โครงการ

การเรียนการสอนเพื่อเสริมประสบการณ์

ชื่อโครงการ การสังเคราะห์ตัวเร่งปฏิกิริยาเชิงแสงจากคอมโพสิทของกราฟีนออกไซด์และสารประกอบเชิงซ้อนโคบอลต์
Synthesis of photoredox catalysts based on composite of graphene oxide and cobalt complexes

ชื่อนิสิต นายพิธิวัฒน์ ชื่นวัฒนา
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ปีการศึกษา 2560

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

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Synthesis of photoredox catalysts based on composite of graphene oxide and cobalt complexes

by

Mr. Pitiwatt Chuenwattana

A Report submitted in Partial Fulfillment of the Requirements
for the degree of Bachelor of Science Program in Chemistry
Department of Chemistry
Faculty of Science
Chulalongkorn University
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Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Bachelor of Science degree

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Date .... Month May Year 2018

The quality of writing of this report is ☑ Excellent ☐ Good ☐ Fair

ชื่อโครงการ การสังเคราะห์ตัวเร่งปฏิกิริยาเชิงแสงจากคอมโพสิทของกราฟีนออกไซด์และสารประกอบเชิงซ้อนโคบอลต์
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บทคัดย่อ

ในปัจจุบันกราฟีนออกไซด์ (GO) เป็นวัสดุที่กำลังได้รับความสนใจและมีแนวโน้มที่จะนำไปประยุกต์ใช้เพื่อเร่งปฏิกิริยาเชิงแสงได้ การเพิ่มประสิทธิภาพของตัวเร่งปฏิกิริยาเชิงแสงโดยทั่วไปนั้น สามารถทำได้โดยการดัดแปรตัวเร่ง ด้วยโมเลกุลที่สามารถดูดกลืนแสงในช่วงที่ตามองเห็นได้หรือการใช้สารย้อมสี ในงานวิจัยนี้มีวัตถุประสงค์เพื่อพัฒนาตัวเร่งปฏิกิริยาเชิงแสงโดยการใช้สารประกอบเชิงซ้อนของโคบอลต์ที่ประกอบไปด้วยอนุพันธ์ของพอร์ไฟรินจับกับกราฟีนออกไซด์ผ่านอันตรกิริยานอนโควาเลนต์ โดยในการศึกษาครั้งนี้จะใช้สารย้อมสีคือ สารประกอบเชิงซ้อนโคบอลต์(II) ที่มี มีโซ-เททระพอร์ไฟรินเป็นลิแกนด์ (CoTPP), โคบาลามินหรือวิตามินบี12 (B12), และ เททระพอร์ไฟริน (H_2TPP) ในขั้นตอนแรกผู้วิจัยได้ทำการเตรียมกราฟีนออกไซด์ด้วยวิธี modified Hummers จากนั้นจึงเตรียมคอมโพสิทของกราฟีนออกไซด์กับสารย้อมสี (GO-dye) ผ่านกระบวนการรวมตัวกันเองด้วยการโซนิเคชัน จากการทดลองจะพบว่าเฉพาะสารย้อมสีที่ไม่ชอบน้ำ (เช่น CoTPP และ H_2TPP) ที่สามารถทำการคอมโพสิทกับกราฟีนออกไซด์ได้ นอกจากนี้อันตรกิริยาระหว่างกราฟีนออกไซด์กับสารย้อมสีสามารถพิสูจน์ได้โดยยูวี วิซิเบิลและฟลูออเรสเซนส์ ช่วงการดูดกลืนแสงของสารย้อมสีในสารประกอบคอมโพสิทระหว่างกราฟีนออกไซด์กับสารย้อมสีจะมีช่วงที่กว้างขึ้นและเกิดการเลื่อนทางแดงเมื่อเทียบกับสารย้อมสีดั้งเดิม การเปลี่ยนแปลงของสเปคตรัมเป็นผลมาจากการรวมตัวกันของสารย้อมสีบนกราฟีนออกไซด์ผ่านอันตรกิริยา ไพ-ไพ และแรงไฮโดรโฟบิค การดับสัญญาณฟลูออเรสเซนส์ของสารย้อมสีด้วยกราฟีนออกไซด์สามารถสังเกตได้จากกระบวนการโฟโตอินดิวส์อิเล็กตรอนทรานสเฟอร์ (PET) ภายใต้การฉายแสง พบว่าสารย้อมสีในสารประกอบคอมโพสิทระหว่างกราฟีนออกไซด์กับสารย้อมสีสามารถแสดงความเสถียรเชิงแสงได้ดีกว่าสารย้อมสีดั้งเดิม ในการศึกษาความว่องไวต่อการเกิดปฏิกิริยาเบื้องต้นของสารประกอบคอมโพสิทระหว่างกราฟีนออกไซด์กับสารย้อมสีที่เป็นตัวเร่งปฏิกิริยาเชิงแสงสำหรับปฏิกิริยาออกซิเดชันของสาร โดยใช้เบนซิลแอลกอฮอลล์เป็นสารตัวแทน โดยจะพบว่าสารประกอบคอมโพสิทระหว่างกราฟีนออกไซด์กับสารย้อมสีสามารถแสดงความว่องไวในการเกิดปฏิกิริยาที่สูงกว่ากราฟีนออกไซด์และสารย้อมสีดั้งเดิม อาจเป็นผลมาจากการทำงานร่วมกันของตัวเร่งปฏิกิริยาเชิงแสง

คำสำคัญ: สารประกอบคอมโพสิทระหว่างกราฟีนออกไซด์กับสารย้อมสี, การเร่งปฏิกิริยาเชิงแสง, สารประกอบเชิงซ้อนของโคบอลต์, การปรับปรุงฟังก์ชันแบบนอนโควาเลนต์

Project Title Synthesis of photoredox catalysts based on composite of graphene oxide and cobalt complexes
Student Name Mr. Pitiwatt Chuenwattana Student I.D. 5733138523
Advisor Name Pannee Leeladee, Ph.D.
Department of Chemistry, Faculty of Science, Chulalongkorn University, Academic Year 2017

ABSTRACT

Recently, graphene oxide (GO) has emerged to be a promising material for photocatalytic applications. Typically, its low photocatalytic activity can be improved by modification with visible light-absorbing molecules or dyes. In this work, we aim to develop an efficient photocatalyst based on GO by noncovalent fabrication with cobalt complexes containing porphyrin-derivative ligands. Meso-tetraphenylporphyrin cobalt(II) complex (CoTPP), cobalamin or vitamin B_{12} (B12), and TPP (for comparison) were used as our dyes in this study. First, GO was prepared by the modified Hummers' method. Then, the dye-functionalized GO composites (GO-dye) were prepared by a simple self-assembly process using sonication method. It was found that only hydrophobic dyes (*i.e.*, CoTPP and TPP) can form composites with GO. In addition, the interaction between GO and dyes was investigated by UV-vis and fluorescence. Absorption bands of dyes in GO-dye were considerably broadened and red-shifted as compared to those of dyes. The spectral changes are likely resulted from the dye aggregation on the GO solid substrate through π-π stacking and hydrophobic property. Fluorescence quenching of dyes by GO was also observed, presumably *via* photoinduced electron transfer (PET) process. Under light irradiation, dyes in GO-dye composites were found to exhibit better photostability than that of the dyes. Preliminary studies on reactivity of GO-dye composites as photocatalysts for substrate oxidation were carried out using benzyl alcohol as a representative substrate. It was found that GO-dyes exhibited higher reactivity than GO and the dyes, possibly due to cooperative photocatalysis.

KEYWORDS: Graphene oxide-dye composite, photocatalyst, cobalt complexes, noncovalent functionalization

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Pitiwatt Chuenwattana

CONTENTS

LIST OF FIGURES

LIST OF SCHEMES

LIST OF TABLES

LIST OF ABBREVIATIONS

Å	angstrom
δ	chemical shift
cm	centimeter
^{o}C	degree Celcius
g	gram
h	hour
MHz	megahertz
µL	microlitre
µmol	micromole
µM	micromolar
mg	milligram
mL	millilitre
mmol	millimole
min	minute
M	molar
mol	mole
nm	nanometer
rpm	round per minute
λ	wavelength

Chapter 1

Introduction

1.1 Introduction to the project and its significance

Graphene oxide (GO) is a two-dimensional carbon sheets (**Figure 1-1**), which can be produced from several methods such as electrochemical exfoliation of graphite and acid exfoliation of graphite. GO is semi-conductor material with wide band gap. The basal plane of GO is surrounded by epoxide and hydroxy groups, and the edges are decorated with carboxyl functional groups. Due to these functional groups, GO can interact covalently or noncovalently with several molecules. GO-based hybrids and composite materials with improved properties have been synthesized with a range of organic and inorganic molecules via covalent bond and noncovalent interactions.[1] It has been used as biosensors[2], drug delivery[3] and photocatalysts[4]. However, in photocatalyst GO has a low efficiency to absorb light, leading to low catalytic performance. Thus, surface sensitization of GO would improve light absorption range and hence improve the photocatalytic reactivity. However, decoration of organic dyes or complexes on GO *via* covalent bond is quite complicated and sometimes requires vigorous conditions for synthesis. Therefore, in this study, we aim to prepare composites of GO and cobalt complexes by sonication method via noncovalent interaction between GO and the complexes (dye) to provide an easy, alternative approach to prepare GO-based photocatalysts.

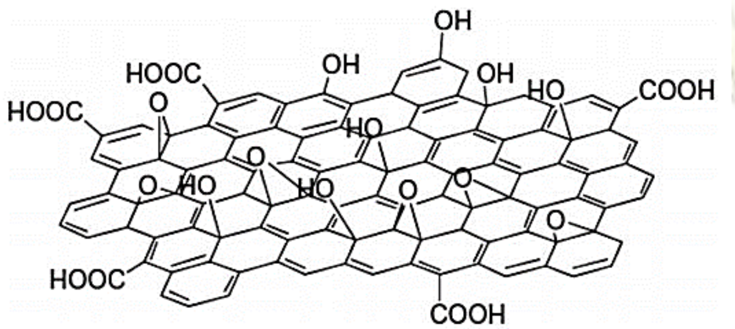


Figure 1-1 Proposed structure of graphene oxide[5]

1.2 Objectives

1. To synthesize composite between GO and cobalt complexes containing porphyrin derivatives.

2. To study reactivity and stability of the synthesized GO-dye composites

1.3 Literature review

Graphene oxide is one of the most promising candidates in the field of nanotechnology owning to its extraordinary mechanical, optical, electronical and thermal properties. These superior properties make graphene oxide be used as a suitable support of the photocatalyst to improve the charge transfer and charge separation. It has been widely reported that graphene oxide incorporated with semiconductor or photosensitizers demonstrated much improved photocatalytic activity for hydrogen generation from water. However, graphene oxide still has limitations including low absorptivity in visible range, charge recombination and low adsorption ability. In the previous works, they have tried to reduce these limitations by grafting with dyes to increase the absorption range, semi-conductor to induce charge separation and also using metal nanoparticles to improve the adsorption ability.

