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ชื่อโครงการ การสังเคราะห์อนุภาคควอนตัมดอท CdS-Fe₃O₄ ที่มีสมบัติแม่เหล็กเพื่อใช้เร่งปฏิกิริยาอินทรีย์
Synthesis of CdS-Fe₃O₄ magnetic nanoparticle for organic catalysis

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โดย
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รายงานนี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตร
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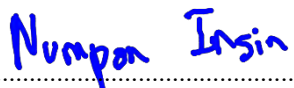
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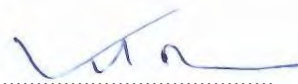
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ชื่อโครงการ การสังเคราะห์อนุภาคควอนตัมดอท CdS-Fe₃O₄ ที่มีสมบัติแม่เหล็กเพื่อใช้เร่งปฏิกิริยาอินทรีย์

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บทคัดย่อ

งานวิจัยนี้มุ่งไปที่การพัฒนาอนุภาคแคดเมียมซัลไฟด์ควอนตัมดอท (CdS QDs) ที่มีสมบัติแม่เหล็กแบบซูเปอร์พาราแมกเนติกเพื่อใช้เป็นตัวเร่งปฏิกิริยารีดอกซ์เชิงแสงในปฏิกิริยาสังเคราะห์เอไมด์ผ่านไทโอเอซิดและคันทาโรลในการสังเคราะห์อนุภาคแคดเมียมซัลไฟด์ควอนตัมดอทที่มีสมบัติแม่เหล็กที่มีสมบัติในการเป็นตัวเร่งปฏิกิริยา อนุภาคแคดเมียมซัลไฟด์ควอนตัมดอทถูกสังเคราะห์โดยวิธีไฮโดรเทอร์มัลและอนุภาคแคดเมียมซัลไฟด์ที่มีสมบัติแม่เหล็กหลากหลายรูปแบบได้ถูกทดลองสังเคราะห์ขึ้นเช่นกัน อย่างไรก็ตามมีอนุภาคควอนตัมดอทแม่เหล็กเพียงสองชนิดที่ได้รับการตรวจสอบเอกลักษณ์และทดสอบในการเป็นตัวเร่งปฏิกิริยา อนุภาคแม่เหล็กทั้งสองได้แก่แคดเมียมซัลไฟด์บนผิวอนุภาคแมกนีไทต์ (CdS-Fe₃O₄) และแคดเมียมซัลไฟด์บนพื้นผิวซิลิกาที่หุ้มอนุภาคแมกนีไทต์ (CdS-SiO₂/Fe₃O₄) อนุภาคทั้งสองชนิดถูกสังเคราะห์โดยการฝังตัวของแคดเมียมซัลไฟด์บนผิวของอนุภาคแม่เหล็กผ่านกระบวนการไฮโดรเทอร์มอล ผลจากกล้องจุลทรรศน์แบบส่องผ่านแสดงให้เห็นว่า CdS-Fe₃O₄ มีโครงสร้างแบบโครงข่ายนาโนแทนที่จะเป็นการสร้างชั้นแคดเมียมซัลไฟด์หุ้มรอบแกนอนุภาคตามที่คาดไว้เบื้องต้น เทคนิคการดูดซับแสงยูวีและเทคนิคการแปลงแสงฟลูออเรสเซนซ์ถูกใช้เพื่อทดสอบสมบัติเชิงแสงของอนุภาคและพบว่า CdS-Fe₃O₄ มีการแปลงแสงฟลูออเรสเซนซ์ที่ต่ำมากในขณะที่ CdS-SiO₂/Fe₃O₄ มีการแปลงแสงเทียบเท่า CdS ปกติ โดยอนุภาคทั้งหมดได้รับแสงกระตุ้นที่ความยาวคลื่น 440 นาโนเมตร สูดทำยอนุภาคทั้งหมดได้ถูกทดสอบในการเป็นตัวเร่งปฏิกิริยาเชิงแสงในปฏิกิริยาระหว่างโพแทสเซียมไทโอซิติเตตและพาราแอนนิซิติน เนื่องจากข้อผิดพลาดของปริมาณตัวเร่งปฏิกิริยาทำให้ไม่สามารถระบุและเปรียบเทียบประสิทธิภาพที่แท้จริงของ CdS-Fe₃O₄ ได้ อย่างไรก็ตามเมื่อเปรียบเทียบระหว่าง CdS และ CdS-SiO₂/Fe₃O₄ แล้วพบว่าทั้งสองให้ปริมาณผลิตภัณฑ์ 24% และ 70% ตามลำดับ โดยปริมาณตัวเร่งที่ใช้ในปฏิกิริยาเท่ากันที่ร้อยละ 0.07 โดยน้ำหนัก ผลการทดลองดังกล่าวหากได้รับการทดลองเพิ่มเติมเพื่อยืนยันจะเป็นแนวทางในการสังเคราะห์อนุภาคแคดเมียมซัลไฟด์ควอนตัมดอทที่มีสมบัติแม่เหล็กเพื่อใช้เร่งปฏิกิริยาต่อไป

