

Electrochemical Study on the TiO₂-CdS Photocatalysis Activity deposited on Graphene

V. Punsan-nga and V. Boonamnuyvitaya.

Abstract—Photocatalytic activity of titanium oxide immobilized on graphene with dopant of cadmium sulfide (TiO₂-CdS/GR) at different weight ratios of CdS were prepared by Hummer's method. The CdS ratios of 0, 0.4, 0.5, 0.6 and 0.7 %wt were varied with the weight ratio of between TiO₂/GR fixed at 1:50. The proposes of this work were to evaluate the photocatalytic activity of the composites by measuring the degradation of methylene blue (MB) solution under ultraviolet and visible light measured by UV-vis spectrophotometry. In addition, the characterizations of composites were investigated by X-ray diffraction (XRD) and transmission electron microscope (TEM). Then, the electrochemical properties of the TiO₂-CdS/GR composite were confirmed by cyclic voltammetry. It is found that TiO₂-CdS/GR composite with 0.5 %wt of CdS results in an excellent degradation of methylene blue. The electrochemical stability in cyclic voltammetry and electrochemical impedance spectroscopic was investigated.

Keywords—electrochemical study, photocatalytic activity, titanium dioxide, cadmium sulfide, graphene.

I. INTRODUCTION

The potential of titanium dioxide (TiO₂) to be used as the catalyst materials have been intensively explored in quite recent years because of its high stability, insolubility, non-toxicity, resistance to corrosion and relative inexpensiveness [1-3]. Also, TiO₂ was widely used as a promising photocatalyst for the environmental remediation and degradation of pollutant process [4]. There were two parts for the degraded mechanism of TiO₂ consisting of the adsorption and the photo oxidation. The adsorption of contaminate organic molecules onto on the TiO₂ surface followed by photo oxidation reaction [5]. However, the disadvantages of TiO₂ of high band gap around 3.2 eV which can be activated only under UV irradiation, the poor adsorption of the surface of TiO₂ and also the recombination of the electron-hole pair of TiO₂ [6-8]. In addition, many studies found that CdS could be a good semiconductor due to its small band gap energy around 2.42 eV which can be used to induce photocatalytic decomposition of water [9]. Also, preparing TiO₂ particles with homogeneously dispersed CdS showed an outstanding

combination because the direct formation of these two semiconductors would provide a strong coupling between them [10-12]. Furthermore, Graphene was a novel material which has intriguing properties such as; high surface area of 2600 m²/g and electron-transferring ability could be efficiently aroused by photoreaction charge separation [13]. Particularly, graphene was assigned as a flat monolayer of carbon atoms tightly pack into a two-dimensional (2D) honeycomb lattice [14]. It was shown that TiO₂-GR composites were an effective adsorption material with good electronic conductivity of graphene due to its π - π conjugation structure [15]. This is because π - π conjugation structure enhances the photocatalytic activity by suppressing the charge recombination of electron-hole pairs. Hence, combining CdS and graphene composite materials could significantly increase the photocatalytic activity of TiO₂ [16]. Then, the possibility to activate TiO₂ in the visible irradiation has been achieved by adding cadmium sulfide (CdS) to the composite whereas its poor adsorption property could be improved by using graphene oxide substrate.

In this work, titanium dioxide (TiO₂), graphene oxide (GR) and cadmium sulfide (CdS) were synthesized by using peroxy titanate acid solution (PTA), Hummer's and hot injection methods. The preparation of TiO₂-GR composites were further used for preparation of TiO₂-GR/CdS particles. The investigation of photocatalytic activity and electrochemical performance were compared among pure TiO₂, TiO₂-GR and TiO₂-GR/CdS with different weight ratios of CdS (CdS at 0.4, 0.5, 0.6 and 0.7 %wt, respectively) while the weight ratio of TiO₂-GR was fixed at 50:1 for all experiments. The intrinsic characteristics of TiO₂-GR/CdS composites were measured by using the X-ray diffraction (XRD) and transmission electron microscopy (TEM). The objective of this work was to investigate the photocatalytic efficiency of the TiO₂-GR/CdS composites under the UV and visible light irradiations. The photocatalytic efficiency of composites was evaluated by measuring the degradation of methylene blue (MB). Especially, the electrochemical performance of photocatalysts were conducted by using cyclic voltammetry and electrochemical impedance spectroscopy (EIS) measurement techniques.

