Enhancing Hydrogen Generation using CdS-modified TiO₂ Nanotube Arrays in 2,4,6-Trichlorophenol as a Hole Scavenger

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Abstract. Nowadays, the lack of renewable energy such as hydrogen, and other environmental issues are problems that must be resolved. 2,4,6-Trichlorophenol (2,4,6-TCP) is classified as a recalcitrant pollutant due to its carcinogenic properties, high toxicity, and dangers to the environment therefore it needs to be eliminated. Hydrogen production using organic pollutant (2,4,6-TCP solution) as a hole scavenger on CdS-TiO₂ nanotube arrays photocatalyst (TNTA-CdS) has been investigated at various CdS loading on TNTA and the initial concentration of 2,4,6-TCP. The TNTA sample was prepared by anodization and followed by an electrodeposition method to decorate CdS on TNTA. The H₂ which was generated by reduction H⁺ and the 2,4,6-TCP removal was performed simultaneously by photocatalysis with TNTA-CdS as photocatalyst. The mole ratio of CdCl₂:CH₃CN:CSNH₂, as precursors of CdS deposited on TNTA (CdS loading) were 0.1:0.06, 0.2:0.12, and 0.4:0.24 and the initial concentration of 2,4,6-TCP were 10, 20, and 40 ppm. Meanwhile, the photocatalytic performance of the variations in CdS loading on TNTA and initial concentration of 2,4,6-TCP toward hydrogen generation was investigated in a photoreactor for 240 minutes under visible light irradiation with a mercury lamp as a photon source. The CdS decorating on TNTA was confirmed by SEM, EDX, and X-ray diffraction (XRD) characterization. According to the UV-Vis and XRD analysis, the TNTA-CdS samples have bandgap energies in the range of 2.71 - 2.89 eV and comprise a 100% anatase phase. Based on the photocatalysis results, the optimum composition of CdS loading is 0.2:0.16 (TNTA-CdS-2) which produced the highest total hydrogen (2.155 mmol/g) compared to the other compositions and produced 1.5 times higher compared to TNTA at 40 ppm of 2,4,6-TCP.

Keywords: 2,4,6-Trichlorophenol, Hole Scavenger, Hydrogen Evolution, Titania Nanotube Arrays, and TNTA-CdS

1. Introduction

The rising consumption of energy, the severe climate change and other environmental challenges, have necessitated the development of alternative/renewable energy that is environmentally friendly (Li et al., 2020; Tian et al., 2020; Fu et al., 2019). To address these issues of fossil fuel depletion and environmental problems, many efforts have been made toward exploring clean and sustainable energy sources with eco-friendly technologies (Xu et al. 2018). The most promising candidate for future energy substitution is hydrogen (H₂) because of its high weight energy density, calorific value, and nonpolluting nature/clean. (Junn Ng et al. 2020; Luo et al., 2020).

Currently, a variety of feedstocks have been used to produce hydrogen, including fossil resources, for instance, coal and natural gas, as well as renewable resources such as water and biomass. Numerous process technologies have been reported for hydrogen generation, including biological, chemical (Holladay et al., 2009), electrolytic (Liu et al., 2020), photocatalytic (Shi et al., 2020), and thermo-chemical (Mehrhooya et al., 2020) processes. These processes are at various stages of development, each offering unique opportunities, benefits, and challenges.

Photocatalysis is a chemical process induced by photo-irradiation in the presence of a photocatalyst. This process is based on a simple concept, where the illumination photon with energy above the photocatalyst’s bandgap excites electrons/e⁻ from the valence band (VB) to the conduction band (CB). Consequently, generating holes/h⁺ in the VB. This photo-induced h⁺ and e⁻ produce oxidation and reduction reaction of chemical species adsorbed on the photocatalyst surface unless they recombine to prevent the redox reaction. Recently, photocatalytic H₂ generation has been mainly used to produce renewable clean fuels which can achieve zero-emission (Christoforidis et al., 2018). Numerous studies have attempted to synthesize semiconductor photocatalysts to achieve efficient photocatalytic hydrogen production (Zhao et al., 2018; Zheng et al., 2020).

