VISIBLE LIGHT INDUCED PHOTOCATALYSIS ON CDS-MODIFIED TiO2 FOR TEXTILE WASTEWATER TREATMENT

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VISIBLE LIGHT INDUCED PHOTOCATALYSIS ON CDS-MODIFIED TiO_2 FOR TEXTILE WASTEWATER TREATMENT

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Abstract - CdS-modified TiO_2 (CdS-TiO_2) has been studied via hydrothermal method for visible-light-driven textile waste degradation. FESEM, TEM, XRD and UV-Vis DRS were used to characterize the as-prepared samples. The photocatalytic performance with loading 1, 5 and 9 w% of CdS on TiO_2 and 1 g of CdS-TiO_2 in 1 L textile waste has been investigated for 6 h degradation under 83% of visible light irradiation. FESEM/TEM analysis indicated that CdS already decorated onto TiO_2 and the prepared sample could red-shift the absorption to visible region with the band gap down to 2.8 eV. The CdS-TiO_2 samples performed higher degradation rate than that of bare CdS-TiO_2, which could be attributed to the intense visible-light response and better separation efficiency of photogenerated electrons-holes.

Keywords - CdS-TiO_2, Visible Light, Degradation, Textile Wastewater.

I. INTRODUCTION

Development of modern society causes crucial issues such as environmental pollutants. The increasing population not only gives positive impact on economic, but also creates negative impact on environment. The textile wastewater is categorized as dangerous waste as it has high content of Chemical Oxygen Demand (COD). One of the potential strategies to solve this problem has to be developed with employing semiconductor-based photocatalytic technique [1]. This technique also can be used for air purification, solar energy conversion, hydrogen production, dye-sensitized solar cells, and wastewater treatment [1-5]. The highly promising photocatalyst is TiO_2 since un expensive, nontoxicity, chemical inertness, high chemical stability and photocatalytic activity [5]. However, TiO_2 has drawbacks of poor visible-light absorption since it has a relatively large band gap around 3.2 eV and therefore, the possibility in employing solar light is limited. Another constrain is the rapid recombination of photogenerated electron-hole pairs that can reduce quantum efficiency. Thus, to overcome these defects, tremendous efforts have been devoted to modify TiO_2 include incorporating non-metal doping (C, N, B, and F), composite the CdS, CdSe, PbS or WO_3 into TiO_2 [1,2,6,7] and deposited metal such as Pd, Pt, Au, or Ag on TiO_2 [5]. Recently, TiO_2 decorated with a narrower band-gab semiconductor is reported as an effective method to enhance the visible light absorption since it participates in the photocatalytic reaction [1]. Moreover, the higher mobility and separation electron-hole could induce a better photocatalytic efficiency. CdS nanomaterial is one of most focus studied samples doe to effective sensitizer.

CdS will be synthesized to TiO_2 due to it has a low band gap (2.45 eV) and higher position of Conduction Band (CB) and Valence Band (VB) than TiO_2. The existence of CdS will separate the photoinduced electrons-holes pairs which suppresses the recombination process and activating response of visible light due to CdS has low energy band gap [1,3,4,7]. Hence, the prepared CdS-TiO_2 nanocomposite can easily capture the visible light and effectively transfer the photogenerated electrons into the TiO_2 CB [7]. Many researchers have studied the CdS-modified TiO_2 nanotube arrays and TiO_2 nanorod arrays for hydrogen generation, solar cell etc [1,3,4,8]. However, to the best of our knowledge, the used of CdS-TiO_2 nanoparticle for photocatalytic degradation of textile wastewater that has high concentration of COD is rarely investigated.

In the presents study, we synthesize CdS on TiO_2 via hydrothermal method. The prepared nanocomposite CdS-TiO_2 samples are characterized by FESEM-EDX/TEM, XRD and UV-Vis DRS. The photocatalytic test was performed for degradation of textile waste under mostly visible light illumination (83%).