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II. EXPERIMENTAL

A. Preparation Titanium dioxide (TiO_2)

Titanyl oxysulfate ($TiOSO_4$, Sigma-Aldrich, 5.0 g) was dissolved in 25 mL of distilled water. After that, the white precipitate of $Ti(OH)_4$ was observed by adding NH_4OH (3 M) to the existing solution and washed with distilled water for several times (pH=7) afterwards. Then, the yellow transparent solution of peroxy titanate acid (PTA) solution was obtained by adding hydrogen peroxide (H_2O_2) 0.98 M into the above solution. The PTA solution was diluted with de-ionized water in the 500 mL volumetric flask. TiO_2 nanoparticles were obtained by refluxing the PTA solution at 100 °C for 10 h [17].

B. Preparation of graphene oxide

Graphene oxide was synthesized by using the Hummer's method [18]. The concentrated H_2SO_4 (32 mL) and $NaNO_3$ (1.0 g) were mixed and stirred in an ice bath, after that natural graphite (1 g) was added into the mixture. $KMnO_4$ (4.5 g) was slowly added to the above mixture under continual stirring at 30 °C for 1 h. Accordingly, the mixture solution was diluted by adding 250 mL of distilled water. The existing mixture was further heated at 98 °C for 1 h. Afterwards, the 10 mL of 30% H_2O_2 was mixed to the existing mixture, then, the dark brown precipitate was separated by centrifugation and washed with distilled water for pH 7.

C. Preparation of GR- TiO_2

Graphene oxide was added at the fixed weight ratios of graphene oxide to TiO_2 of 1:50 into the TiO_2 (PTA refluxed at 100 °C for 10 h) colloidal suspension (50 mg/L) in ethanol (70%). Then, graphene oxide- TiO_2 suspension were irradiated with two 8 W UVA lamps for 48 h [19].

D. Preparation of cadmium sulfide solution (CdS)

$CdCl_2 \cdot H_2O$ (0.8 g) was firstly dissolved in 200 mL of dimethylformamide (DMF), after that the solution was ultrasonicated at 25 °C for 30 minute. Also, 0.1 g of thiourea was dissolved in 3 mL of dimethylformamide (DMF). Both of existing solutions were mixed in three necked flask and were refluxed with stirring at 130 °C for 6 h.

E. Preparation of silica solution

Methyltrimethoxysilane (MTMOS), methanol (MeOH), distilled water (DI water) and hydrochloric acid (HCl) were stirred at 25 °C for 1 h (solution A) with a ratio of 4.43: 8.22: 2: 0.5 mL, respectively. Then, methanol (MeOH) and ammonia hydroxide (NH_4OH) with a ratio of 8.22: 3.2 mL were stirred at 25 °C for 1 h and were mixed together with the solution A at 25 °C for 5 minutes.

F. Preparation of TiO_2 -GR/CdS

Graphene oxide of 0.01 g was added to PTA solution with a ratio between TiO_2 and GR of 50:1, after that it was ultrasonicated at 25 °C for 45 minutes. Also, 20 mL of ethanol

was added to the TiO_2 -GR suspensions, afterwards it was irradiated by using UVA lamp for 24 h. Cadmium sulfide solution was in addition mixed to TiO_2 -GR suspensions (20 mL) with volumes of 28, 24, 20 and 16 mL (0.7, 0.6, 0.5 and 0.4 %wt), respectively. Then, silica solution (10 mL) were added to pure TiO_2 , TiO_2 -GR and TiO_2 -GR/CdS solutions, and it was stirred at 25 °C for 15 minutes afterwards. Substrate glasses were used for dipping TiO_2 -GR/CdS solution, and dried with using hot air dry at 80 °C for 6 h.

G. Characterization

The crystalline of TiO_2 photocatalyst was investigated by using X-ray diffractometer (Bruker, D8- Discover) with a generated voltage of 40 kV and a current of 40 mA, scanned at a speed of 0.18/s and step size of 0.02° at an angular range of 20-80°. Also, the crystalline sizes of anatase and rutile TiO_2 were calculated by using Scherrer's equation, as follow:

$$D = K\lambda / \beta \cos \theta \quad (1)$$

where D is the crystallite particle size, " λ " is the wavelength of $CuK\alpha$ irradiation (0.15406 nm), K is a constant of 0.9, β is the full width at half maximum, and θ is the Bragg's angle of the anatase (1 0 1) plane [20]. The morphology of catalysts was observed by using a transmission electron microscope (TEM, JEOL, JEM-2100). The absorption edge wavelength of catalysts was recorded by UV-Vis spectrometer (UV1900, UV/VIS. Hitachi). Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) test were measured by using automated potentiostat (ACM Instrument, Gill AC). The electrochemical test consists of three following electrode cell configurations: standard Ag/AgCl as a reference electrode, inert platinum (Pt) sheet as a counter electrode and a working electrode was immersed in the 0.1 Na_2SO_4 electrolyte. A black light blue (BLB, " λ " = 365 nm, Philips) and fluorescent lamp (" λ " = 420 nm, Osram) were used as the source of the UV and visible light, respectively.

H. Photocatalytic activity test

Photocatalytic activity of pure TiO_2 , TiO_2 -GR, and TiO_2 -GR/CdS at varies weight ratio series samples were evaluated by a degradation of methylene blue (MB) aqueous solution (4 ppm). Also, the light sources were placed parallel to another one at the same distance of 20 mm from the photoreaction bottles. The experiment was conducted in two steps. Firstly, the catalyst thin film dispersed in 30 mL of 4 ppm MB solution was kept in the dark for 5 h in order to ascertain the adsorption-desorption equilibrium. Secondly, the samples were exposed to UV and visible light for every 1 h under ambient conditions. The concentration of MB within the sample was determined by UV-Vis spectrophotometer (U1900 UV/VIS, Hitachi) at a wavelength of 664 nm. Then, the photocatalytic activity of pure TiO_2 , TiO_2 -GR, and TiO_2 -GR/CdS at various weight ratio series were measured in terms of degradation efficiency (%) of MB by following equation [21]:

$$\text{Degredation efficiency} = \frac{C_0 - C_i}{C_0} \times 100 \quad (2)$$

where C_0 is the initial concentration of MB after the dark condition while C_i is the concentration of MB solution after UV and visible light irradiation.

I. Electrochemical test

All electrochemical experiments were performed with three electrode configurations including working electrode, counter electrode, and reference electrode. Pure TiO_2 , TiO_2 -GR and TiO_2 -GR/CdS with varying weight ratios were used as the working electrode. Also, platinum sheet and Ag/AgCl (3 M KCl) were used as the counter electrode and the reference electrode, respectively. Cyclic voltammetry was tested on automated potentiostat (ACM Instrument, Gill AC) in 0.1 M Na_2SO_4 electrolyte with the scan rate of 600 mV/min within the range between -400 mV to 600 mV. The surface area of the working electrode exposing to the electrolyte was 12.56 cm^2 . The electrochemical impedance spectroscopy (EIS) measurements were performed with 10 mV signals and a frequency range from 0.01 Hz to 1000 Hz. Accordingly, the cyclic voltammetry and electrochemical impedance spectroscopy (EIS) tests were investigated under the UV and visible light conditions.

III. RESULTS AND DISCUSSION

A. Characterization of synthesized material

Fig.1 shows the X-ray diffraction (XRD) patterns of TiO_2 (PTA refluxed at 100 °C for 10 h). This figure shows that there are five distinctive TiO_2 peaks at 25.3°, 37.9°, 48.0°, 54.6° and 62.8° which correspond to the anatase phase (JCPD 21-1272) [22, 23]. The crystal size of TiO_2 (PTA refluxed at 100 °C for 10 h) was calculated from Scherrer's equation is 14.8 nm.

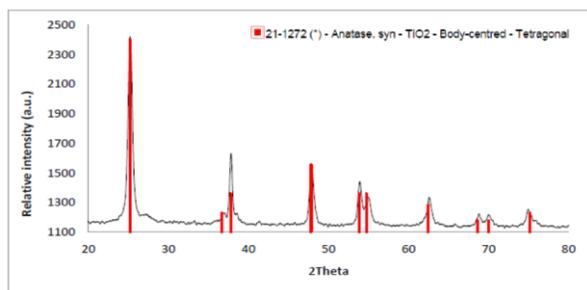


Fig. 1. XRD diffraction patterns of TiO_2 (PTA reflux at 100 °C for 10 h)

Fig. 2 illustrates the X-ray diffraction (XRD) patterns of cadmium sulfide (refluxed at 130 °C for 6 h). There are six peaks at 25.0°, 26.5°, 28.2°, 43.6°, 47.80° and 51.80° which correspond to the hexagonal of cadmium sulfide (CdS) phase (JCPDS 41-1049) [24, 25].