CdS, a narrow bandgap (2.45 eV) and narrow conduction band edge positions semiconductor, is one of the promising photocatalysts in hydrogen production (Gholipour et al., 2015). Furthermore, CdS can reduce...
protons/H⁺ to H₂ due to the absorption of visible light with a long wavelength in photocatalysis which is not limited to its application to solar photocatalysis. However, this photocatalyst has drawbacks such as its instability under irradiation, a small bandgap leading to the recombination of photoexcited electrons-holes, as well as high susceptibility to corrosion by excited holes (Gholipour et al., 2015; Zhao et al., 2016). Therefore, pure CdS must be combined with other semiconductors to overcome these limitations. For this reason, several studies, including morphological control (Wang et al., 2018; Zhao et al., 2019) and modification (Ba et al., 2019) have been carried out to enhance the photocatalytic performance of CdS.

Nowadays, titanium dioxide (TiO₂) was the most common and promising photocatalyst used in hydrogen production (Slamet et al., 2017; Zhao et al., 2016), waste minimalization (Elyasbath et al., 2021; Sharotri et al., 2016), dye-sensitized solar cells (Zhao et al., 2016). It is commonly used as a semiconductor due to the compound’s stability, pollutant-free nature, availability in nature, inexpensiveness, and resistance to corrosion (Acar et al., 2016). In photocatalytic H₂ generation, several processes have been performed to enhance the utilization efficiency of TiO₂ photocatalyst under visible light, increase the surface area and reduce the electron-hole recombination. These processes include depositing with nonmetal and metal ions to be active with visible light and reducing the recombination of photogenerated e⁻ and h⁺ (Sharotri et al., 2016; Slamet et al., 2017), getting morphology modifications in the forms of nanotubes (Elyasbath et al., 2021), and combining with narrow bandgap semiconductors such as CdS (Tian et al., 2015; Zhao et al., 2016). TiO₂-CdS is a common composite system, which is rich with TiO₂ nanoparticle or TiO₂ nanotube arrays (TNTA) as a semiconductor has shown remarkable performances in the field of photocatalytic performance. For instance, several studies using TiO₂/TNTA-CdS for H₂ production (Junn Ng et al., 2020; Wang et al., 2014; Zhao et al., 2016; Zhu et al., 2015), methane production (Park et al., 2016), and for degrading dye and diclofenac pollutants (Elongovak et al., 2021; Li et al., 2015). This photocatalyst was selected to minimize the recombination and enhance the activating response to visible light. The presence of CdS on TNTA increased the mechanical stability and produced more hydrogen (Liu et al., 2011). TiO₂ with the morphology of nanotube arrays produced by the anodizing process is widely used due to the high surface area (Elizabeth et al., 2021; Slamet et al., 2017).

Numerous reports have shown organic compounds containing hole scavengers tend to reduce recombination and serve as H₂ source to enhance hydrogen generation through oxidation reaction (Luo et al., 2009; Slamet et al., 2017). Examples of organic compounds containing hole scavengers modified with TiO₂ nanoparticle or TiO₂ nanotube arrays (Sharma et al., 2017), methanol (Levy et al., 2012), and ethanol (Hippargi et al., 2018). Furthermore, 2.4,6 TCP, a hazardous pollutant, is also a suitable hole scavenger/sacrificial agent for H₂ production. This process could help in eliminating waste while producing renewable energy. 2.4,6-TCP needs to be degraded since it causes carcinogenic effects and is dangerously toxic for life even at low concentrations. According to International Agency for Research on Cancer (IARC), it is categorized as carcinogenic 2B Group (Ali et al., 2019). This waste comes from pharmaceutical, petrochemical, textile, and pesticide waste. Some studies have been performed to photodegrade 2.4,6-TCP using TiO₂/graphene (Ali et al., 2019), MgO-MgFe₂O₄ (Ramirez et al., 2019), CdS (Khodadad et al., 2016), TiO₂-Carbon (Lavand et al., 2015), and g-C₃N₄ (Ji et al., 2013). In addition, biological degradation, coagulation, adsorption, and AOP method were also performed to eliminate 2.4,6-TCP (Ali et al., 2019; Khoshandeh et al., 2018). However, 2.4,6-TCP can present an attractive renewable material that can be degraded and converted to H₂ simultaneously. Therefore, this would be profitable as a new source for H₂ production and waste reduction. Few studies have been conducted for hydrogen production using TNTA-CdS and degrading 2.4,6-TCP either separately or simultaneously. H₂ production and 2.4,6-TCP degradation simultaneously has been performed previously using TiO₂ nanotube/graphene composite (Slamet et al., 2017). Unfortunately, the application of TNTA-CdS composite in hydrogen production and degrading with 2.4,6 TCP simultaneously has not been studied in detail.