คำสำคัญ: ควอนตัมดอท, สมบัติแม่เหล็ก, ตัวเร่งปฏิกิริยาเชิงแสง

Project Title Synthesis of CdS-Fe₃O₄ magnetic nanoparticle for organic catalysis

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Abstract

This research focuses on developing CdS quantum dots (CdS QDs) with superparamagnetic property to be used as a heterogeneous photocatalyst in thioacid-mediated amide formation and exploring the most suitable means to synthesize CdS magnetic quantum dots (CdS MQDs) with high photocatalytic activity. CdS QDs were synthesized using hydrothermal method and various CdS MQDs were obtained, but only two types of CdS MQDs were well characterized and tested, namely CdS-Fe₃O₄ MQDs and CdS-SiO₂/Fe₃O₄ MQDs. These two types of MQDs were synthesized by growing CdS QDs on the surface of the preformed magnetic nanoparticles using hydrothermal method. TEM was used to study the morphology of CdS QDs and CdS-Fe₃O₄ MQDs, and the results showed that CdS-Fe₃O₄ MQDs formed a nanonetwork structure instead of the expected core-shell structures. UV/vis spectroscopy and fluorescence spectroscopy were used to study their optical properties. CdS-Fe₃O₄ MQDs showed low fluorescence intensity when excited with 440 nm light; on the other hand, CdS-SiO₂/Fe₃O₄ MQDs still retain high fluorescence, almost identical to bare CdS QDs. When used as a photocatalyst in the reaction between Potassium thioacetate and *p*-anisidine, CdS-Fe₃O₄ and CdS QDs cannot be compared together due to the difference in catalyst amount. However, CdS-SiO₂/Fe₃O₄ MQDs gave higher quantity of product compared to the bare CdS QDs, 70% and 24% respectively, when present in the reaction in low quantity (0.07 wt%). The results showed that with some more experiments, these methods could be used to synthesize CdS magnetic quantum dots with photocatalytic property.

Keywords: quantum dots, magnetic property, photocatalyst

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ABBREVIATION

APTES	(3-aminopropyl)triethoxysilane
CdCl ₂	cadmium chloride
CdS	cadmium sulfide
CdTe	cadmium telluride
CH ₃ COOH	acetic acid
Fe ₃ O ₄	magnetite
FeCl ₂	ferrous chloride
FeCl ₃	ferric chloride
P25	Photocatalytic grade titanium dioxide nanoparticle
MNPs	magnetic nanoparticles
MPS	(3-mercaptopropyl)trimethoxysilane
MQDs	magnetic quantum dots
N ₂	nitrogen
Na ₂ S	sodium sulfide
NaBH ₄	sodium borohydride
NaOH	sodium hydroxide
NH ₃	ammonia
QDs	quantum dots
SiO ₂	silica
TEM	transmission electron microscope
TEOS	tetraethyl orthosilic
TGA	thioglycolic acid
UV	ultraviolet
vis	visible
wt%	percent by weight

Chapter 1

Introduction

1.1 Problems and significance

Synthesis of organic substances could be a complex and detailed job for all chemists. An organic reaction could need days under high temperature, high pressure, and exact pH to yield a few percentages of product. One way to reduce these complexities is using catalyst to shorten the time and make the reaction complete more swiftly. Photocatalyst is a type of catalyst that converts the energy from incident light to chemical energy, controlled by intensity and energy of the light itself. Normally, organic dyes and transition metal complexes are utilized as photocatalysts and generally exhibiting high catalysis activity. However, they suffer from being homogenous catalyst and cannot be separated and recycled by mechanical means.¹⁻⁴

Heterogeneous catalyst such as quantum dots (QDs) are emerging as a new solution for photocatalytic reaction. S. Das *et al.* found that cadmium sulfide quantum dots (CdS QDs) can be used as photocatalysts in the reaction between amine and thioacid to form amide at room temperature and neutral condition.⁵ The reaction between 2 mmol of both thiobenzoic and aniline with 10 mg CdS QDs under visible light could yield 98% product after 5 hrs. While using P25 as a photocatalyst under the same conditions only yielded a trace amount of product

The CdS QDs used in the photocatalytic reaction proved to be an excellent photocatalyst. However, the particle cannot be separated from the reaction mixture via simple mechanical methods, thus making it unpractical in industrial scale. The composites between CdS QDs and magnetic nanoparticle (MNPs) such as Fe₃O₄ called CdS magnetic quantum dots (MQDs) could possibly provide the ability for the particles to be removed from the mixture when put in a magnetic field.