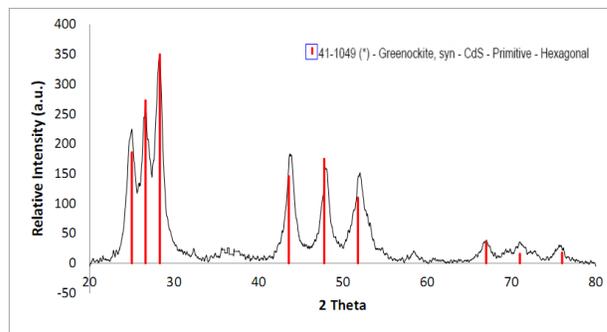


Fig. 2. XRD diffraction patterns of CdS (reflux at 130 °C for 6 h)

Fig. 3 illustrates the X-ray diffraction patterns of TiO_2 -GR/CdS composites. It is shown that TiO_2 contains five peaks at 25.3°, 37.9°, 48.0°, 54.6° and 62.8° which indicate the anatase phase (JCPD 21-1272). Cadmium sulfide (CdS) shows six peaks at 25.0°, 26.5°, 28.2°, 43.6°, 47.80° and 51.80° which correspond to the hexagonal of cadmium sulfide (CdS) phase (JCPDS 41-1049). Graphene shows one peak only at 26.5° which corresponds to carbon group of graphene.

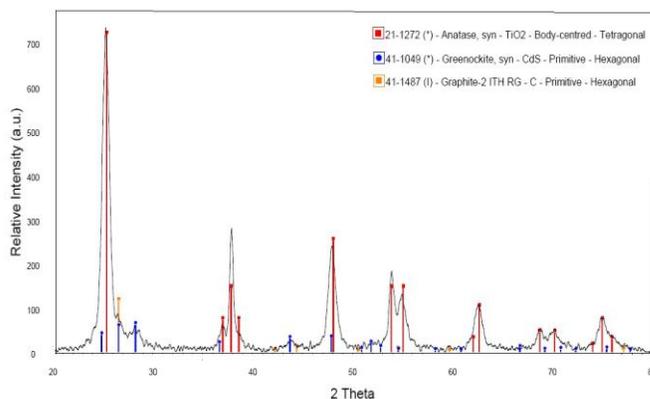


Fig. 3. XRD diffraction patterns of TiO_2 -GR/CdS

The wrinkled two-dimensional structure of graphene oxide can be clearly observed in Fig. 4(a). In case of TiO_2 , the needle-like or rhombus anatase crystals have an average length of 40-80 nm and diameter of 10-20 nm, as shown in Fig. 4 (b). Also, the TEM image of TiO_2 -GR is shown in Fig. 4 (c). It is indicated that the diffraction rings of TiO_2 -GR index to (1 0 1), (0 0 4), (2 0 0) and (1 0 5) crystal planes of anatase TiO_2 which is consistent with the XRD analysis. Then, the results confirm that TiO_2 nanoparticles are successfully loaded onto graphene sheet.

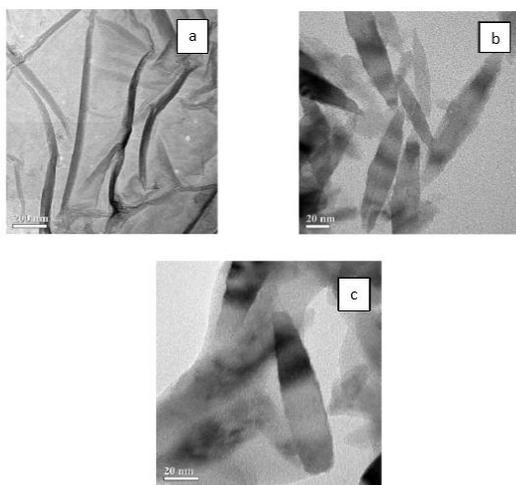


Fig. 4 TEM image of (a) graphene, (b) TiO_2 (PTA refluxed at 100°C for 10 h), (c) $\text{TiO}_2\text{-GR}$

In addition, the UV-vis absorption spectra of TiO_2 , $\text{TiO}_2\text{-GR}$ and $\text{TiO}_2\text{-GR/CdS}$ (CdS at 0.4, 0.5, 0.6 and 0.7 % wt) catalysts are presented in Fig. 5. The spectra of TiO_2 , $\text{TiO}_2\text{-GR}$ catalysts show a red shift in the band gap transition with increasing cadmium sulfide dopant. It is also shown that TiO_2 demonstrates the lowest absorption wavelength, while $\text{TiO}_2\text{-GR/CdS}$ demonstrates a maximum wavelength. Furthermore, Fig. 5 shows that the high adsorption wavelength affects the low band gap energy of catalysts.