This study reports a combination of degradation and H₂ production using TNTA-CdS photocatalyst with 2.4,6-TCP as a hole scavenger. Modification of TNTA with CdS was carried out by the electrodeposition process. Subsequently, the TNTA-CdS was characterized by SEM-EDX, XRD, and UV-Vis DRS analyses. The effect of loading CdS on TNTA, and the initial concentration of 2.4,6 TCP in H₂ generation were also evaluated.

2. Materials and Methods

2.1. Materials

Nitric acid (HNO₃, 65%), 2.4,6 Trichlorophenol (2.4,6 TCP, 98%), and hydrofluoric acid (HF, 65%) were purchased from Merk. Furthermore, Glycerol solution (98%, 8%) was procured from Brataco, while thioacetamide (CH₃CSNH₂, 98%) and cadmium chloride (CdCl₂, 99%) were obtained from Sigma Aldrich. All the chemicals used without further purification and the aqueous solutions were prepared using distilled water.

2.2. Preparation of TNTA

Titanium foils (0.3 mm thickness, 99.6%) were mechanically polished with sand using cc1500cw, chemically polished for 2 minutes with a mixture of HF, HNO₃, and H₂O (1:3:6), rinsed with deionized water, then dried. The anodization process was performed using Pt electrode (2 mm thickness) as the cathode and Ti foils as the anode, in an electrochemical cell equipped with a DC power supply (ESCORTEL 6030SD). At room temperature, the Ti foils were anodized for 2 hours at 50 V in a 60 ml glycerol electrolyte solution containing 0.5 wt% NH₄F and 25 wt% water, with continuous stirring at 150 rpm (NESCO79-1A) to produce TNTA. Subsequently, the TNTA was rinsed with deionized water and calcined for 3 hours at 500°C in an atmospheric furnace as previously reported with slight modification (Ratnawati et al., 2014).

2.3. Modification of TNTA with CdS

TNTA-CdS was prepared through electrodeposition in a TPC 015 ultrasonic bath, where Pt electrode and TNTA served as the anode and cathode, respectively. The electrolyte consists of CdCl₂ and CH₃CSNH₂ in various mole per Liter ratios, to obtain TNTA-CdS-1 (0.1:0.06), TNTA-CdS-2 (0.2:0.12), and TNTA-CdS-3 (0.4:0.24). Furthermore, the electrodeposition process was performed at 1.5 V for 0.5 hours. Subsequently, the TNTA-CdS was performed on the TNTA-CdS-3 samples, with 100 watt power, in a TPC 015 ultrasonic bath.
produced was washed with distilled water and annealed for 2 hours at 350°C in an atmospheric furnace.

2.4. Characterization of catalyst

The morphological structure of TNTA-CdS was evaluated using a Scanning Electron Microscope (SEM, JSM-6510LA) equipped with an energy dispersive X-ray analyzer (EDX) to know the elemental composition. The energy bandgap of the photocatalyst produced was measured using UV–Vis diffuse reflectance spectra (UV-Vis DRS) analysis (Shimadzu 2450 Spectrophotometer). The samples’ absorbance and reflectance were then determined at ambient conditions in the wavelength of 200 to 600 nm. To evaluate the photocatalyst’s crystalline phase, X-ray diffraction (Shimadzu 7000 X-ray diffractometer) was used at 40 kV and 30 mA with Cu Kα (λ = 0.154184 nm). Meanwhile, the Scherrer equation was employed to calculate the crystallite sizes of the TNTS-CdS estimated from full width at half-maximum (FWHM) (Slamet et al., 2017).