P. Sun *et al.* successfully synthesized CdTe MQDs by forming of disulfide bond between TGA-capped CdTe QDs and SH-SiO₂/Fe₃O₄ nanoparticles.⁶ The composite preserved the

photoluminescence properties of CdTe QDs and showed superparamagnetic behavior. With some modification, the method is worth trying and could prove successful in synthesis of CdS MQDs as well. However, photocatalyst with disulfide bond may not be suitable for thioacid mediated amide synthesis, which, according to S. Das, the reaction mechanism includes the formation and bond breaking of disulfide bond. The disulfide bond on the surface of catalyst composite may involve in the reaction, by reacting with reagents and converting them into other by-products. Also, the component that linked together with disulfide bonds, in our case the QDs and Fe₃O₄ MNPs, will be separated apart when the bond is broken, leading to the loss of superparamagnetic character from the photocatalyst. Therefore, the other form of CdS MQDs composite should also be studied.

Gao JH *et al.* suggested that CdS (or CdSe) QDs could be grown directly on the surface of MNPs and form magnetic particle with fluorescence property.⁷ Their work showed how 2 types of CdS/FePt can be synthesized by controlling the order between sulfur and cadmium precursors. The resulted composite showed excellent fluorescence and magnetic property. Moreover, the composite synthesized by Salgueiriño-Maceira *et al.* using growth of CdTe on the surface of SiO₂/Fe₃O₄ MNPs also showed good fluorescence property, almost the same as bare CdTe QDs.⁸ These two kinds of composites could be used as the model to synthesize disulfide-free CdS MQDs.

In this work, we focus on the synthesis of CdS MQDs using various method and study the photoluminescence properties of the composites as well as determine the ability of the composite as photocatalyst in the thioacid mediated amide bond synthesis reaction. Moreover, we hope to find the most suitable CdS MQDs to be adopted as a useful photocatalyst.

1.2 Purposes

1. To synthesize CdS MQDs that could be dispersed well in water
2. To study photocatalytic activity of the synthesized CdS MQDs

1.3 Theories and literatures

Quantum dots

Quantum dots (QDs) are semiconductive nanoscale particles that exhibit unique optical and electrical properties compared to their respective bulk materials. Due to quantum effects, electrons and holes in the particle can co-exist and recombine together at specific amount of energy.⁹ This energy often shown in the form of light; thus, the wavelength of this light can be adjusted by controlling their size and composition.¹⁰ In solid state chemistry, this phenomenon is explained with the band gap model. Normally, electrons in semiconductor will occupy the valence band. When these electrons are excited by light, heat, or other form of energy, they will move to conduction band and leave electron vacancy (holes) in valence band. When excited electron in conduction band relaxes and moves back to valence band, or recombines with the hole, it will release excessed energy in the form of light which its wavelength depend on the energy difference between both bands. This energy difference is called a band gap and is crucial for optical and chemical properties of QDs.⁹