Since the discovery of the photocatalytic splitting of water on TiO_2 electrodes by Fujishima and Honda in 1972 (**Figure 1-2**), a progress has been made in the area of highly active oxide semiconductor photocatalysts because of their application in solar energy conversion and environmental protection. Several semiconductors (e.g., ZnO, WO_3 and CdS) could act as photocatalysts for light-induced chemical transformations due to their unique electronic structure composed of a filled valence band (VB) and an empty conduction band (CB). When a photon with energy matches or exceeds the band gap energy (Eg) of the semiconductor, an electron in the VB would be excited into the CB, leaving a positive hole in the VB. However, the photogenerated electrons and holes in the excited states are unstable and can easily recombine.[6]

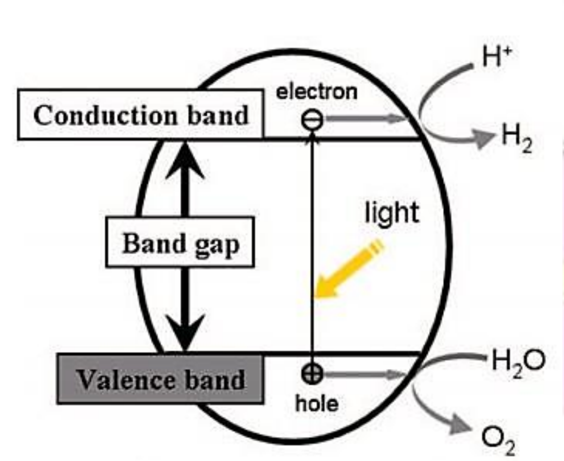


Figure 1-2 Fundamental principle of semiconductor-based photocatalytic water splitting for hydrogen generation[6]

In another work, Majid *et al.* synthesized CdO-graphene oxide to enhance visible light driven photocatalytic degradation of organic pollutants. They reported that graphene oxide plays an important role for the enhancement of photocatalytic activity of the composite. Because GO composite provides better charge separation of the photogenerated electron–hole pairs and prolongs the excited state lifetime. From the result, they observed the photodegradation of methylene blue by CdO composited with graphene oxide. The percentage of photodegradation by CdO-GO composite and pristine CdO were 93.3 and 11.8, respectively. Therefore, graphene oxide could efficiently increase the %photodegradation of methylene blue by promoting the charge separation between CdO and itself which improves the photodegradation performance (**Figure 1-3**).[7]

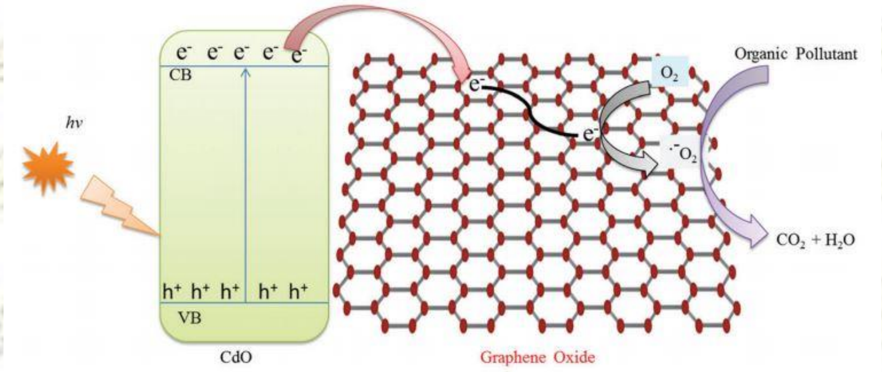


Figure 1-3 The high charge separation in the CdO/GO nanocomposites[7]

Yang *et al.* have successfully synthesized a nanohybrid composed of *cis*-dithiocyanato-bis(2,2´-bipyridine-4,4´-dicarboxylate) ruthenium(II) (N3) covalently bound with reduced graphene oxide to enhance the visible light absorptivity, charge separation efficiency, and lifetime extension of the photoexcited state, leading to the enhancement of photocatalytic activity (**Figure 1-4**). The amount of hydrogen increased to 6.03 µmol/mg from 2.98 µmol/mg by RGO and N3-RGO as catalyst respectively.[8]

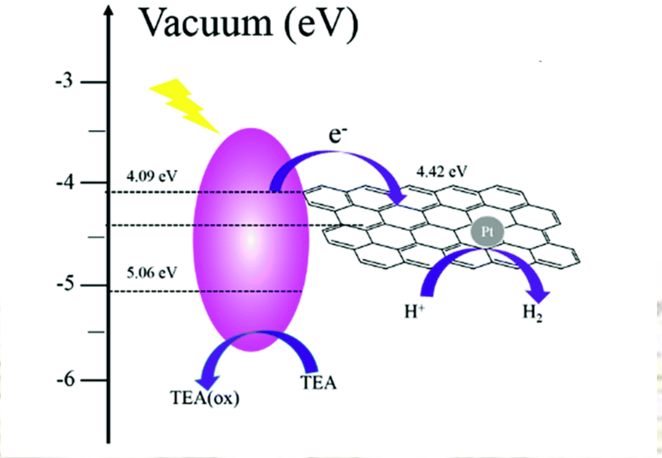


Figure 1-4 Energy band structure diagram of heterostructure between RGO and N3[8]

From the above previous work, they have prepared the composites of GO and dyes via covalent bonds. However, the complicated and vigorous synthesis of highly-reactive functionalized graphene oxide were required such as the transformation of carboxylic edge group to acyl chloride. Therefore, to avoid the difficult procedures and harmful chemicals, an alternative way to form composite of graphene oxide and dyes has been introduced via noncovalent interactions.

Noncovalent or supramolecular interactions are found in many types of materials that experience attractive and/or repulsive forces between them. These interactions are found in many natural and synthetic systems for recognition or detection.[9] For GO, the basal plane is relatively similar to graphene (G) except for defects by epoxides or hydroxides bound to the carbon atoms. For this reason, similar π-interactions will likely occur as shown with G. On GO, there are both hydrogen-bond donors and acceptor moieties from the epoxides, alcohols, ethers, carboxylic, and carboxylate oxygen bearing moieties that can contribute additional modes for interactions.

Ma *et al.* synthesized cobalt phthalocyanine–graphene oxide nanocomposite through π-stacking system. The nanocomposites also had a complicated mutual electronic interaction between the two components. From the result, the Q bands and Soret band of pristine CoPc are at 661 and 598 nm, respectively. After compositing with GO, the Q-bands was slightly red-shifted to 604 nm for 1%CoPc–GO and were further red-shifted to 667 nm for 2.6%CoPc–GO, respectively. These indicated the adsorption/intercalation of CoPc onto/into the carbon sheets, by which the strong π-π interaction between CoPc and GO leading to relocation of the electrons from graphene sheets to the phthalocyanine group of CoPc[10] and thereby reducing the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbitals (LUMO) gap of the CoPc (**Figure 1-5**).[11] In addition, the prepared composites were used for detection of drug by cyclic voltammetry because the changing of redox ability of Co-center in CoPc onto/into graphene oxide sheets.

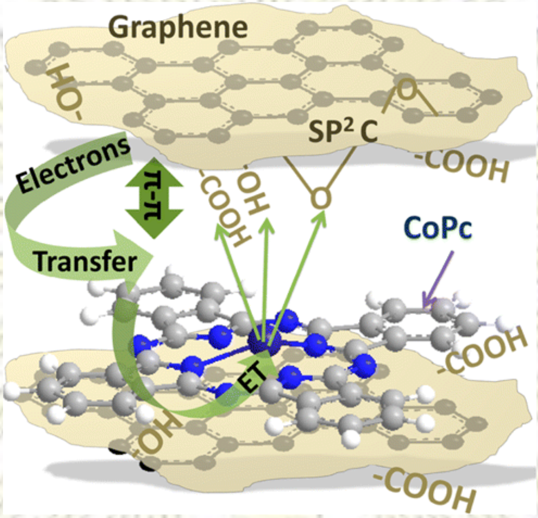


Figure 1-5 The interaction between cobalt phthalocyanine and graphene oxide nanocomposite[11]

One of the most well-known dyes in nature is chlorophyll-an important light antenna for facilitating sunlight in photosynthesis process. The aromaticity and electron delocalization in dye molecules provide an efficient UV-Vis absorption and electron/energy transfer for the photocatalytic process. In our perspective, our chosen dyes should contain porphyrin derivatives which mimic the ability of chlorophyll from the natural source. For the metal center, Co is the interesting metal for porphyrin derivatives because of the suitable of ion radius for complexation. The several oxidation states of Co also provide an opportunity to be used as oxidation and reduction catalysts. Therefore, porphyrins and Co(II)porphyrin derivatives (such as Co(II)TPP and Cobalamin) were our selected dyes for this research (**Figure 1-6 and 1-7**). The study of increasing light absorption range of graphene oxide by dyes via **π-π** interaction is quite rare for oxidation reaction, especially for non-covalent graphene oxide composites. Therefore, in this study, we aim to prepare composites between graphene oxide and dyes via noncovalent interactions and to investigate their photocatalytic reactivity toward oxidation of organic substrates.