2.5. Photocatalytic Hydrogen Production

The photocatalyst’s activity was investigated for hydrogen production from the reactant (200 mL of 2,4,6-Trichlorophenol solution) through the photocatalysis reaction conducted in a 500 mL Pyrex glass reactor equipped with two mercury lamps (Philips HPL-N 250 W/542 E40 HG ISL with 83% visible light and 17% UV) as a photon source to stimulate the reaction, as well as a magnetic stirrer to homogenize the reactant. The mercury lamps were then placed 1 cm away from the photoreactor, and the photocatalytic reactor system was placed in a reflector box for 4 hour-irradiation. Before the irradiation, the TNTA-CdS in reactant within the reactor flask was magnetically stirred and purged with argon to eliminate air that could hamper the H₂ generation and to test the photoreactor’s leakage. The photoreactor is equipped with a cooling system in the form of 2 exhaust fans which are placed on the walls of the reflector box, and after 75 minutes of irradiation, the temperature became constant around 80°C.

Subsequently, the H₂ produced was analyzed by online sampling every 30 min using Gas Chromatograph (Shimadzu GC 2014) equipped with a molecular sieve (MS Hydrogen 5A, 80 - 100 mesh) column for hydrogen analysis which was connected to a personal computer.

Meanwhile, the signal/peak of hydrogen was recorded using a Thermal Conductivity Detector (TCD) system with high purity argon/Ar (99.99%) at 50 cm² min⁻¹, as a carrier gas. Figure 1 presents a schematic diagram of the photoreactor.

3. Results and Discussion

3.1. Semiconductor Analysis

The present study investigates the morphological analysis of TNTA-CdS using scanning electron microscope (SEM) imaging. The SEM images in Figures 2a and 2b show the TNTA were regularly and perpendicularly self-organized. Meanwhile, Figure 2c confirms the presence of CdS on the surface of the tube which tends to be brittle due to sonication in the modification process. According to the Figure, CdS nanoparticles are deposited on the TNTA surface and some CdS nanoparticles are observed outside the nanotubular structures (the space between the tubes). This result is in line with the reports of previous studies (Liu et al., 2011; Xie et al., 2016). Based on the EDX analysis on TNTA, the components detected were Ti, O, C, F, Cd, and S (Table 1). The C, N, and F were obtained from glycerol and NH₄F (Slamet et al., 2017), however, for TNTA-CdS, there are additional components: Cd and S. The mass percentage of Cd was much larger, compared to S, indicating Cd⁺² formed compounds other than CdS. These results confirmed CdS was successfully deposited on TNTA. The diameter ranges for TNTA and TNTA-CdS were 123-144 nm and 130-152 nm, respectively, while the tube thickness was 25-27 nm and 22-28 nm, respectively. According to the previous study, the tube height of TNTA formed after anodizing and annealing with air was about 1500 nm (Slamet et al., 2017). The competition between chemical dissolution within the tube’s mouth and inside wall and the oxidation reaction at the tube’s bottom, influence the highly ordered morphology of TNTA.

UV–Vis diffuse reflectance spectra (DRS) were recorded to investigate the TNTA’s light absorption ability and the variations of TNTA-CdS. In comparison with bare TNTA, the light absorbance edge of TNTA-CdS-1, TNTA-CdS-2, and TNTA-CdS-3 photocatalyst were significantly red-shifted to the visible region (Figure 3). This is possible due to the decorating of CdS on TNTA, which has been reported to improve the visible light capability of TNTA-CdS (Elangovan et al., 2021; Li et al., 2015). By extrapolating the Tauc plot of the transformation of Kubelka-Munk [F(R).hv]¹/² vs energy (hv) in the linear section and intersecting on the x-axis, the bandgap of photocatalyst can be evaluated (Elangovan et al., 2021), with F(R) according to equation 1.