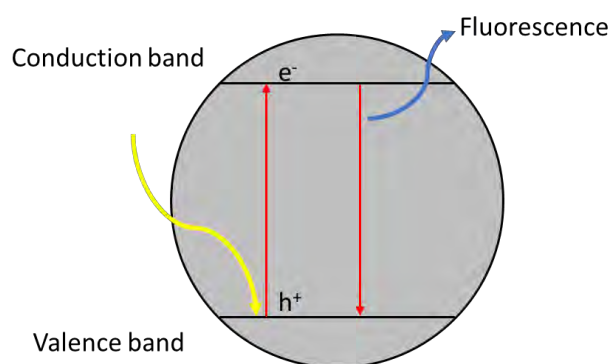


Figure 1.1 : band structure and photoluminescence property of quantum dots

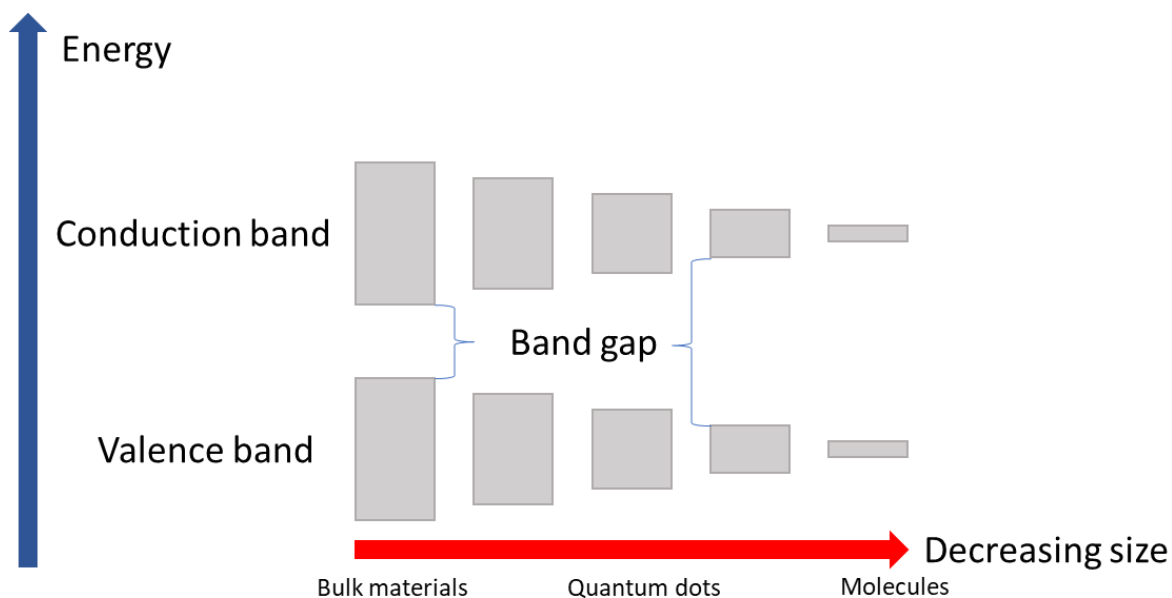


Figure 1.2 : Correlation between particle size and band gap energy

Typically, quantum dots are composed of 2 components, normally metal and p-block nonmetal, such as cadmium sulfide, cadmium telluride, zinc selenide and indium phosphide. There are also other types of quantum dots such as graphene quantum dots, perovskite quantum dots, 3-components quantum dots, core-shell quantum dots. Every types and composites of quantum dots have their own specific optical, electrical, and biological properties.¹¹

Ultraviolet/visible light spectroscopy and Fluorescence spectroscopy

UV/vis spectroscopy is the study of light absorption in ultraviolet and visible light regions. In this range of electromagnetic wave, atoms or molecules undergo electronic transitions.¹² The light absorbed by the materials affect their color. Principle of UV/vis absorption is that electrons (bonding and non-bonding) in certain orbitals can absorb light and are excited into high-energy orbitals, the larger the difference between the two orbitals, the shorter wavelength of the absorbed light.¹³



Figure 1.3 : Simplified working scheme of UV/vis spectrophotometer: light from the lamp past through the sample, and the light that not absorbed by the sample will meet with the detector.

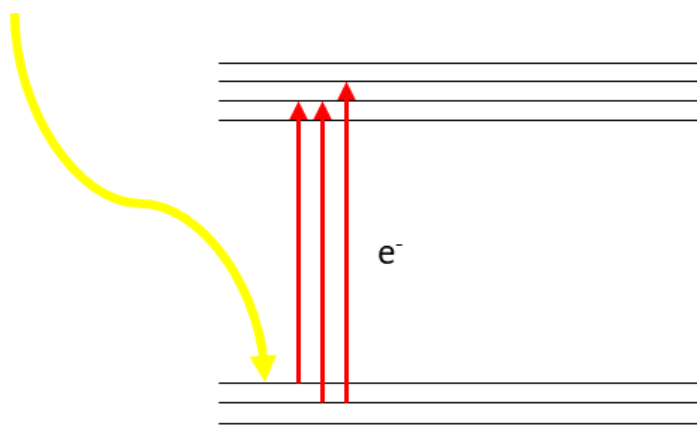


Figure 1.4 : Mechanism of light absorption: electrons will absorb incident light and be excited to excited state.

According to Beer-Lambert law, absorption intensity equals the path length through the sample times the extinction coefficient times concentration of the particle;¹³

$$A = \epsilon c L$$

where A : absorbance

ϵ : extinction coefficient (M⁻¹cm⁻¹)

c : concentration (Molar)

L : path length (cm)

This equation shows that the absorption intensity (absorbance) is directly proportional to the concentration. With calibration curves, one can calculate the concentration of the particle. However, this equation is true only at low concentration.