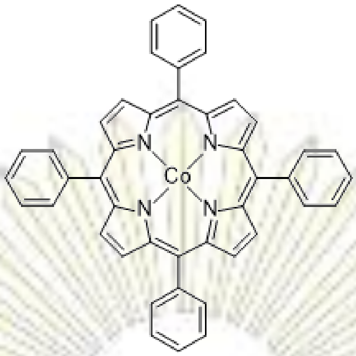


Figure 1-6 Structure of cobalt(II) tetraphenylporphyrin

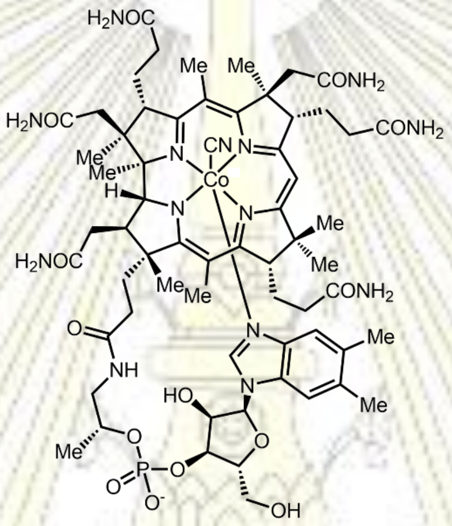


Figure 1-7 Structure of cobalamin (B12)

Chapter 2

Experimental Section

2.1 Materials

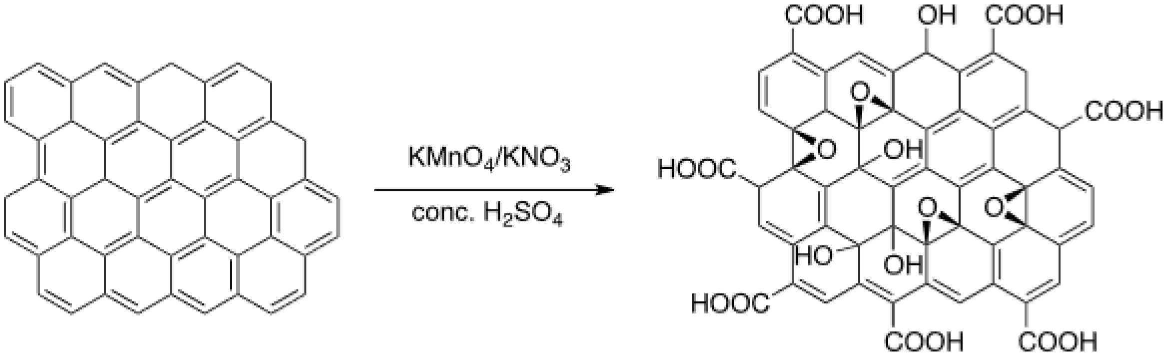
All solvents and chemicals used in the experiments were analytical grade and used without further purification unless otherwise noted. Pyrrole was distilled prior to use to get rid of the yellow stain from degradation. All liquid chemicals were dried over 3 Å molecular sieves for at least 12 h before used.

2.2 Instruments

UV-Vis absorption spectra and fluorescence emission spectra were collected using Varians Cary 50 Probe and Varians Cary Eclipse, respectively. The spectra were recorded at room temperature using a quartz cell with an optical path length of 1 cm. IR absorption spectra were recorded on Nicolet iS10 ATR-FTIR spectrometer on ATR mode. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX 400 spectrometer operating at 400 MHz for ^{1}H-NMR signal.

2.3 Experimental Procedures

2.3.1 Synthesis of graphene oxide



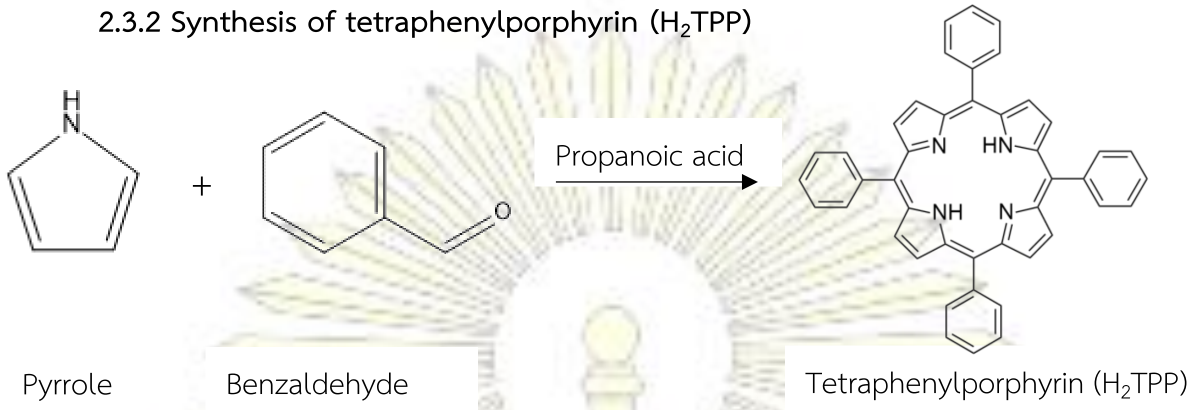
Graphene

Graphene oxide (GO)

Scheme 2-1 Synthesis of graphene oxide (GO)

Graphene oxide was prepared as shown in **Scheme 2-1** by adding conc. H_2SO_4 (25 mL, 0.47 mol) into a 125 mL conical flask containing graphite powder (0.805 g), and $NaNO_3$ (0.4 g, 4.71 mmol) in an ice bath and stirred for 20 min. Next, $KMnO_4$ (2.64 g, 16.71 mmol) was slowly added into the reaction for 10 min and stirred for 6 h. After that, $KmnO_4$ (2.44 g, 15.44 mmol) and conc. H_2SO_4 (10 mL, 0.188 mol) was added into the reaction. The reaction mixture was stirred overnight. Then the reaction mixture was poured into 250 mL beaker containing ice cube (~150 mL) and H_2O_2 (5 mL, 0.21 mol) and stirred for 1 h. The washing step was performed by centrifugation at 4,000 rpm for 10 min with following washing solution; Milli-Q water, 6M HCl, Milli-Q water, 0.5M K_2HPO_4, Milli-Q water x2, respectively. After adding each washing solution into the centrifuged tube, the crude product was consequently washed with washing solution for 5-10 min before directly centrifuged, except for K_2HPO_4 solution which required overnight stirring. Finally, the obtained slurry of graphene oxide was dried in vacuum for at least 12 h to remove excess water. GO was characterized by UV-Vis spectroscopy and IR spectroscopy.

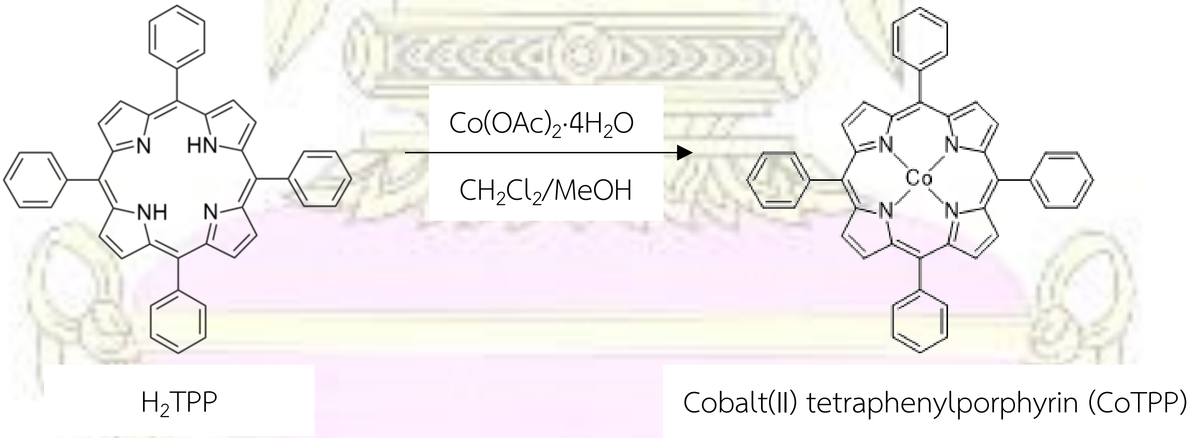
2.3.2 Synthesis of tetraphenylporphyrin (H_2TPP)



Scheme 2-2 Synthesis of tetraphenylporphyrin (H_2TPP)

H_2TPP was prepared as shown in **Scheme 2-2** by mixing benzaldehyde (7.33 mL, 71.91 mmol) and pyrrole (5 mL, 72.16 mmol) in a 100 mL round bottom flask, and propanoic acid (50 mL) was added into solution. After that, the solution was refluxed and stirred for 1 h, followed by aging for 1 h. The reaction was cooled down at room temperature for 24 h. Next, the solution was extracted with boiling DI water (200 mL) and ethanol (200 mL). Finally, the obtained product was dried in vacuum for 6 h to give 0.428 g H_2TPP (4% yield). Porphyrin was characterized by ^{1}H-NMR and UV-Vis spectroscopy.

2.3.3 Synthesis of cobalt(II) tetraphenylporphyrin (CoTPP)



Scheme 2-3 Synthesis of cobalt(II) tetraphenylporphyrin (CoTPP)

CoTPP was prepared as shown in **Scheme 2-3** by dissolving H_2TPP (49.56 mg, 0.08 mmol) in 20 mL CH_2Cl_2 and purging with N_2 for 30 min. In another flask, $Co(OAc)_2{\cdot}4H_2O$ (0.256 g, 1.03 mmol) was dissolved in 15 mL MeOH and stirred to give a pink solution. Then, the $Co(OAc)_2{\cdot}4H_2O$ solution was added into H_2TPP solution and stirred for 6 h under nitrogen atmosphere. The reaction was monitored by TLC (1:1 CH_2Cl_2: n-hexane + 5% triethylamine). After that, the solution was extracted with DI water 3 times. The organic layer was collected, dried over $MgSO_4$ and concentrated under vacuum to give 18.85 mg CoTPP (34% yield) CoTPP was characterized by UV-Vis spectroscopy.

2.3.4 Preparation of graphene oxide-porphyrin composite (GO-TPP), graphene oxide-cobalt(II) porphyrin composite (GO-CoTPP) and graphene oxide–cobalamin (GO-B12) composite

In the typical reaction, the separated vials, 4 mL H_2O was added to GO (11.91 mg) in the first vial. In the second vial, 2.5 mL DMF was added to H_2TPP (44 mg, 0.07 mmol) (18.85 mg, 0.03 mmol CoTPP or 44.08 mg, 0.03 mmol cobalamin). Two vials were separately sonicated for 1 h. Next, the GO dispersion was added into H_2TPP solution then the mixture was sonicated for 2 h in ice bath. Then, the solution was filtered by cotton wool and washed with milliQ water. The filtrate was centrifuged at 10,000 rpm for 50 min to remove the non-composite graphene oxide. Then, the supernatant was decanted and 10 mL milliQ water was added to the composite. The solution was sonicated for 2.5 h in ice bath and centrifuged at 4,000 rpm for 10 min (if there were still some precipitates left, the supernatant was decanted and washed with 10 mL milliQ water and centrifuged at 4,000 rpm for 10 min)

2.3.5 Photostability Examination

In the typical procedure, the photostability examination of CoTPP and GO-CoTPP were examined by UV-Vis spectroscopy upon light irradiation was applied for 0-24 h. Before the irradiation of light, CoTPP solution was prepared by adding 10 mL DMSO into CoTPP (5.37 mg, 8×10^{-3} mmol). Then the 15 µL CoTPP solution was pipetted into a cuvette with 1985 µL DMSO and monitored by UV-Vis spectroscopy. For GO-CoTPP solution, 40 µL GO-CoTPP was pipetted into 1960 µL DMSO and monitored by UV-Vis spectroscopy. After collecting data from the solutions without the irradiation, the stability test is the determination of dye content remaining in irradiated solutions. In the separated vials, 9 mL milliQ-water was added to 1 mL GO-CoTPP to extract CoTPP from GO-CoTPP with CH_2Cl_2 (33 mL) in the first vial. Then, the organic layer was collected and concentrated under vacuum. After that 10 mL DMSO was added to CoTPP and the UV-Vis absorption was measured to calculate the percentage of CoTPP in GO using standard curve. The second vial containing 2 mL GO-CoTPP was irradiated with LED light for overnight. After that, 1 mL GO-CoTPP was pipetted into 9 mL milliQ-water and extracted with CH_2Cl_2 (33 mL). Then, the organic layer was collected and concentrated under vacuum before measuring the UV-Vis absorption and calculating the concentration with standard curve.