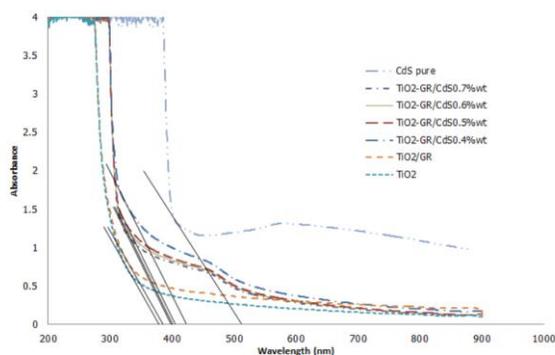


Fig. 5. UV-vis absorption spectra of TiO_2 , $\text{TiO}_2\text{-GR}$ and $\text{TiO}_2\text{-GR/CdS}$ catalysts with different weight ratios of cadmium sulfide (CdS at 0.4, 0.5, 0.6 and 0.7 % wt).

B. Photocatalytic activity

The adsorption of MB on photocatalysts reached equilibrium in 5 h under dark condition. The photocatalytic activities of TiO_2 , $\text{TiO}_2\text{-GR}$ and $\text{TiO}_2\text{-GR/CdS}$ catalysts with different weight ratios of cadmium sulfide (0.4, 0.5, 0.6 and 0.7 % wt) under UV and visible light irradiation are presented in Figs. 6 (a) and (b) respectively. The orders of photocatalysts degradation of MB under UV irradiation are as following: $\text{TiO}_2\text{-GR} > \text{pure TiO}_2 > \text{TiO}_2\text{-GR/CdS } 0.4\% \text{ wt} > \text{TiO}_2\text{-GR/CdS } 0.7\% \text{ wt} > \text{TiO}_2\text{-GR/CdS } 0.6\% \text{ wt} > \text{TiO}_2\text{-GR/CdS } 0.5\% \text{ wt}$. Under visible light irradiation, the degradation

efficiency of MB are as follows: $\text{TiO}_2\text{-GR/CdS } 0.5\% \text{ wt} > \text{TiO}_2\text{-GR/CdS } 0.4\% \text{ wt} > \text{TiO}_2\text{-GR/CdS } 0.7\% \text{ wt} > \text{TiO}_2\text{-GR/CdS } 0.6\% \text{ wt} > \text{TiO}_2\text{-GR} > \text{pure TiO}_2$. As shown in Fig. 6 (a), $\text{TiO}_2\text{-GR}$ demonstrates higher degradation (85.20%) than pure TiO_2 (75.73%) owing to the electron transferred between conduction band (CB) and valence band (VB) in TiO_2 band gap may be recombined by graphene oxide. Additionally, graphene oxides on TiO_2 have high surface area for adsorption of MB, therefore $\text{TiO}_2\text{-GR}$ can degrade MB better than pure TiO_2 . Moreover, $\text{TiO}_2\text{-GR/CdS}$ has a lowest degradation of MB because the cadmium sulfide (CdS) can be reacted only in the visible light, then the UV light transmitted to $\text{TiO}_2\text{-GR}$ may be obstructed by CdS doped particles.