II. DETAILS EXPERIMENTAL

2.1. Materials and Procedures

All chemicals, including thioacetamide (CH_3CSNH_2, 98%), cadmium chloride ($CdCl_2$, 99%), ethanol (80%) and chemicals for COD treatment were obtained from Sigma Aldrich. TiO_2-P25 (79% anatase and 21% rutile) were purchased from Evonic Industry. Aqueous solutions were made by mixing with deionized water.

The CdS was prepared by mixing certain amount of $CdCl_2$ and CH_3CSNH_2 in the ethanol solution for 24 h. Precipitate of CdS formed was then whased repeatedly and dried at 150 ^oC. In this study, CdS-TiO_2 samples (0, 1, 5 and 9w% of CdS in 1 g TiO_2-P25) were prepared via hydrothermal method. The sol of CdS was mixed with TiO_2 under ultrasonic wave for 1 h, heated until the paste of CdS-TiO_2 was

formed, and followed by drying at 150 ^{o}C for 2 h. The as obtained samples were then calcinated at 550 ^{o}C for 30 minutes in the muffle furnace. Subsequently, these photocatalysts were used to treat textile wastewater (1 g of CdS-TiO_2 in 1 L waste).

The morphological analysis of the CdS-TiO_2 was performed by Transmission Electron Microscopy, TEM (FEI Tecnai G2-STWIN 200 kV) and Field Emission Scanning Electron Microscope, FESEM (JEOL Multi beam System 4610F). Energy dispersive X-ray analyzer (EDX) is attached to the FESEM to determine the composition of the samples. The energy band gap of the sample is decided by a UV-Vis DRS using Spectrophotometer Shimadzu 2450 type in the wavelength range of 200-600 nm. The crystalline phases of the samples were identified using Shimadzu XRD 7000 X-ray diffractometer with the scan rate at 2^{o} min^{-1} over the 2θ range of 10–80^{o} and it was operated at 40 kV and 30 mA. The source of the X-ray radiation was Cu Kα (λ = 0.154184 nm). The crystallite sizes of the samples were estimated from FWHM (full-width at half-maximum) of XRD using Scherrer equation.

The photodegradation was carried out in an 1L Pyrex flask (contains 500 ml of waste with 0.5 g of CdS-TiO_2) equipped with a mercury lamp of Philips HPL-N 250 W/542 E40 HG ISL as a photon source (17% of UV and 83% of visible light) to trigger the photocatalytic reaction and, magnetic stirrer to mix the waste. The photoreaction system was placed inside a reflector box, and the lamp was set up 15 cm away from the surface of liquid waste that already contained with CdS-TiO_2. Photodegradation was started at room temperature 28ºC and stirred for 60 min without irradiation of photon to allow the system reached an adsorption-desorption equilibrium. After 6 h irradiation, the COD were evaluated. The COD value was calculated according to SNI 6989.2:2009 with DRS-8000 UV-Vis spectrophotometer on the wave number of 600 nm.

III. RESULTS AND DISCUSSION

The crystalline CdS was synthesized according to the reaction that could be described as follows [1]:

$CH_3CSNH_2 + 2H_2O \rightarrow NH_3 + CH_3COOH + H_2S$ (1)

$CdCl_2 + H_2S \rightarrow CdS + 2\ HCl$ (2)

3.1. Characterization of Photocatalyst

FESEM/EDX characterization determines the morphology and elemental composition of CdS-TiO_2. Fig.1. depicts the elemental composition and mapping of modified TiO_2. The EDX results of prepared sample indicated that CdS were detected and it gave evident the successful decoration of CdS on TiO_2. This result is accordance with the study reported by Liu et al. [8]. From Selected area electron diffraction (SAED) patterns results, a diffraction spots with d spacing 0.175 nm could be obviously observed and revealing the indication to the (311) plane of CdS characteristic as shown in Fig.2a. [4]. Fig.2b. and Fig. 3. performed the TEM image of fabricated sample. It can be seen that the photocatalyst is TiO_2 nanoparticles with lattice spacing of 0.351 nm attribute to the (101) crystal plane of anatase and 0.324 nm belong to (110) plane of rutile [4]. As shown in Fig.3., the CdS were uniformly deposited onto the surface of TiO_2.