Fluorescence spectroscopy is complementary to UV/vis spectroscopy, fluorescence spectroscopy is the study of emitted light when electron transition from excited state back to ground state.^{12, 13} Both absorption and fluorescence are unique for each material, depending on its composition, structure, size, shape. However, fluorescence is more specific, belonging to certain kind of molecules, and it can be used to characterize these molecules with more accuracy.¹²

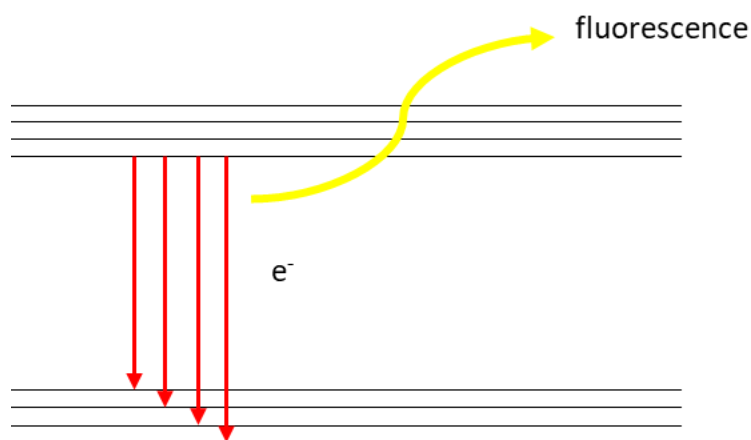


Figure 1.5 : Mechanism of fluorescence: excited electrons will relax and transit to lower ground state and release the energy in the form of light.

For quantum dots, the particle absorb light at shorter wavelength than their bulk materials. The smaller the particle is, the shorter absorption wavelength and the sharper absorption peak it shows.¹⁴ This absorption wavelength depends on its diameter, so we can calculate the size of

QDs from UV/vis spectroscopy. QDs will often absorb one specific wavelength of light greatly and absorb the shorter wavelength light proportion to energy of the light.¹⁴

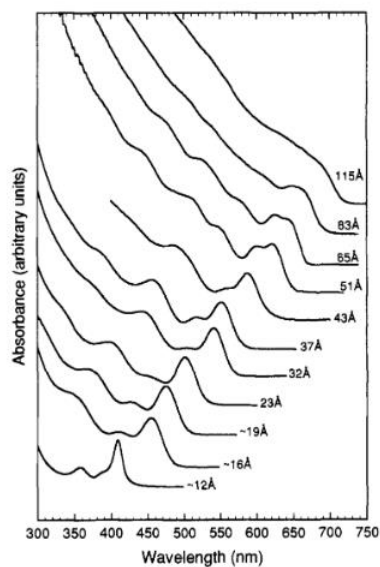


Figure 1.6 : Effect of quantum dots' size on UV/vis absorption

However, UV/vis spectroscopy cannot be used with solid particle of opaque colloidal mixture because the particle itself will block the light, and the detector will not be able to determine the light absorbed by the particle. For this reason, UV-DRS spectroscopy is invented.¹² Meanwhile, researchers need data from UV/vis spectroscopy to study the materials with fluorescence spectroscopy because the excitation wavelength in fluorometer need to be adjusted properly. Excitation wavelength that the materials cannot absorb will not excite the electron and provide no fluorescence, and excitation wavelength that is too short may generate fluorescence overtone that overlay with fluorescence spectrum.¹⁵ This fluorescence overtone will be generated at multiplicity of the excitation wavelength and have very high intensity.

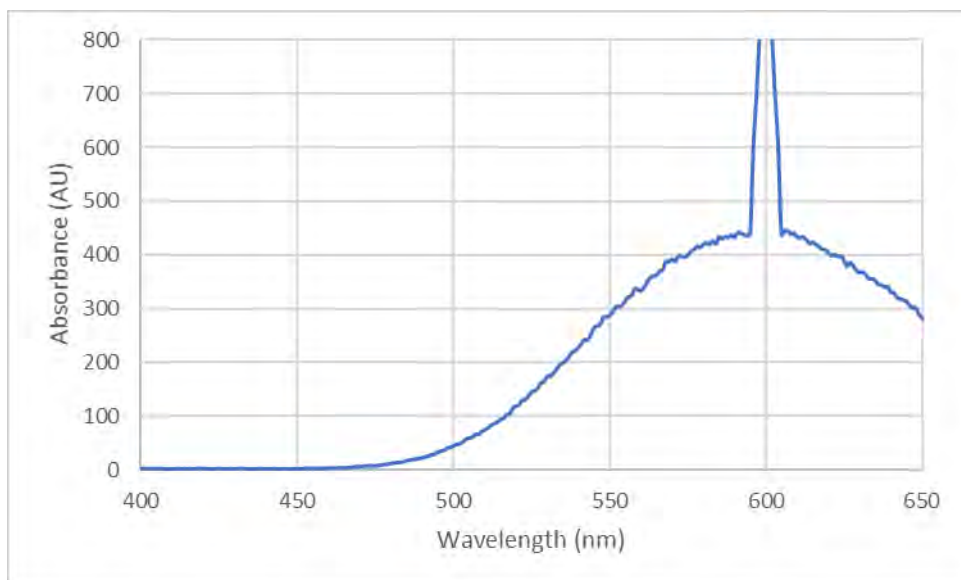


Figure 1.7 : Fluorescence overtone at 600 nm when excitation wavelength is 300 nm, overtone signal overlaps with fluorescence of the particles.