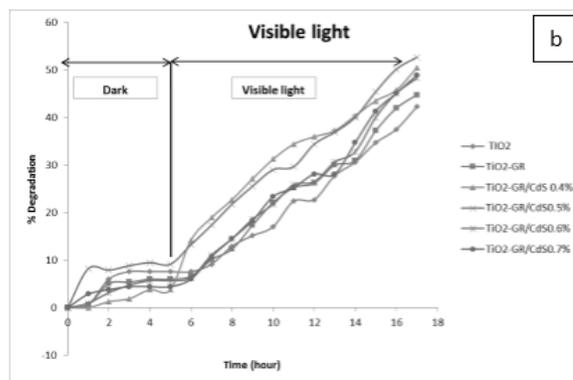
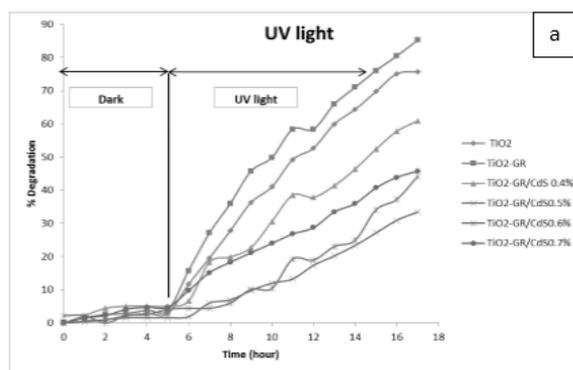
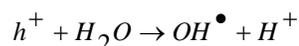
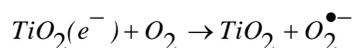
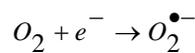
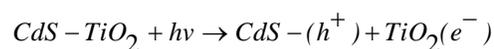


Fig. 6. Photocatalytic degradation of MB solution over pure TiO_2 , $\text{TiO}_2\text{-GR}$ and $\text{TiO}_2\text{-GR/CdS}$ catalysts with different weight ratios of cadmium sulfide (CdS at 0.4, 0.5, 0.6 and 0.7 % wt) (a) under UV irradiation, (b) under visible irradiation

Fig.6 (b) illustrates that $\text{TiO}_2\text{-GR/CdS}$ with 0.5%wt has higher degradation of MB (52.70%) than other catalysts and TiO_2 shows the lowest degradation of MB (42.28%) in visible irradiation. This may be attributed to the electrons in the conduction band (CB) were generated on the surface of TiO_2 when it was irradiated by the light with the energy equal to or exceed its band gap energy. Theoretically, pure TiO_2 cannot be excited by visible light irradiation. However, the photocatalytic activity of TiO_2 under visible light was improved by introducing CdS particles. Then, the degradation of MB proves that electrons were generated in the

mineralization of MB. It was clearly shown that TiO₂-GR/CdS performs good photocatalytic activity than pure TiO₂ and TiO₂-GR composites due to an addition of graphene oxides which enhance electron transport and mobility of charge carriers. However, the various percentage weight ratios of CdS on TiO₂-GR result in different effects. In this study, TiO₂-GR/CdS 0.5%wt indicates an optimum weight ratio confirmed by the highest degradation of MB in the visible light irradiation. Under the visible irradiation, the graphene sheets acts as good electron acceptors and it can accept the electrons generated by light irradiation. Meanwhile, CdS is also excited and it produce electrons and holes in its conduction band (CB) and valence band (VB). The electrons accepted by graphene sheets were transferred to CdS and TiO₂ particles, therefore the reactions will be induced by increasing the number of electrons as well as the rate of transferred electrons. Thus, the photocatalytic activity of TiO₂ can be enhanced by adding graphene oxide and CdS composites. The electrons (e⁻) reacts with dissolved oxygen molecules in order to produce oxygen peroxide radicals (O₂^{•-}). On the other hand, the positive charged hole (h⁺) can react with OH⁻ derived from H₂O to form hydroxyl radicals OH[•]. Then, the dye molecules of MB were photocatalytically degraded by the peroxide and hydroxyl radicals to CO₂, H₂O. The photocatalytic reaction of MB by TiO₂-GR/CdS can be written as following equation:



C. Electrochemical performance

Cyclic voltammetry

Fig.7 (a) and (b) show the cyclic voltammograms of pure TiO₂, TiO₂-GR and TiO₂-GR/CdS catalysts with different weight ratios of cadmium sulfide (CdS at 0.4, 0.5, 0.6 and 0.7 %wt) under UV and visible light irradiation, respectively. It was found that the current densities of UV irradiation condition were significantly decreased as the potential swept negatively. The peaks of negative current density indicate a reduction of the photocatalytic reaction, whereas the positive current densities are caused by the oxidation reaction peaks. In Fig. 7 (a), the results under UV light irradiation are as follows: TiO₂-GR > pure TiO₂ > TiO₂-GR/CdS 0.4%wt > TiO₂-GR/CdS 0.7%wt > TiO₂-GR/CdS 0.6%wt > TiO₂-GR/CdS 0.5%wt. It is shown that TiO₂-GR demonstrates highest reduction peak, while TiO₂-GR/CdS 0.5%wt demonstrates the lowest reduction peak. Then, TiO₂-GR performs good excellent reduction reaction because TiO₂ can be excellently reacted in UV light, also the graphene oxide deposited on TiO₂ has better electron transfer properties from TiO₂ to electrolyte. On the other hand, TiO₂-GR/CdS 0.5%wt