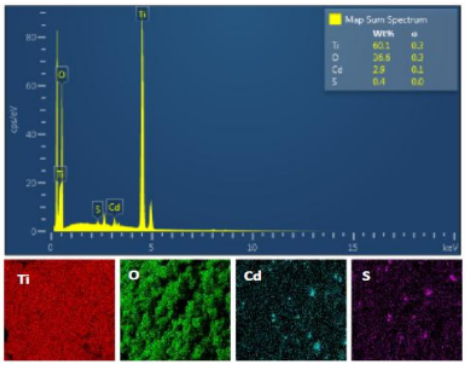

Fig.1. EDX analysis and elemental mapping of the CdS-TiO_2

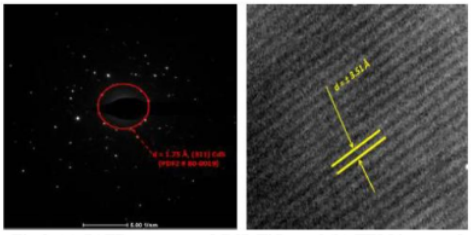

Fig.2. (a) SAED patterns of CdS-TiO_2 and (b) TEM image of CdS-TiO_2

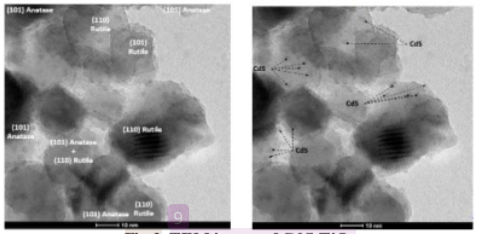

Fig.3. TEM image of CdS-TiO_2

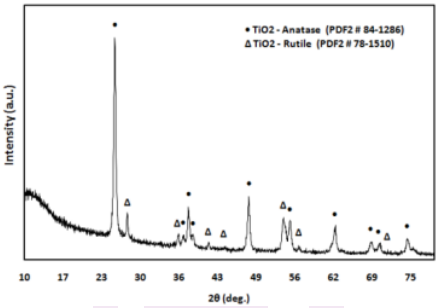

Fig. 4. XRD patterns of CdS-TiO_2

The XRD patterns of CdS-TiO_2 demonstrated that after deposition no obvious diffraction bands belong to CdS (Fig.4.). From Fig.4., it is obvious that no phase transition occurs during modification process since only anatase (PDF # 84-1286) and rutile (PDF # 78-1510) phase were observed. The anatase and rutile crystallite size of TiO_2 is 20 and 23 nm respectively. It is suggested that the concentration of CdS may be too low to be detected and highly dispersed. This result is in accordance with the previous study that conducted by Zhu et al [4]. The hexagonal phase at 2 θ value of 26.5°, 43.9° and 52.1° correspond to the (111), (220) and (311) planes of CdS-TiO_2 nanotubes were detected in high concentration of CdS as reported by Cheng et al [1,9].

The band gap energy of the CdS modified TiO_2 was estimated by the Kubelka- Munk function and Tauc plot [1], and Fig.5. shows the UV-Vis absorption spectra of photocatalyst. There was a certain redshift after TiO_2 is composited with CdS. Furthermore, the band gap of TNTAs and TNTAs-CdS could also be calculated through the following photon energy formula:

$$E = {}^{h.c}/_{\lambda} \quad (3)$$

where E, h, c and λ are band gap energy, plank's constant, speed of light and wave length of the light, respectively. After calculating, the band gap of CdS-TiO_2 was 2.8 eV, and the decreasing of the band gap is due to the depositing CdS onto the TiO_2, which was in accordance with the EDX/TEM results. This result indicated that there is an effective electronic interaction between CdS and TiO_2 which influence the absorption capability of the TiO_2 [4, 8, 10].