2.3.6 Fluorescence study

To investigate interaction between GO and dyes, 0.25 mM stock solution of dye (H_2TPP and CoTPP) was prepared and fluorescence study was performed. In a typical procedure, a 0.25 mM solution of dye (H_2TPP and CoTPP) was prepared in DMSO. The suspension of GO (2 mg/mL) was prepared in water. From these stock solution, the mixtures of GO and dye were prepared in various concentrations as shown in **Table 2-1**. Fluorescence measurements of these mixtures were carried out in conditions shown below

Conditions for H_2TPP: Emission mode, Excited at 415 nm, Start at 425 nm, Scan rate medium, Photomultiplier manual 750 volts

Conditions for CoTPP: Emission mode, Excited at 415 nm, Start at 425 nm, Scan rate medium, Photomultiplier manual 800 volts

Table 2-1 Sample preparation for fluorescence study

Vials	Volume (μL) of H_2TPP or CoTPP	Volume (μL) of GO suspension	Volume (μL) of DMSO
1	5	6.25	1988.75
2	5	12.50	1982.50
3	5	18.75	1976.20
4	5	25.00	1970.00
5	5	31.25	1963.75
6	5	37.50	1957.50
7	5	43.75	1951.25
8	5	50.00	1945.00
9	5	62.50	1932.50
10	5	75.00	1920.00

2.3.7 Catalytic oxidation of benzyl alcohol under light irradiation

Product analysis by ^{1}H-NMR. The reactivity of GO-dye composites was examined via oxidation reaction of benzyl alcohol. The concentration of catalyst was prepared in 100% (%/w compared to 5 mg of benzyl alcohol) and milliQ-water was added to adjust volume into 2 mL. Then, the solution was added 5 μL (0.05 mmol) benzyl alcohol, and the solution was irradiated for 24 h. After that, the solution was filtered by syringe filters (0.45 and 0.22 μm) to remove GO-dye composites from solution and extracted with 600 μL $CDCl_3$. The organic layer was collected and monitored by NMR spectroscopy for product analysis.

Product analysis by GC. The catalyst (GO, GO-TPP, or GO-CoTPP) was prepared in 5 concentrations; 25%, 50%, 75%, 100% and 200% (%/w compared to 5 mg of benzyl alcohol), respectively. Then, 5 μL (0.05 mmol) of benzyl alcohol was added into each vial. After that, the solution was irradiated for 24 h. Then, the solution was filtered by syringe filters (0.45 and 0.22 μm) to remove GO from solution. Then, organic compounds in the filtrate were extracted by CH_2Cl_2 (2.0 mL). The products of benzyl alcohol oxidation were analyzed by GC-FID.

Chapter 3

Results and Discussion

In this work, GO-TPP, GO-CoTPP, and GO-B12 were prepared and investigated for photocatalytic activity. Because H_2TPP, CoTPP, and B12 contain π-π conjugated system in molecules, they could exhibit π-π interaction with GO. The characterization of these composites was done by UV-Vis spectroscopy. Moreover, photoinduced electron transfer was investigated by Fluorescence spectroscopy. Finally, the prepared composites were used as photocatalyst in alcohol oxidation reaction.

3.1 Synthesis and Characterization

3.1.1 Graphene oxide (GO)

Graphene oxide was synthesized following the reported procedure.[12] The product was obtained as black sheet product, and was characterized by UV-Vis spectroscopy and IR spectroscopy. From FTIR spectrum in **Figure 3-1**, the stretching and bending peaks of GO were found at 1000, 1150, 1650, 1750 and 3350 cm^{-1} corresponding to C–O, C–OH, C=C, C=O, and O–H, respectively. UV-Vis spectrum in **Figure 3-2** showed the absorption peak at 231 nm corresponding to π-π^* transition of aromatic C-C bonds. The FTIR and UV-Vis spectra confirmed our successful synthesis of GO and were in an agreement with the results obtained previously.[13]

GO UV-Vis: λ_{max} = 231 nm

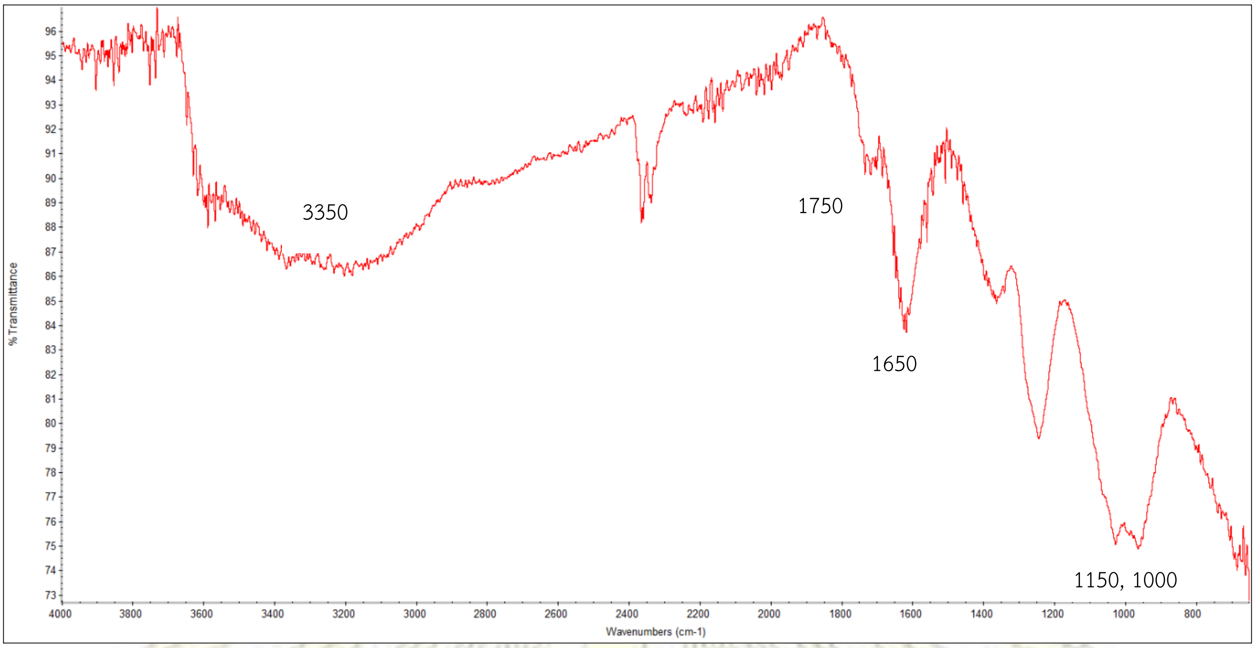


Figure 3-1 FTIR spectrum of GO

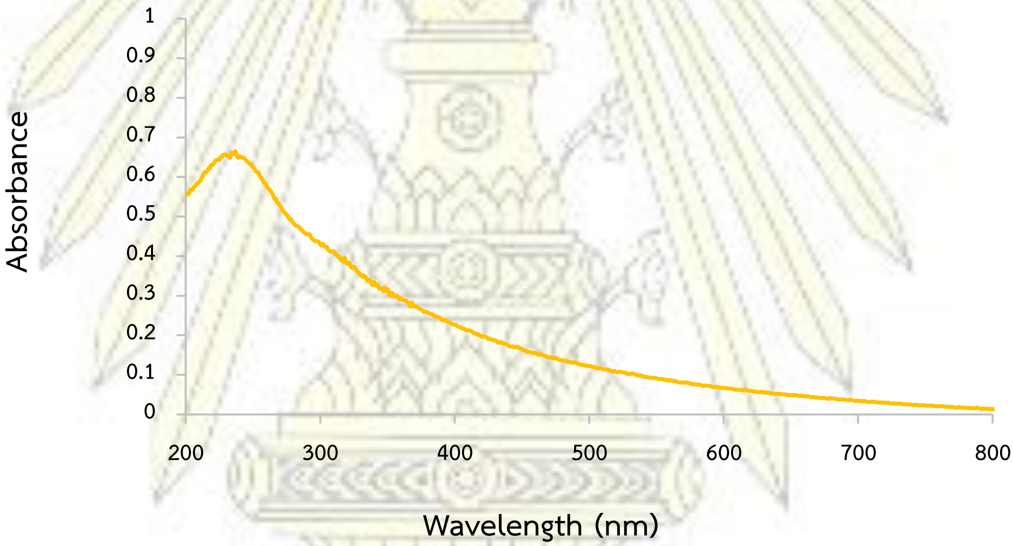


Figure 3-2 UV-Vis spectrum of GO

3.1.2 Tetraphenylporphyrin (H_2TPP)

Tetraphenylporphyrin was synthesized following the reported procedure.[14] The product was obtained as blue solid with 4% yield and characterized using UV-Vis and NMR spectroscopy. The yellow spectrum in **Figure 3-3** showed two main absorption peaks at 417 nm and 520 nm corresponding to Soret band and Q band, respectively which are the characteristic features of H_2TPP.[15] ^{1}H-NMR spectrum of H_2TPP showed at δ 8.84 (s, 8H), 8.22 (d, 8H), 7.76 (t, 8H), 7.76 (t, 4H) was consistent with previous work.[16]

