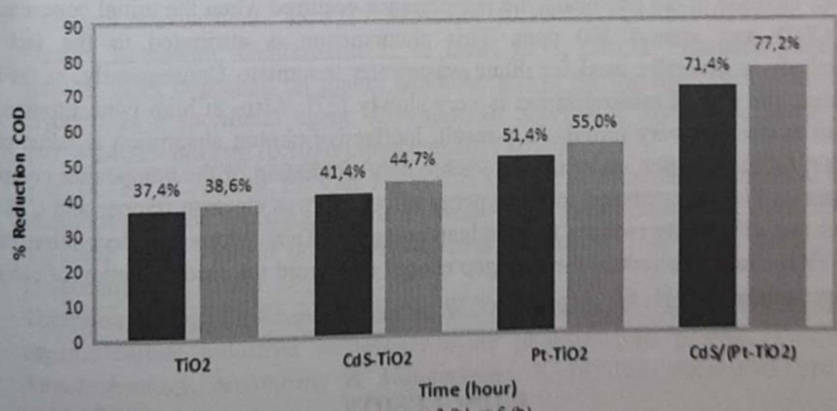

Figure 4. Percent COD reduction on various photocatalysts as a function of irradiation time (1 g photocatalyst in 1000 ml waste with initial COD 500 ppm).

It meant that the role of Pt as electrons trapper that result in lowering the recombination of electron-hole pairs and also reducing the bandgap is more dominant than that of the role of CdS in reducing the bandgap and separating photo-induced electron-hole pairs. CdS/(Pt-TiO_2) shows a much higher photocatalytic performance compare to the Pt-TiO_2 and CdS-TiO_2. The existence of a synergetic effect could cause this phenomenon due to vectorial electron transfer driven by the excitation of TiO_2 and CdS with Pt as a mediator [1]. When photocatalysis was performed in 6 h, only a little change/even constant occurred in % COD reduction, and it is a little higher than that of 3 h irradiation, as shown in Figure 4. It meant that 3 h irradiation performed the best time. This condition is likely caused by the amount of photocatalyst that may not be enough to degrade or recalcitrant organic matter that still exists in the waste that is difficult to degrade.

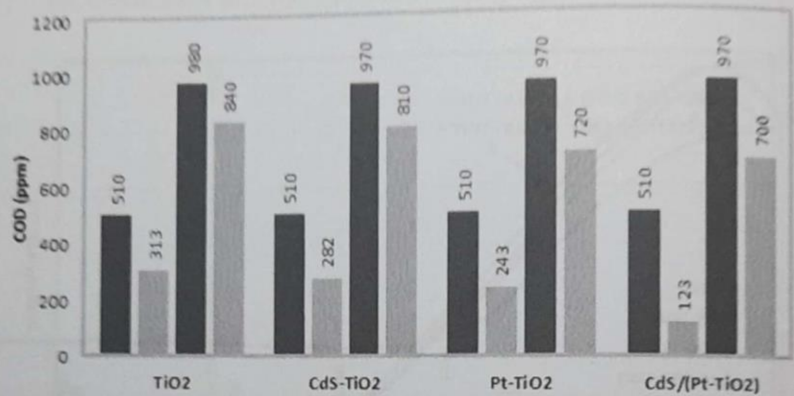

Figure 5. Percent COD reduction of various photocatalysts as a function of initial COD concentration (1 g photocatalyst in 1000 ml waste).

Figure 5 depicts the % COD reduction with different initial concentrations (approximately 500 and 1000 ppm) of wastewater for 6 h irradiation. It can be said that the significant increase of the photocatalytic performance occurred when the initial concentration of the COD was around 500 ppm. This phenomenon is attributed to the fact that photocatalysis is generally used for dilute wastewater treatment. Consequently, at the high COD value, the rate of mineralization is very slowly [27]. Also, at high concentration, the palm wastewater was very turbid. As a result, ineffective photon absorption is taken place. The higher COD reduction under mostly visible light irradiation of the composites compared to the bare of TiO_2 is attributed to the synergy effect of Pt as electron trapper and CdS as a sensitizer that effectively reduces the bandgap energy of TiO_2. Moreover, decoration Pt and CdS on TiO_2 could also reduce the bandgap energy and avoid the recombination of electron-hole pairs, respectively [1, 5].

CONCLUSION

Deposition of Pt and CdS on TiO_2 via chemical reduction and hydrothermal methods has been successfully performed, evidenced by FESEM results. The decorating Pt and CdS on TiO_2 can alleviate the recombination of photogenerated electrons-holes and reduce the bandgap energy, and therefore enhance its photocatalytic activity in degrading the palm wastewater. The addition of 1w% of Pt and CdS on TiO_2 (CdS/Pt-TiO_2) performs improvement towards an effective separation of electron-hole pairs, efficient charge transfer, and shows capable of absorbing the visible light in the degradation of palm wastewater comparing with Pt-TiO_2, CdS- TiO_2, and bare TiO_2.

Acknowledgments

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As Professor at the Universitas Pembangunan Jaya, with daily activities in lecturing, doing research, as well as water resources development planning, I really praise Nova Science Publishers for publishing selected papers from "2020 International Conference on Urban Sustainability, Environment, and Engineering (CUSME 2020)". This publication would be useful for professionals, reseachers, scholar, policymakers, and NGO. I believe that currently, many professionals would like to give more attention to the development of sustainable urban. In addition, this publication could be used as a reference for city authorities to make appropriate policy choices to protect the provision of equitable housing, health, and transportation services.

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Urban Development and Lifestyle are trend issues for cities around the world. Learning from experience is the most effective way to support cities to be sustainable developed. This book offers knowledge sharing among countries and covers a variety of cities' issues. It also provides great lessons for researchers, officers and policy-makers who are coping with several urban problems.
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