Photocatalytic reaction

Photocatalytic reaction is the reaction that can be accelerated by irradiation of electromagnetic wave, normally UV or visible light, in the presence of catalyst. It was designed to improve the efficiency of photoreaction, reaction that use light energy for activation, without alteration of the final product or catalyst's structure, and the catalyst is termed 'photocatalyst'. In photocatalytic reaction, light is absorbed by photocatalyst to create electrons and holes, which will act as active species and react with another reagent.¹⁶ This new pathway requires less activation energy, and thus the reaction can be conducted at lower temperature with higher conversion.

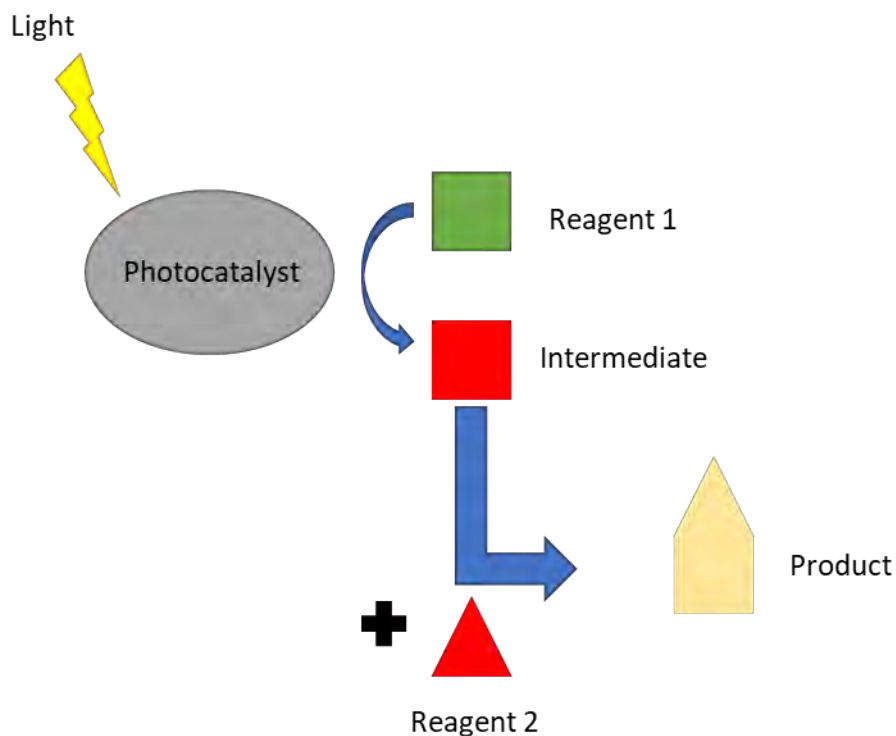


Figure 1.8 : Simplified scheme for photocatalytic mechanism

Thioacid-mediated amide synthesis

Amide synthesis reaction is an important part in modern industry due to amide being the main component of various polymers. The reaction usually starts with amine and acid halide or carboxylic acid.¹⁷ The reaction between amine and carboxylic acid often yield a low amount of amide; on the other hand, reaction between amine and acid halide yields a high amount of amide, but the reaction must be conducted in controlled environment due to high reactivity of acid halides.¹⁷ Both low yielding and difficult handling makes the amide synthesized unavailable in mass production.

R.V. Kolakowski *et al.* proposed the mechanism of thioacid/azide amide formation in 2006¹⁸. The reaction has 2 pathways depending on the functional group on azide, and this reaction provide a new method for amide synthesis. This method gives a high amount of product with great selectivity. However, their method still requires some expensive or toxic chemicals. Their proposed mechanism is shown below in Fig.1.9¹⁸