H_2TPP UV-Vis: λ_{max} = 417 nm and 520 nm

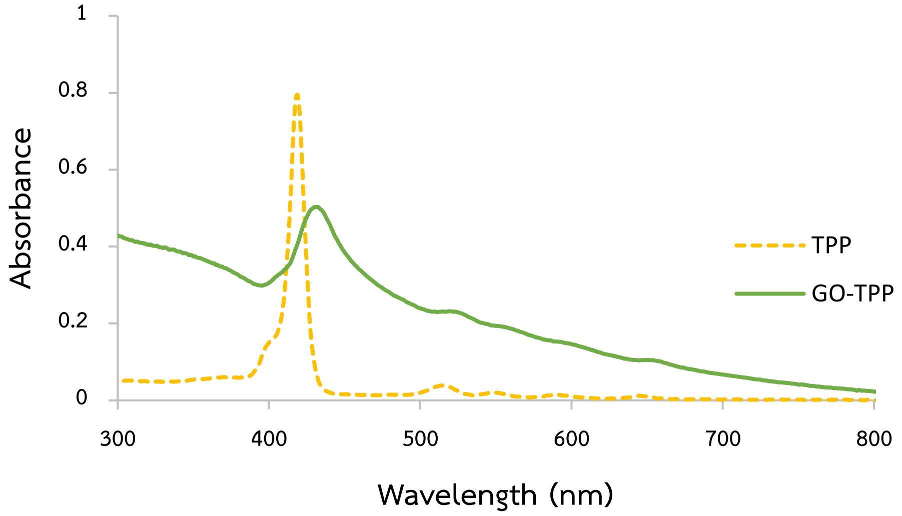
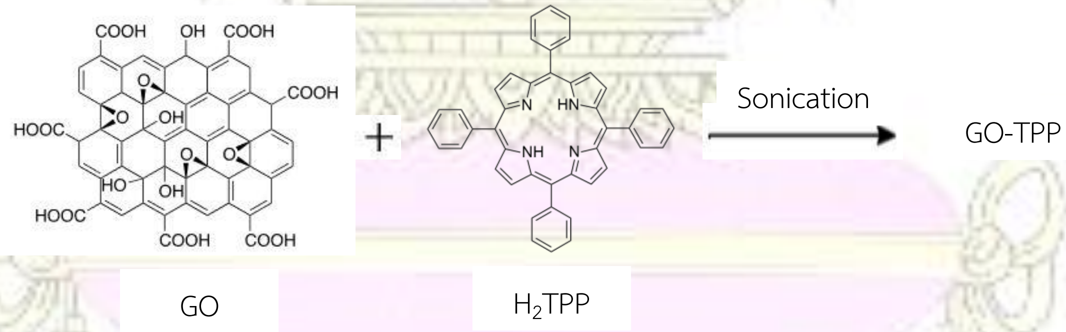


Figure 3-3 UV-Vis spectra of H_2TPP and GO-TPP

3.1.3 Graphene oxide–tetraphenylporphyrin (GO-TPP)



Scheme 3-1 Preparation of graphene oxide-tetraphenylporphyrin (GO-TPP)

Graphene oxide – porphyrin composite was prepared by sonication method. The product was characterized by UV-Vis spectroscopy. The percentage of loaded TPP in GO-TPP was around 80% compared with the starting dye amount. The spectrum of GO-TPP in **Figure 3-3** showed absorption peak at 436 nm and 527 nm while the spectrum of H_2TPP showed absorption peak at 417 and 520 nm. The spectrum of GO-TPP was broaden and red-shifted compared to that of H_2TPP. The broadening of spectrum indicated the formation of composites between GO and H_2TPP. The observed red-shift from the spectrum suggested the strong π-π interaction between GO and H_2TPP leading to delocalization of electrons from GO to H_2TPP.[11] This data confirmed our successful preparation of GO-TPP.

GO-TPP UV-Vis: λ_{max} = 436 nm, 527 nm

3.1.4 Cobalt(II) porphyrin (CoTPP)

Cobalt(II) porphyrin was synthesized following the reported procedure.[17] The product was obtained as red-purple solid with 34% yield, and characterized using UV-Vis spectroscopy. The green spectrum in **Figure 3-4** showed two main absorption peaks at 416 nm and 526 nm corresponding to Q-band and Soret band respectively which are the characteristic features of CoTPP.[17]

UV-Vis: λ_{max} = 416 nm, 526 nm

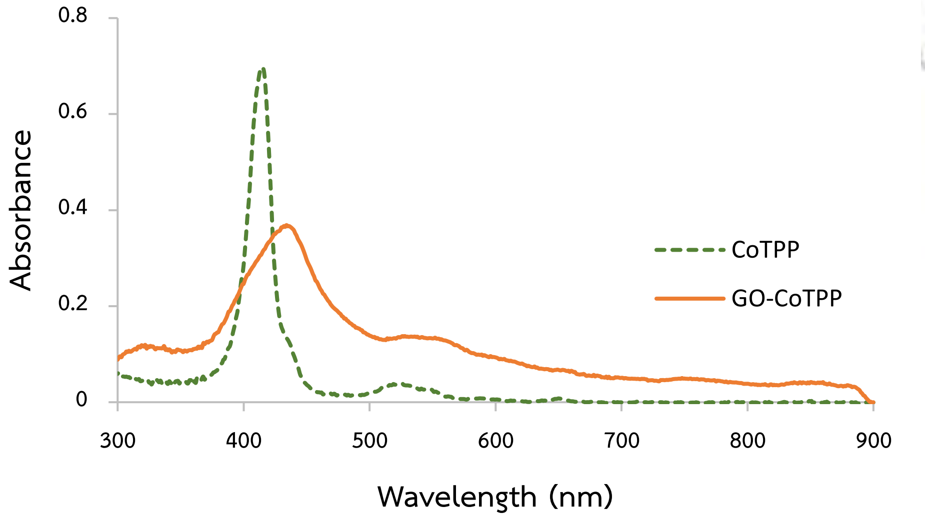
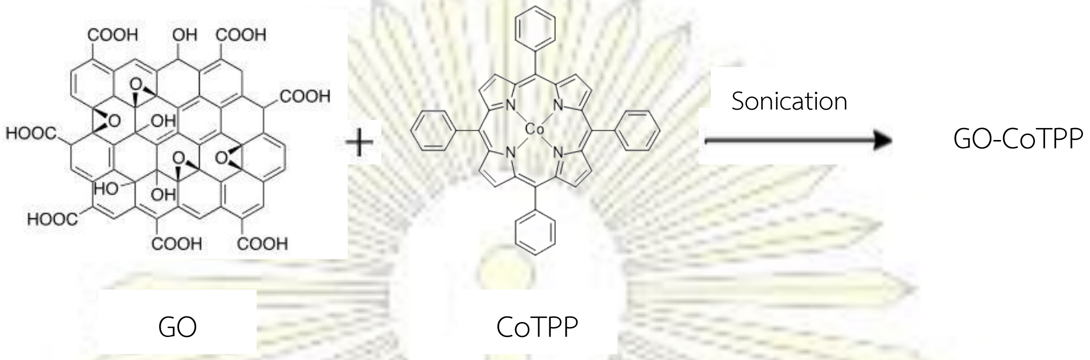


Figure 3-4 UV-Vis spectra of CoTPP and GO-CoTPP

3.1.5 Graphene oxide - cobalt(II) tetraphenylporphyrin (GO-CoTPP)



Scheme 3-2 Preparation of graphene oxide-cobalt (II) tetraphenylporphyrin (GO-CoTPP)

Graphene oxide – cobalt(II) porphyrin composite was prepared by sonication method. The product was characterized by UV-Vis spectroscopy. The amount of dye in composite is determined by 1 mL of GO-CoTPP in 9 mL of Milli-Q water extracted by CH_2Cl_2 (3 times/100 mL) and concentrated under vacuum. After that, CoTPP from extraction was dissolved in 10 mL DMSO. Then the 10 μL of solution was pipetted into 1990 μL of DMSO and measured by UV-Vis spectroscopy to calculate the concentration of CoTPP in GO-CoTPP composite by calibration curve. The % of loaded CoTPP in GO-CoTPP was around 28% compared with the starting dye amount. The UV-Vis spectrum of GO-CoTPP in **Figure 3-4** showed two main absorption peaks at 434 nm and 527 nm. The comparison between GO-CoTPP and CoTPP spectrum showed that the spectrum of GO-CoTPP was red-shifted and broaden. This data suggested the successful preparation of GO-CoTPP composite through π-π interaction.

GO-CoTPP UV-Vis: λ_{max} = 434 nm, 527 nm

3.1.6 Graphene oxide - cobalamin (GO-B12)

Graphene oxide – cobalamin composite was prepared by sonication method. The product was characterized by UV-Vis spectroscopy. The composite of GO and B12 could not be generated because B12 can dissolve in water. In preparation of composite, the composite was washed by milliQ water to remove the excess dye. At this step, most of B12 in composite was dissolved into the filtrate. Therefore, a few amounts of B12 was remained in the prepared composite. In addition, from the spectrum as shown in **Figure 3-5**, there was only little amount of B12 in the composite, and no shifting was observed. From these results, it can be concluded that GO-B12 composite could not be prepared by this method due to solubility of B12 in water.

GO-B12 UV-Vis: λ_{max} = 362 nm

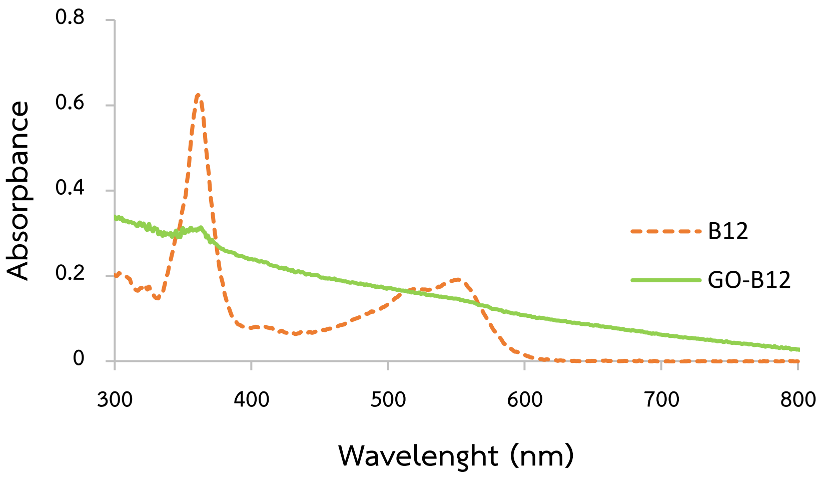


Figure 3-5 UV-Vis spectra of B12 and GO-B12

From the above results, it was demonstrated that H_2TPP and CoTPP were composited with GO while B12 could not. This is because of H_2TPP and CoTPP are hydrophobic dyes which could be composited with GO in water. Meanwhile, B12 is a hydrophilic dye which could be washed by water during the preparation. In this study we would like to perform photocatalytic reactivity in water. Therefore, GO-TPP and GO-CoTPP were chosen for studies in the next steps.

3.2 Stability test

Normally, the graphene oxide is the exfoliated graphite oxide. Its stability depends on the distance of each sheet of graphene oxide. If sheets get closer to each other, the loss of oxygen-containing functional group would be thermodynamically occurred. After a few weeks, the disperse ability would be lost because there is no oxygen-containing functional group left. After the preparation of the composites (GO-TPP, GO-CoTPP), it was shown that H_2TPP and CoTPP could enhance the light absorption range of GO. Unfortunately, it was precedented that porphyrin derivatives dyes can generate singlet oxygen which is a nonselective oxidant. The excited electrons of dye can transfer to the triplet state which consequently transfer their energy to triplet oxygen leading to the formation of singlet oxygen and dye decomposition. In our assumption, graphene oxide is a great UV block agent and a good quencher. If the excited electron from dyes was transferred to graphene oxide, the generation of singlet oxygen would be inhibited providing the stability of dye.