Table 1

<table>
<thead>
<tr>
<th>Component</th>
<th>TNTA</th>
<th>TNTA-CdS-2</th>
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</thead>
<tbody>
<tr>
<td>Ti</td>
<td>63.87</td>
<td>50.16</td>
</tr>
<tr>
<td>O</td>
<td>32.95</td>
<td>28.08</td>
</tr>
<tr>
<td>C</td>
<td>0.71</td>
<td>1.17</td>
</tr>
<tr>
<td>N</td>
<td>1.65</td>
<td>1.22</td>
</tr>
<tr>
<td>F</td>
<td>0.83</td>
<td>0.37</td>
</tr>
<tr>
<td>Cd</td>
<td>-</td>
<td>18.71</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>0.34</td>
</tr>
</tbody>
</table>
Fig. 2. The SEM image for (a) TNTA from the top, (b) TNTA at an angle of 45°, (c) TNTA-CdS-2 from the top at 50,000x magnification.

Fig. 3. The DRS spectra of bare TNTA and variations of TNTA-CdS photocatalysts.

Fig. 4. The Tauc plot for determination of bandgap of photocatalyst samples.

\[ F(R) = \frac{(1-R)^2}{2R} \quad (1) \]

Where \( R \) is the converted reflectance (%) of the UV adsorption spectra, \( h \) = plank’s constant, \( v \) = frequency.

The Tauc plot of transformed Kubelka-Munk function vs energy (eV) for various TNTA-CdS photocatalysts for calculation of bandgap is presented in Figure 4, and the evaluation of the bandgap is using indirect band gap (Chen et al., 2013).

Based on Figure 4, the bandgap of TNTA, TNTA-CdS-1, TNTA-CdS-2, and TNTA-CdS-3 was found to be 2.91, 2.89, 2.8, and 2.71 eV, respectively. This means CdS deposited in TNTA modifies the photocatalyst due to a reduction in the bandgap energy. Therefore, higher CdS loading on TNTA will result in even lower bandgap energy due to the low bandgap of CdS (2.45 eV). This is in line with the report of the previous studies (Li et al., 2015). The enhanced ability of the TNTA-CdS in absorbing visible light makes the composite potentially suitable for solar-driven applications.

Figure 5 depicts the XRD patterns of TNTA and TNTA-CdS-2 samples. The diffraction peak observed at \( 2\theta = 25.3^\circ, 37.80^\circ, 48^\circ, 54.3^\circ, \) and \( 55.05^\circ \) indicates anatase crystals of TNTA derived from (101), (004), (200), (105), and (221) crystallite orientations (JCPDS no 21-1272). However, there is no indication of rutile phase of TNTA because there were no diffraction peaks at \( 2\theta = 27.4^\circ \) and \( 36^\circ \) (JCPDS No.21-1276) (Slamet et al., 2017). Furthermore, after depositing, TNTA-CdS-2 exhibited a weak diffraction peak at around \( 2\theta = 43.7^\circ \) assigned to the (110) plane of hexagonal phase CdS according to JCPDS#41-1049 (Xie et al., 2016, Yu et al., 2021). These results confirm the successful decoration of CdS on the TNTA surface, which is in accordance with the SEM and EDX results. Also, the diffraction peaks at around \( 2\theta = 23.6^\circ, 30.56^\circ \) and \( 50.12^\circ \) indicate the presence of CdCO3 impurities formed during the electrodeposition process (JCPDS = N°Data 421342) (Moreira et al., 2017; Veeraputhiran et al., 2017). The anatase crystal size of TNTA and TNTA-CdS-2 were discovered to be 20.4 and 27.17 nm, respectively using Scherrer’s equation (Li et al., 2015; Slamet et al., 2017). This shows depositing with CdS led to a significant increase in the crystal size. The calcination temperature and duration also play an important role in enhancing the crystalline anatase phase (Aphairaj et al., 2011).
In the synthesis of TNTA-CdS, there were 2 calcination processes, which were at 500 °C for 3 hours and at 350 °C for 2 hours. This caused the increase of anatase crystals; however, no rutile crystals were identified. Therefore, the CdS depositing on TNTA enhanced the diffraction and crystallinity (Li et al., 2015).