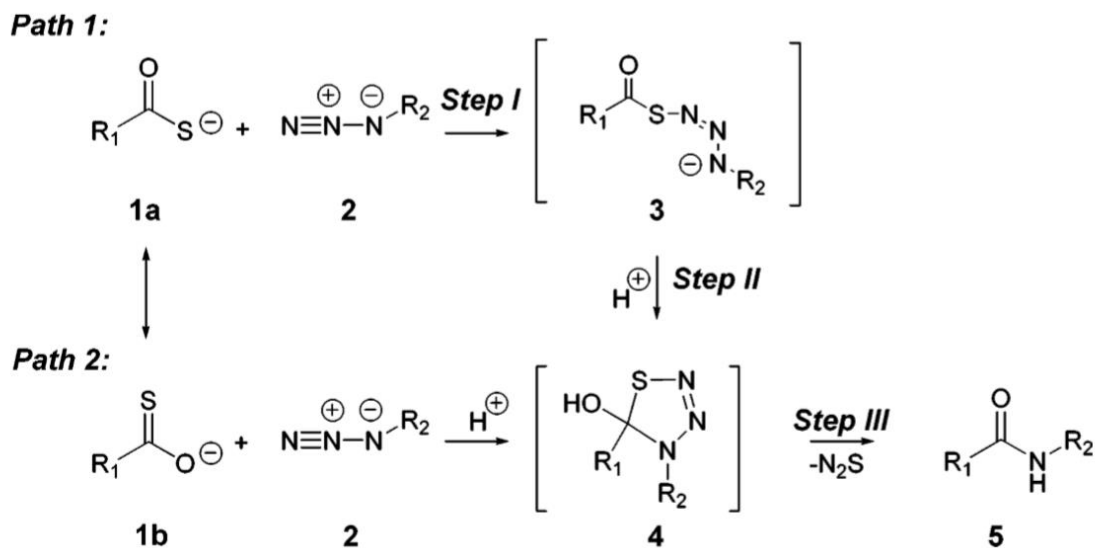


Figure 1.9 : Kolakowski's proposed mechanism for thioacid/azide amidation

In 2017, S. Das *et al.* has studied the possibility of using CdS QDs as photocatalyst in thioacid-mediated amide synthesis and proposed a mechanism of the reaction as shown in Fig.1.10.⁵ The reactions were conducted at room temperature and gave high yield without the addition of other catalyst or reagents. The CdS QDs play important role as an oxidizer for disulfide bond formation, due to CdS QDs' valence band potential, which is close to reduction potential of thioacid, and amide bond forms after amine attack the disulfide bond. The reaction was completed after 4 hours at room temperature with water as solvent and gave up to 98% yield.

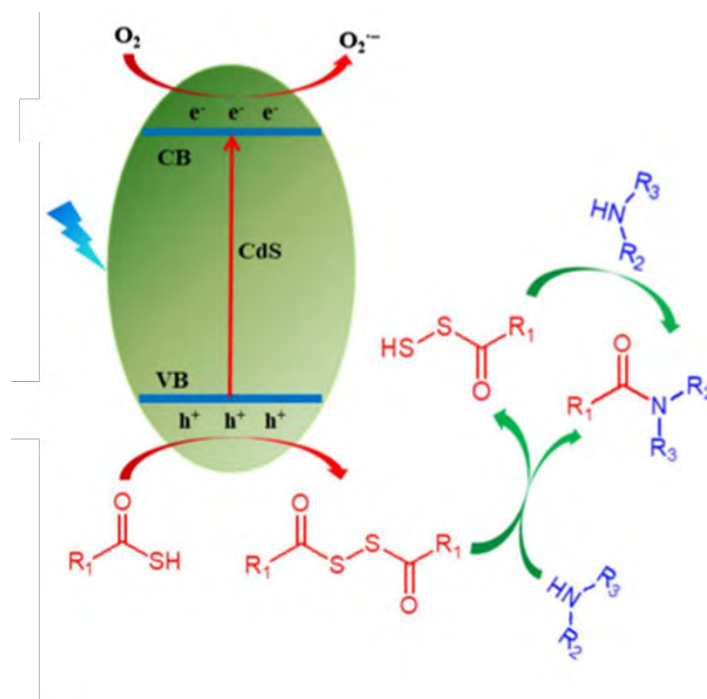


Figure 1.10 : Das' proposed mechanism for thioacid-mediated amidation using CdS QDs as photocatalyst.

This mechanism suggested that photocatalysts with disulfide bond (or other bond with the same reactivity) in their structure are not suitable for the reaction. The disulfide bond in the catalyst's composite may react with amine and inhibit the thioacid from the reaction. Also, the new bond form amine and thiol on the particle would break the old disulfide bond, disconnecting the QDs from MNPs.

Chapter 2

Experiment

2.1 Instruments

1. Heating mantle
2. Schlenk line
3. Condenser
4. Gas tube
5. Magnetic stirrers
6. Digital scales
7. Nitrogen gas system
8. Centrifuge machine and tubes
9. Beakers
10. pH paper
11. 3-neck flasks

2.2 Chemicals

1. FeCl_3
2. FeCl_2
3. Sulfur powder
4. 25% NH_3 solution
5. NaBH_4

6. CdCl_2
7. CH_3COOH
8. Tetraethyl orthosilicate (TEOS)
9. 1 M NaOH solution
10. Thioglycolic acid (TGA)
11. Acetone
12. (3-Mercaptopropyl)trimethoxysilane (MPS)
13. (3-Aminopropyl)triethoxysilane (APTES)