3.2.1 Stability test of H_2TPP compared with GO-TPP

The UV-Vis spectra of H_2TPP in **Figure 3-6** showed two main absorption peaks at 417 and 520 nm. Upon irradiation of H_2TPP up to 24 h, the absorbance at peaks 417 and 520 nm were constantly decreased. This was presumably due to generation of singlet-oxygen molecules. Singlet-oxygen molecules were generated from triplet-oxygen molecules[18] in **Figure 3-9**. First the electron in ground state of H_2TPP was excited into excite state. After a few nanoseconds, the porphyrin undergoes an intersystem crossing to a triplet state. From the triplet state, the energy is transferred to oxygen molecules by switching them from a triplet ground state into an excited singlet state.[18] Once the singlet-oxygen molecules were generated they would react with H_2TPP resulting in decomposition of dye. Therefore, concentration of H_2TPP was decreased and related to their absorbance. On the other hand, the UV-Vis spectra of GO-TPP showed absorption peak at 436 nm in **Figure 3-7**. When this composite was irradiated up to 9 h, the absorbance of two peaks was only slightly changed. This is because GO served as an electron acceptor instead of triplet-oxygen molecules, resulting in inhibition of singlet-oxygen generation. In conclusion, the composite between GO and H_2TPP provides the dye stability. From this reason, the UV-Vis spectra of extracted TPP in GO-TPP before and after irradiation as shown in **Figure 3-8** was slightly dropped.

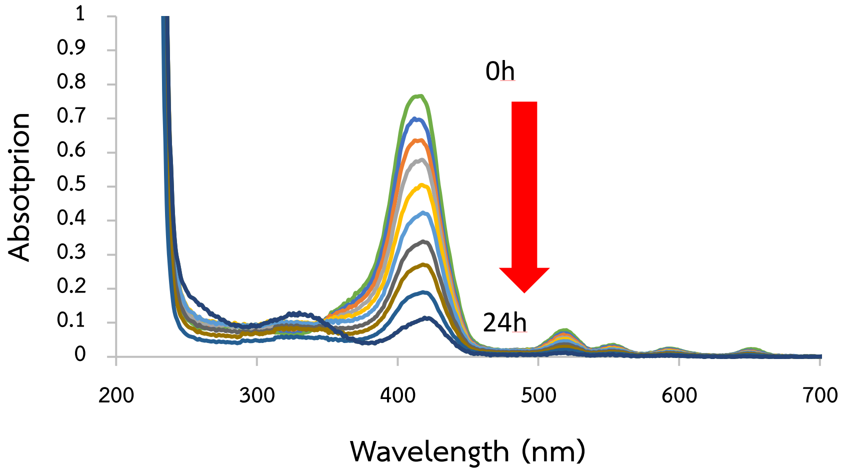


Figure 3-6 Photodecomposition of H_2TPP in DMSO/H_2O under light irradiation

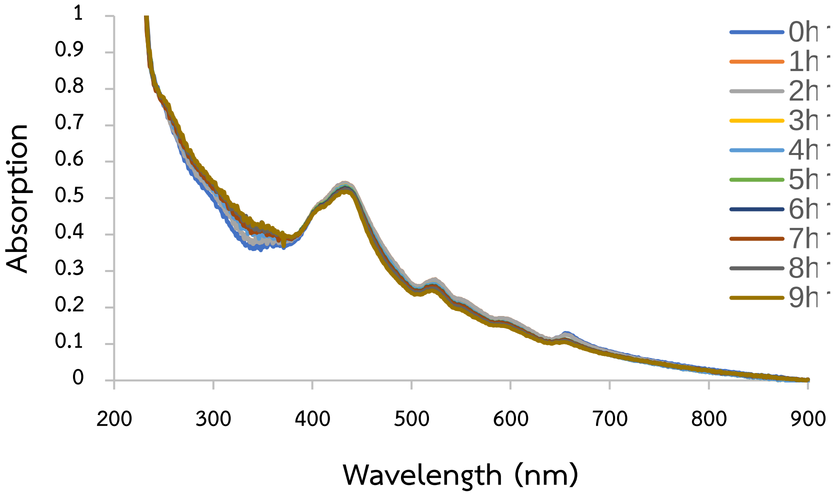


Figure 3-7 Photodecomposition of GO-TPP in water under light irradiation

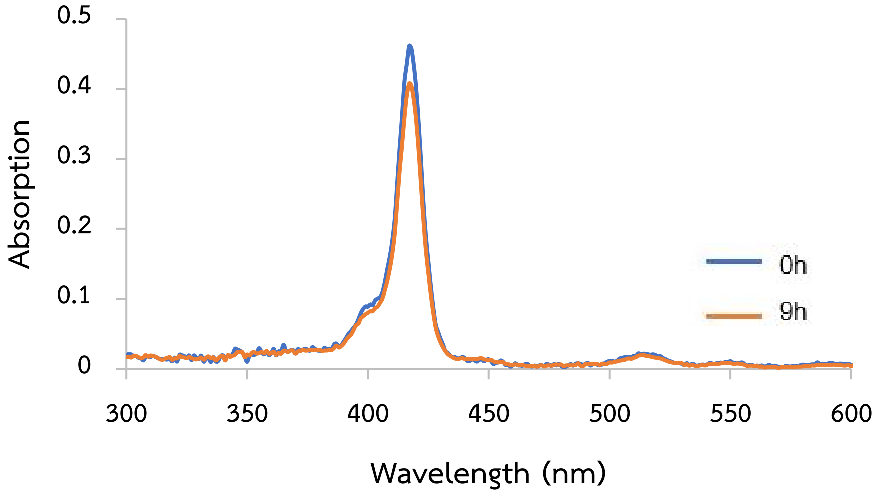


Figure 3-8 Absorption of extracted TPP in GO-TPP before and after irradiation

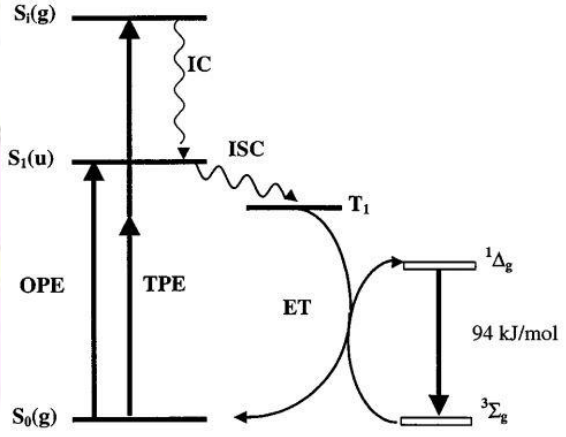


Figure 3-9 Diagram showing the generation of singlet oxygen[18]

3.2.2 Stability test of CoTPP compared with GO-CoTPP

The UV-Vis spectra of CoTPP in **Figure 3-10** showed two main absorption peaks at 416 and 526 nm. Upon irradiation of CoTPP up to 24 h, the Soret band at 416 nm decreaswd while a new peak at 433 nm was observed due to decomposition of CoTPP. This was because singlet-oxygen molecules were generated which then decomposed CoTPP. Therefore, concentration of CoTPP was decreased and it related to their absorbance. Moreover, the UV-Vis spectra of GO-CoTPP in **Figure 3-11** showed absorption peak at 426 nm. Upon irradiation of GO-CoTPP up to 9 h, the absorbance at 426 nm was only slightly changed. This is because GO still served as an electron acceptor, similar to the result observed for GO-TPP. As a result, the UV-Vis spectra of extracted CoTPP in GO-CoTPP before and after irradiation with light in **Figure 3-12** was only slightly dropped when compared with those of CoTPP.