performs poor reduction reaction in UV light. For the under visible light irradiation as shown in Fig. 7 (b), the peaks of reduction reaction are ranked in the following order: TiO₂-GR/CdS 0.5%wt > TiO₂-GR/CdS 0.4%wt > TiO₂-GR/CdS 0.7%wt > TiO₂-GR/CdS 0.6%wt > TiO₂-GR > pure TiO₂. TiO₂-GR/CdS 0.5%wt shows the highest reduction reaction attributed to CdS that excellently reacted in visible light. Meanwhile, pure TiO₂ shows the lowest reduction reaction because TiO₂ can be only reacted in UV light.

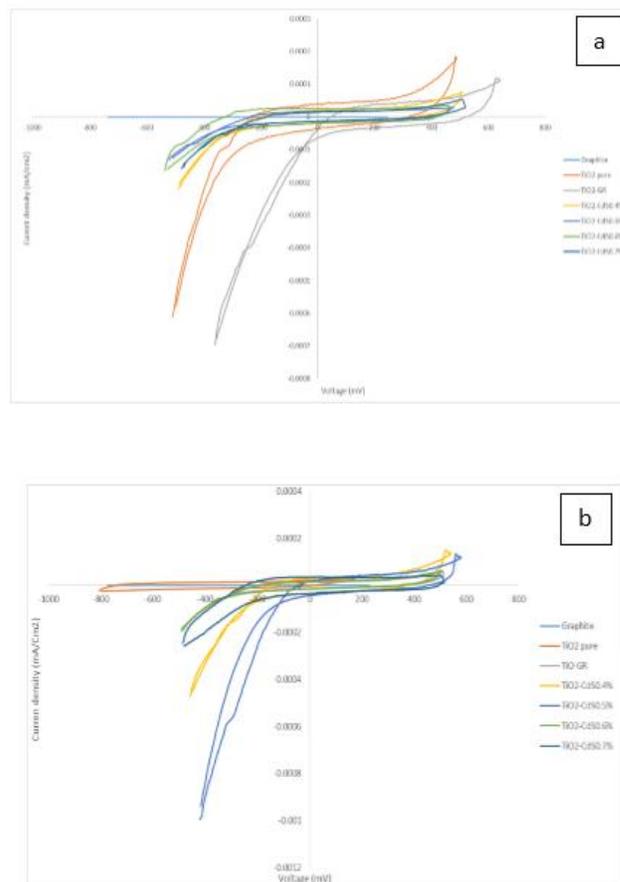


Fig. 7. Cyclic voltammograms of TiO₂ pure, TiO₂-GR and TiO₂-GR/CdS catalysts of cadmium sulfide (CdS at 0.4, 0.5, 0.6 and 0.7 %wt respectively) (a) under UV light irradiation, (b) under visible light irradiation.

IV. CONCLUSIONS

In this work, TiO₂-GR/CdS photocatalysts were prepared with the fixed weight ratio of TiO₂/GR 1:50, and cadmium sulfide (CdS) at weight ratios of 0.4, 0.5, 0.6 and 0.7 %wt, respectively. The XRD diffraction patterns show the presence of an anatase phase of TiO₂ and also the hexagonal peaks of cadmium sulfide. However the intensity of the peaks were diminished due to the presence of graphene. In addition, the TEM analysis gave an images of the structural view in nanoscale that the TiO₂ particles were loaded onto graphene sheets. Furthermore, the photocatalytic activity was also studied by the MB degradation of pure TiO₂, TiO₂-GR and TiO₂-GR/CdS catalysts with different weight ratios of

cadmium sulfide under UV and visible light irradiation condition. The TiO₂-GR shows the high degradation of MB (85.20%) in UV irradiation while TiO₂-GR/CdS 0.5 %wt demonstrates the high degradation of MB (52.70%) in visible irradiation. Also, the electrochemical performance of composites were investigated by a cyclic voltammetry. The results show that the TiO₂-GR has highest reduction reaction observed at a current density of -0.0007 mA/cm² in the UV light irradiation while TiO₂-GR/CdS 0.5 %wt has highest reduction reaction at current density of -0.001 mA/cm² in visible light irradiation.

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