3.2. Hydrogen Production and 2,4,6 TCP Elimination

In terms of morphology, TNTA reportedly produces 5 times more hydrogen, compared to P25-TiO2, considering the two photocatalysts produced 1.503 and 0.298 mmol/g of H2, respectively (data not presented). This is because the neat arrangement of TNTA tubes enables photons to enter more easily, compared to P25-TiO2. Also, P25-TiO2 has higher band gap energy, as well as a lower surface area of 53.6 m²/g (Slamet et al., 2017), compared to TNTA, which has lower bandgap energy and a higher surface area of 285 m²/g (Zhao et al., 2009).

Figure 6 shows the H₂ production (mmol/g) on TNTA-CdS with various CdS loading. During the process, the reactor temperature was measured using a thermocouple and after 75 minutes of irradiation, the temperature was kept constant at about 87°C using exhaust fans. The accumulative hydrogen production on the TNTA, TNTA-CdS-1, TNTA-CdS-2, and TNTA-CdS-3 was approximately 1.503 mmol/g, 1.796 mmol/g, 2.155 mmol/g, and 0.814 mmol/g, respectively. TNTA-CdS-2 produced greater hydrogen, compared to TNTA and TNTA-CdS-1, indicating hydrogen generation increased with an increase in the CdS loading. The highest hydrogen production by TNTA-CdS-2 might be due to the synergy effect of appropriate loading amount and uniformly distributed CdS on TNTA that result in effective separation of h⁺ and e⁻ pairs.

CdS can minimize recombination activity because TNTA has a more positive conduction band (CB), compared to CdS, which causes the electrons to move from the CB of CdS to the CB of TNTA. Meanwhile, CdS has a more negative valence band (VB), compared to TNTA, and consequently, the hole moves from the TNTA VB to the CdS VB. The hole and electron transfer caused differences in the exact locations; therefore, recombination was minimized due to the separation effect (Xu et al., 2018, Zhao et al., 2016) as depicted in Figure 7. Optimal photon absorption was also achieved due to the reduction in the bandgap.

The enhanced photocatalytic activity up to optimum loading could be due to effective charge transfer, uniformly distributed, strong interaction between CdS and TNTA, responds positively to the visible light, high crystallinity, and large surface area (Elangovan et al., 2021). The presence of CdS also strengthens the mechanical stability and increases the photoanode material’s efficiency (Liu et al., 2011). However, TNTA-CdS-3 showed weak performance in hydrogen production. This phenomenon might be due to the presence of an excess CdS loading that causes accumulation of CdS on TNTA surface and has increased particle size which results in the reduction of the surface area since aggregation of CdS causes low dispersion. In another word, the CdS are not dispersed uniformly on the TNTA surface which would reduce the contact area and photocatalytic performance (Elangovan et al., 2021; Zhao et al., 2016). Moreover, smaller CdS quantum dots inject more effectively e⁻ into TNTA than the bigger ones as reported by Robel et al., 2007 in the previous study. Furthermore, CdS loading greater than optimum conditions could also cause CdS aggregates to become larger and clog the mouth of TNTA (Zhu et al., 2015). Although TNTA-CdS-3 has the strongest absorption indicated by the lowest band gap (2.71 eV), this blocking will affect light absorption in the inner TNTA.

![Figure 5](image5.png) **Fig. 5.** The XRD patterns of bare TNTA, TNTA-CdS-2 and TiO2-P25 photocatalysts where T = Ti, A = Anatase, R = Rutile, C = CdS, CO = CdCO3.

![Figure 6](image6.png) **Fig. 6.** The relationship between time and hydrogen production on various photocatalysts as a function of irradiation time with an initial 2,4,6-TTCP concentration of 40 ppm.