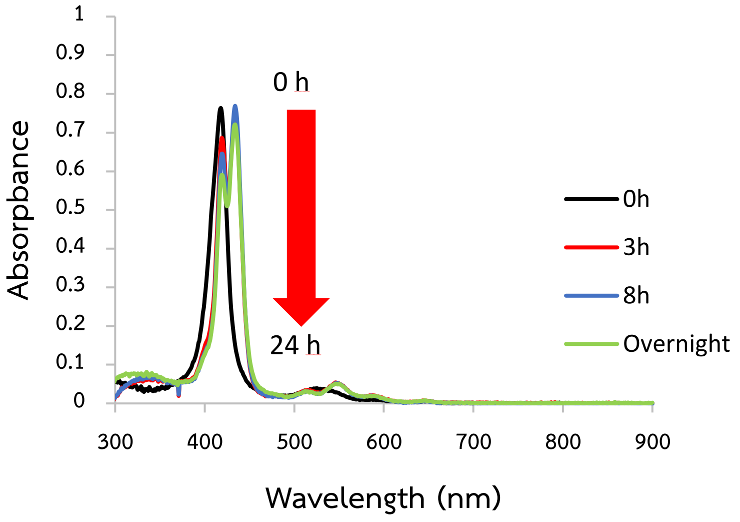


Figure 3-10 Photodecomposition of CoTPP in DMSO

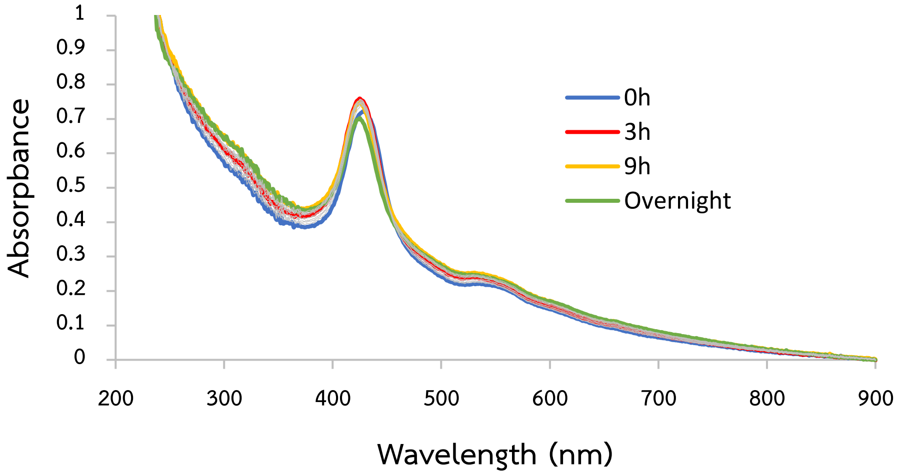


Figure 3-11 Photodecomposition of GO-CoTPP in water

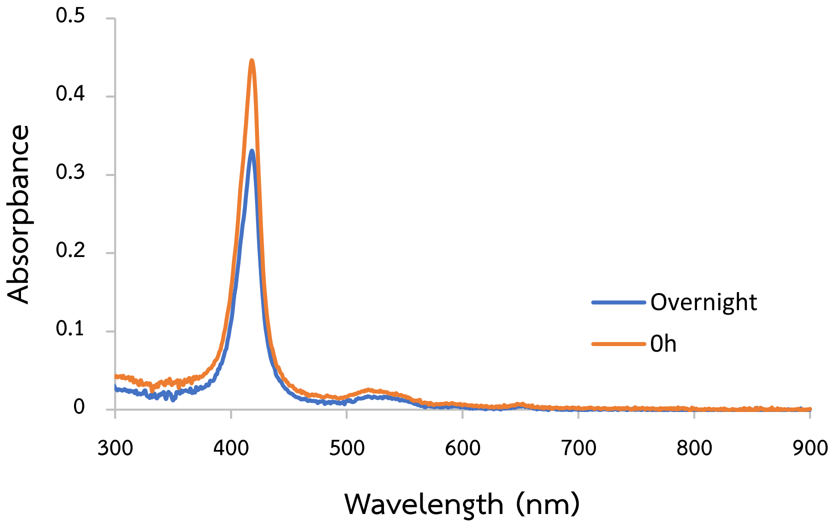


Figure 3-12 Absorption of extracted TPP in GO-CoTPP before and after irradiation

3.3 Fluorescence study

From the result of stability test, it was proposed that H_2TPP and CoTPP were decomposed by singlet-oxygen. Therefore, we used GO to interrupt the generation of singlet-oxygen. GO serves as an electron acceptor instead of triplet-oxygen. Herein, the fluorescence study was performed to investigate the interaction between GO and dyes.

The fluorescence spectra dyes upon addition of excess GO were shown in the appendix. The excitations of H_2TPP, CoTPP, GO-TPP and GO-CoTPP were located at 415 nm. From this result, it showed that fluorescence signals from H_2TPP and CoTPP were completely quenched in the presence of GO, implying that GO acts as a fluorescence quencher.

The fluorescence titration spectra of H_2TPP and CoTPP were shown in **Figure 3-13** and **Figure 3-14**. The fluorescence intensity of H_2TPP and CoTPP were decreased upon addition of GO. Fluorescence quenching is the quenching of electron singlet excited state, through non-radioactive transition back to the ground state by either energy transfer or electron transfer. For this study, the excited electron from H_2TPP and CoTPP transfered to GO, resulting in a decrease in fluorescence intensity. Percent fluorescence quenching of H_2TPP and CoTPP are 80 and 64 respectively. These results suggested that the fluorescence of H_2TPP could be quenched by GO more efficiently than that of CoTPP.

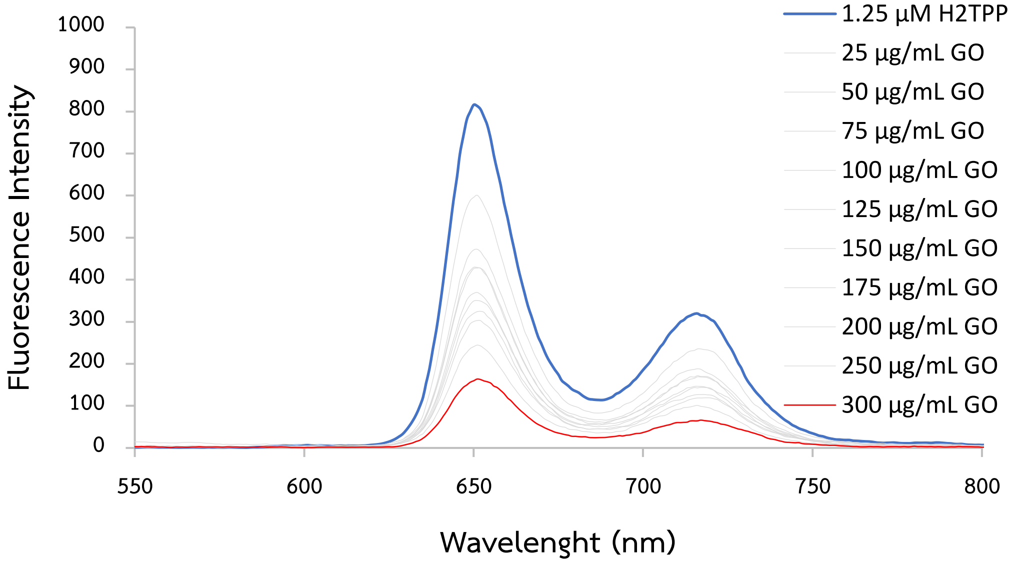


Figure 3-13 Fluorescence titration of H_2TPP by GO

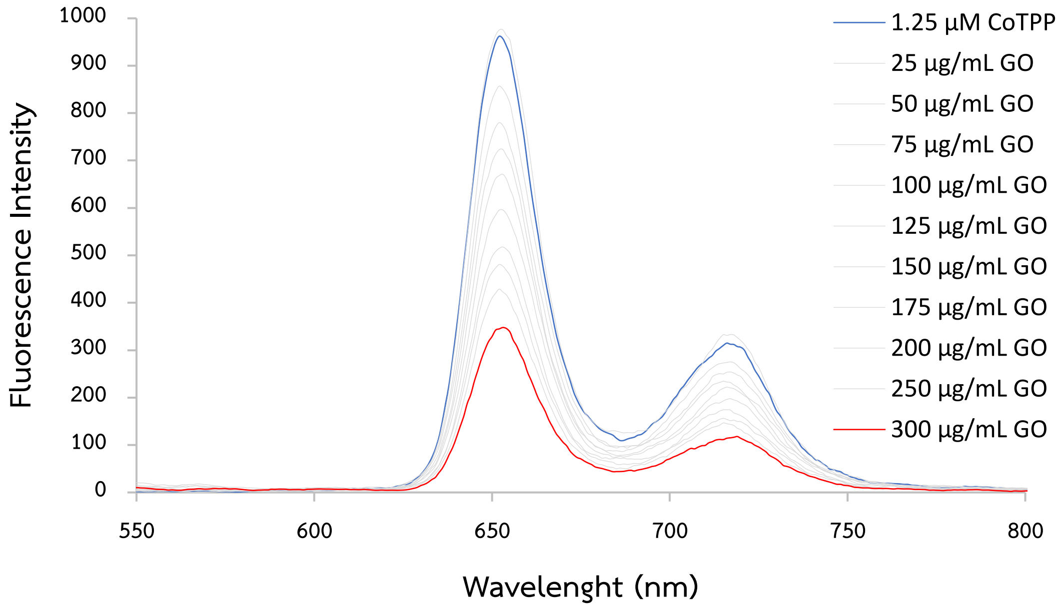
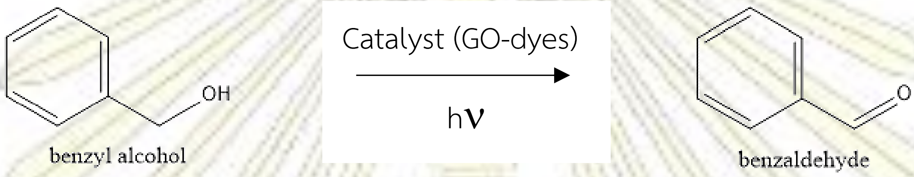


Figure 3-14 Fluorescence titration of CoTPP by GO

3.4 Reactivity studies

The oxidation of organic substrate was commonly used transition-metal-based as catalyst. Transition metal-based catalysts also had disadvantage such as expensive, difficult to remove, toxic and limited. In recent years, graphene oxide had been used as a catalyst because graphene oxide is a readily available and inexpensive materials. In this study, we would like to use catalyst based on graphene oxide.

For this study, the reactivity of GO, GO-TPP and GO-CoTPP were examined *via* oxidation reaction of benzyl alcohol. The product was found to be benzaldehyde as shown in **Scheme 3-3**.



Scheme 3-3 Oxidation of benzyl alcohol by GO and GO-dyes as catalyst

From ^{1}H-NMR spectra of GO, CoTPP and GO-CoTPP, only those from GO and GO-CoTPP showed chemical shift at 10 ppm corresponding to aldehyde group of the benzaldehyde product. This indicated that GO and GO-CoTPP could oxidize benzyl alcohol into benzaldehyde. However, pristine GO and CoTPP could not exhibit the good reactivities as compared to that of the prepared composite. This suggested that GO and CoTPP exhibited cooperative reactivity. It was proposed that the oxidation of benzyl alcohol occurred *via* epoxy groups on GO[20], while dye enhanced the visible light absorption.

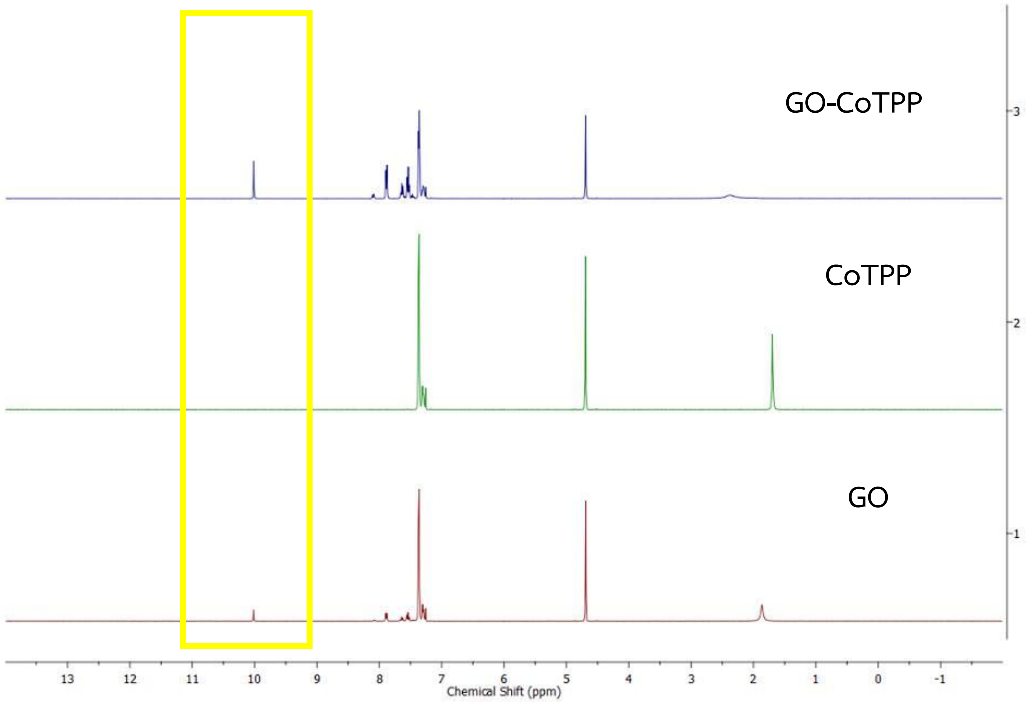


Figure 3-15 ^{1}H-NMR of crude product from benzyl alcohol oxidation using GO-CoTPP, CoTPP and GO as catalysts, respectively

In addition, the optimization of GO, GO-TPP and GO-CoTPP was also performed by varying the composite into 5 concentrations in separated vials (%/w compared to 5 mg of benzyl alcohol), 25%, 50%, 75%, 100% and 200%. Every vial was irradiated with LED light and detected the products by GC-FID twice. %yield of benzaldehyde was shown in **Figure 3-16**. In the previous work, they proposed that the oxidation of benzyl alcohol was occurred *via* epoxy group on GO[20] as shown in **Figure 3-17**. From the result, the %yield of benzaldehyde was raised when the concentration of dye in composite was increased and become constant at 100%/w. Because dyes can efficiently increase the light absorption range in composite. Moreover, GO-TPP got the highest %yield of benzaldehyde compared to GO-CoTPP because CoTPP might interact with epoxy group in graphene oxide, blocking the active site for catalysis. Therefore, it caused the lower %yield of benzaldehyde than that catalyzed by GO-TPP.