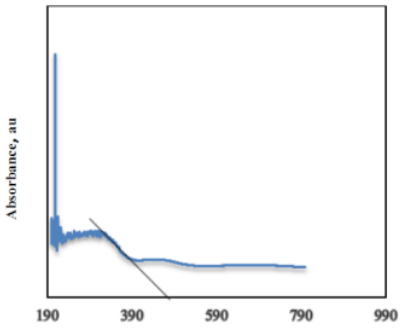

Fig.5. The UV-Vis diffuse reflectance absorption spectra of CdS-TiO_2

3.2. Photocatalytic performance

The visible light photodegradation of textile waste is performed to evaluate the photocatalytic performance. After 6 h irradiation, degradation process indicated that the initial COD value of textile wastewater (1190 ppm that resulted from production process) is reduced by 5, 11, 9 and 6% with the loading of CdS on TiO_2 are 0, 1, 5 and 9 w% respectively. The insignificant reduction of COD is may be caused by the low oxidation rate. Photocatalysis is usually used for dilute wastewater and therefore, complete mineralization is very slowly [11]. Furthermore, the waste was very turbid. As a consequence, photon absorption was disturbed and occurred ineffectively. The 1% loading CdS on TiO_2 presents best result since at low loading of CdS, a considerable part of holes oxidized the organic pollutant. As a result, the reduction of COD value is better. Photodegradation of textile wastewater with initial COD concentration of 500 ppm (obtained from equalization tank) was conducted with CdS loading of 1 w%. Result indicated that after 6 h irradiation, COD value were reduced by 34% and 50% using of bare TiO_2 and CdS-TiO_2 photocatalyst respectively. Similar phenomenon also happened that the higher CdS loading, the smaller the oxidation rate. For 0, 1, 5, 9 w% CdS loading, COD elimination were 34, 50, 44 and 38% respectively. The higher photocatalytic activities under mostly visible-light of CdS-TiO_2 compare to pure TiO_2 attributed to the decreasing of band gap energy of CdS-TiO_2 to 2.8 eV and better charge separation of electron-hole that avoid recombination [4]. After TiO_2 was sensitized with CdS and it is illuminated, electrons can be easily excited from the valence band (VB) to conduction band (CB) of CdS as depicted in Fig.6 and followed by the jumped of those electrons to the CB of TiO_2 doe to its lower Fermi Level. Subsequently, the departed electrons could be migrated to the surface and could react with the adsorbed O_2 to form OH radicals (•OH) which responsible to the degradation of organic pollutants. Furthermore, the residual holes in the CB of CdS could also react with water to form OH radials. The detail reaction could be presented as followed (Eq. 4, 5 & 6) and the schematic diagram charge transmission route of CdS-TiO_2 can be depicted in Fig. 6. [4].

$$e_{cb}^- + O_2 \rightarrow O_2\bullet^- \quad (4)$$

$$2O_2\bullet^- + 2H_2O \rightarrow 2\bullet OH + 2OH^- + O_2 \quad (5)$$

$$h^+_{vb} + H_2O \rightarrow \bullet OH + H^+ \quad (6)$$

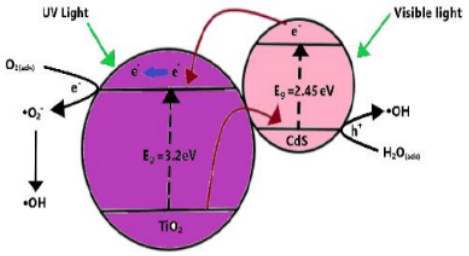

Fig.6. Schematic diagram of CdS-TiO_2 and its charge transmission route

The final COD in this study is not fulfill the Indonesian Government Regulation (PP No 5, Year 2014) since COD concentration that allowed to the

discharge standard quality is 150 ppm. Some variations need to be performed for the next study.

IV. CONCLUSION

The composite of CdS-TiO_2 has been synthesized by hydrothermal method and applied for the degradation of textile wastewater. The conclusions of this study are as follows:

1. The immobilization of CdS on TiO_2 did not affect the structure of TiO_2. Meanwhile, reducing band gap was occurred.
2. The existence of CdS on TiO_2 is crucial to increase photocatalytic COD reduction in the waste as they extend the optical absorption in visible light region. As a result, higher photodegradation rate was taken place. CdS loading which contributed the best results of the COD elimination was found to be 1 w% of CdS on TiO_2.

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