![Figure 7](image7.png) **Fig. 7.** Electron and hole generation, transfer, and separation between TNTA and CdS in a TNTA-CdS nanocomposite under visible light.
The following reaction may be occurred in the photocatalytic process: 

\[ \text{TNTA-CdS} + \text{hv} \rightarrow \text{CdS (h^+)}/\text{TNTA (e^-)} \]  

The elimination of 2,4,6 TCP is proportional to the H\(^+\) concentration of 40 ppm and the H\(^+\)/recombination decreases with an increase in the initial concentration. For the 2,4,6 TCP (CdH\(_2\)Cl\(_2\)OH) degradation, the possible pathway could be presented according to Equation (7) to (11).

\[ \text{h}^+ + \text{H}_2\text{O} \rightarrow \bullet \text{OH} + \text{H}^+ \]  

\[ \text{e}^- + \text{O}_2 \rightarrow \bullet \text{O}_2 \]  

\[ \bullet \text{O}_2 + \text{e}^- \rightarrow \text{H}_2\text{O}_2 \]  

\[ \text{CdH}_2\text{Cl}_2\text{OH} + (\text{h}^+\bullet \text{OH} \bullet \text{O}_2\bullet \text{H}_2\text{O}_2) \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{small molecule compounds} \] \hspace{1cm} (10)  

\[ \text{or CdH}_2\text{Cl}_2\text{OH} + (\text{h}^+\bullet \text{OH} \bullet \text{O}_2) \rightarrow \text{intermediate} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Cl} \] \hspace{1cm} (Ramirez et al., 2019) \hspace{1cm} (11)

The oxidizing agent that plays a role in the degradation (h\(^+\)\bullet \text{OH}\bullet \text{O}_2\bullet \text{H}_2\text{O}_2) depends on the photocatalyst used. When TiO\(_2\) is used, \bullet \text{OH} plays a very crucial role in the degradation of 2,4,6 TCP. In contrast, \bullet \text{O}_2\bullet \text{e}^- plays a major role in the degradation if the photocatalyst was MgO-MgFe\(_2\)O\(_3\) (Ramirez et al., 2019).

Figure 10 shows the relationship between the elimination of 2,4,6 TCP and the H\(^+\) generation at various initial 2,4,6 TCP concentrations. At the initial concentration of 10, 20, and 40 ppm, the elimination/reduction of the concentration of the pollutants was 9.7, 17.2, and 32 ppm while the accumulative H\(^+\) production was 1.814; 1.910; and 2.155 mmol/g respectively. The elimination of 2,4,6 TCP and the H\(^+\) production was discovered rising, along with an increase on the initial concentration up to 40 ppm. This phenomenon is due to the presence of sufficient or abundant surface area/active site of the TNTA-CdS in absorbing the incident light and the photocatalyst was uniformly distributed. The higher the initial concentration of 2,4,6-TCP up to 40 ppm, the more H\(^+\) is produced and the more 2,4,6-TCP is degraded since the more reactants are degraded and converted.
In the H₂ generation mechanism, reactant (2,4,6-TCP) serves as a hole scavenger that increases the H₂ production due to it reducing the recombination of photogenerated electrons-holes. As a result, more electrons reduce H⁺ to generate H₂.

4. Conclusions

TNTA modified with CdS was successfully produced by using the electrodposition method. According to the SEM images, XRD analysis, and EDX spectra, the CdS nanoparticles were dispersed and deposited on the TNTA surface. The UV-Vis DRS results showed the effect of CdS deposited on TNTA reduced the band gap of TNTA-CdS photocatalyst from 3.10 to 2.71 eV, therefore it shifted to the visible light domain. It indicates the photocatalyst was more responsive to visible light absorption. The deposition CdS on TNTA enabled better electron-hole separation, compared to TNTA alone. However, CdS loading on TNTA more than the optimum condition (TNTA-CdS-2) produced lower photocatalytic activity which is likely due to CdS aggregate clogging the mouth of TNTA that affected light penetration in the inner tube. In addition, excess CdS caused accumulation of CdS on TNTA surface which reduced the contact area. Although TNTA-CdS-3 has the strongest absorption indicated by the lowest band gap (2.71 eV), this blocking would affect light absorption in the inner TNTA. The amount of CdS deposited in TNTA and the initial concentration of 2,4,6 TCP were discovered to influence the performance in photodegradation of 2,4,6 TCP, as well as the hydrogen production. In this study, the TNTA-CdS-2 photocatalyst was found to produce the most optimal hydrogen generation and 2,4,6-Trichlorphenol degradation.

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