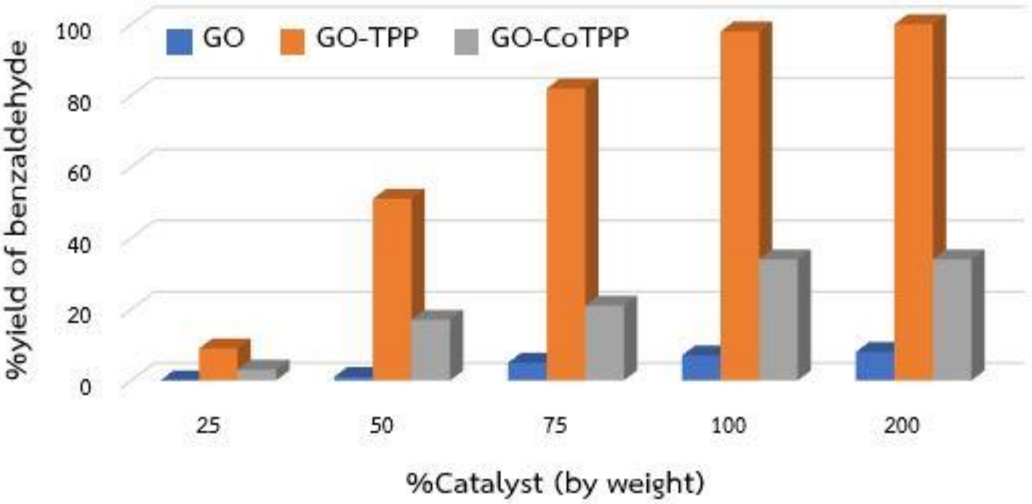
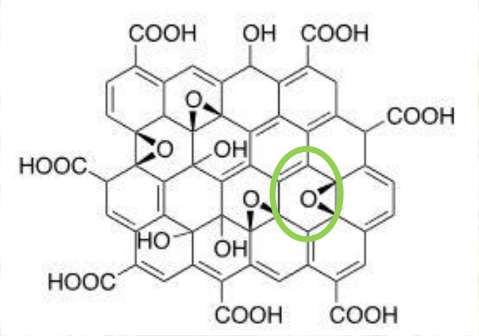


Figure 3-16 Production of benzaldehyde from oxidation of benzyl alcohol catalyzed by GO, GO-TPP and GO-CoTPP under light irradiation



GO

Figure 3-17 Epoxy group on GO as a proposed active site for oxidation of benzyl alcohol

Chapter 4

Conclusion

In summary, GO, H_2TPP, CoTPP, GO-TPP, Go-CoTPP, GO-cobalamin were prepared and characterized by various techniques. H_2TPP and CoTPP were obtained in 4 % and 34 % yield, respectively. H_2TPP and CoTPP were successfully composited with GO while B12 could not. This is because H_2TPP and CoTPP are hydrophobic dyes which could be composited with GO in water. Meanwhile, B12 is a hydrophilic dye which could be washed by water during preparation. The UV-Vis spectra of GO-TPP and GO-CoTPP showed a red shift because of a strong π-π interaction between GO and dyes. The photostability of GO-TPP and GO-CoTPP were studied by UV-Vis, showing that dyes in the composite were more stable than the original dyes under light irradiation. The interaction of GO and dyes were observed by fluorescence spectroscopy. The fluorescence intensity of H_2TPP and CoTPP were quenched upon addition of GO, confirming the interaction between GO and dyes. The composites GO-TPP and GO-CoTPP were then investigated for photocatalytic activity with oxidation of benzyl alcohol. The result showed that GO-dyes gave the higher %yield of product than GO. This is because dyes can efficiently increase the light absorption in visible region and lead to more surface sensitization of GO. The %yield from photocatalytic studies of GO, GO-TPP and GO-CoTPP were 8, 100 and 34 % respectively.

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APPENDIX

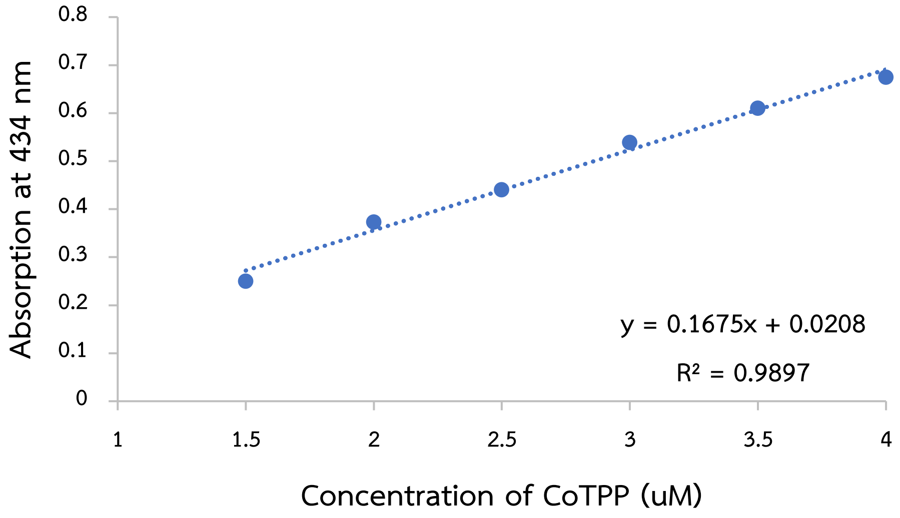

Figure A-1 Standard curve of CoTPP in DMSO

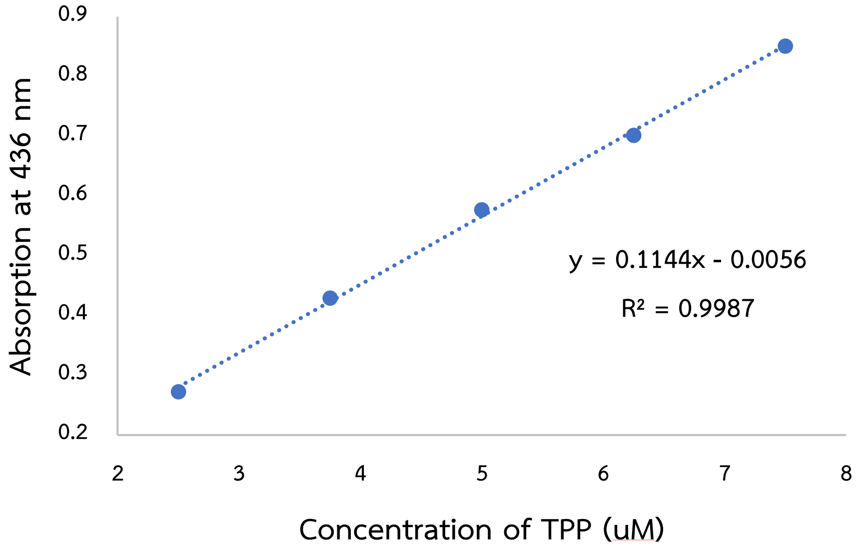

Figure A-2 Standard curve of H_2TPP in DMSO/DI

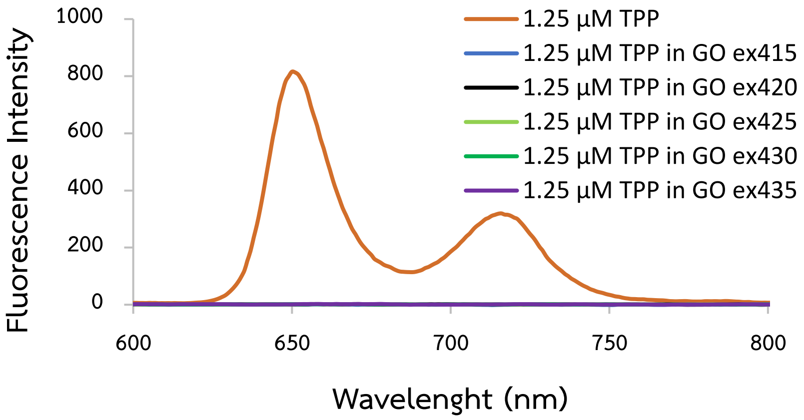

Figure A-3 Fluorescence intensity of H_2TPP and GO-TPP

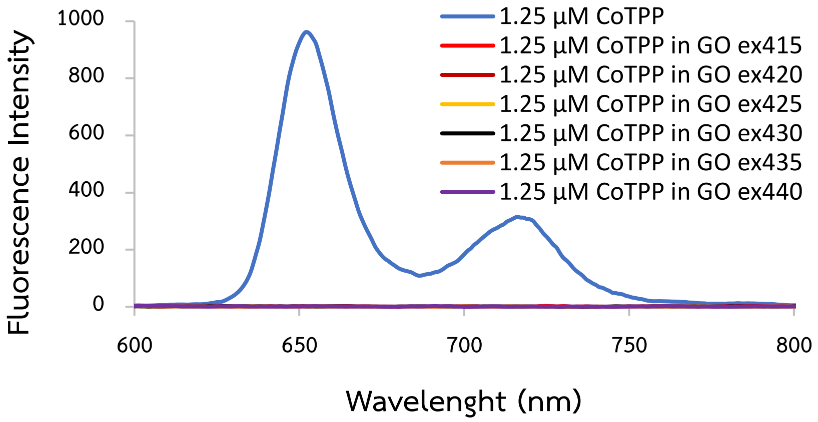

Figure A-4 Fluorescence intensity of CoTPP and GO-CoTPP

VITAE

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