2.3 Methods

2.3.1 CdS QDs synthesis

Following G.L. Wang et al., 0.09 g CdCl_2 was dissolved in 50 mL DI water and added into a 3-neck flask. The solution was stirred under N_2 atmosphere in Schlenk line. Then 250 μL of TGA was added and the solution turned opaque. 1 M NaOH was added dropwise to adjust the pH to 9.0 and make clear solution. 5.0 mL 0.1 M Na_2S (prepared from reaction between sulfur and NaBH_4) then added slowly to form CdS QDs. The mixture was mechanically stirred and heated at 120°C under N_2 atmosphere for 4 hours. Ethanol was added to form yellow CdS QDs precipitate. The precipitate was centrifuged and washed with DI water and ethanol to rinse out the excess reagent. CdS QDs were dispersed in DI water and kept in cold and dark place. The process is shown in Fig.2.1.¹⁹

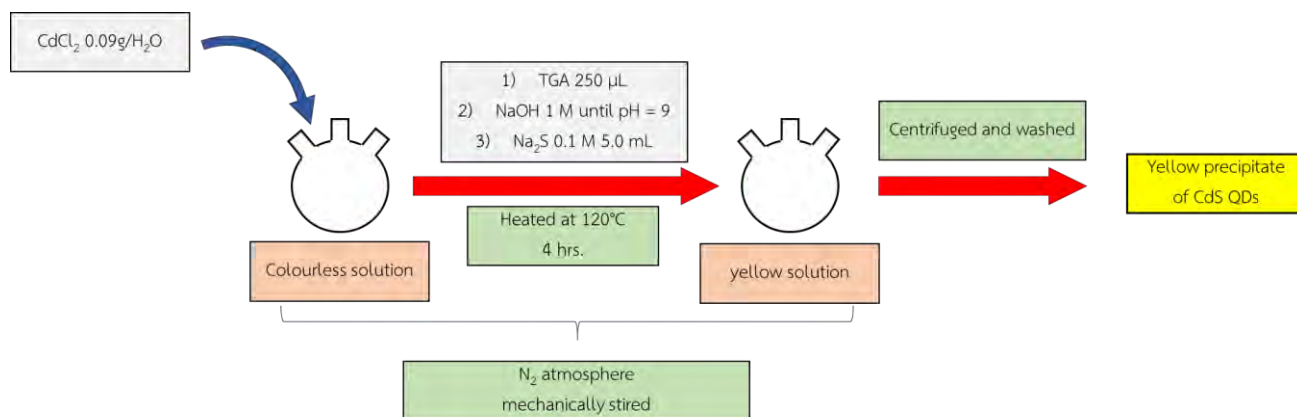


Figure 2.1 : Synthesis of CdS QDs

2.3.2 MNPs synthesis

2.3.2.1 Fe₃O₄ MNPs

Adapted from Massart's method, 50 mL of 1 M FeCl₃ and 10 mL of 2 M FeCl₂ was mixed and carefully dropped into 20 mL of 25% NH₃ under mechanical stirring. The mixture was stirred at room temperature for 30 minutes. Yielded particles were washed with DI water until the pH reach 7.0 and then dispersed in DI water.²⁰

2.3.2.2 SiO₂/Fe₃O₄ MNPs

10 mL of Fe₃O₄ MNPs in water was mixed with 5 mL of 25% NH₃. Then 30 mL of DI water and 25 mL of ethanol was added. The mixture was stirred for 10 minutes, then 2 mL of TEOS and 30 mL of ethanol was added to initiate the sol-gel process. The reaction was done under room temperature and normal pressure for 6 hours. The particle was separated with magnet and washed with DI water and acetone. Washed particle was dried at 60°C for 2 hours and kept in dry place.

2.3.2.3 SH-SiO₂/Fe₃O₄ MNPs

Follow the method reported by P. Sun *et al.*, 50 mg of SiO₂/Fe₃O₄ was dispersed in a mixture of 10 mL DI water and 35 mL ethanol. 5mL of 25% NH₃ was then added, and the mixture

was stirred for 10 minutes before adding 2 mL MPS to begin sol-gel process. The reaction mixture was stirred under room temperature and normal pressure for 12 hours. The particle was separated with a magnet and washed with DI water then dispersed in DI water.⁶

2.3.2.4 $\text{NH}_2\text{-SiO}_2/\text{Fe}_3\text{O}_4$ MNPs

Adapted from Sun's method, 50 mg of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ was dispersed in a mixture of 10 mL DI water and 35 mL ethanol. 25% NH_3 was then added and the mixture was stirred for 10 minutes before adding 2 mL APTES to begin sol-gel process. The reaction mixture was stirred under room temperature and normal pressure for 4 hours. The particle was separated with magnet and washed with DI water then dispersed in DI water.⁶

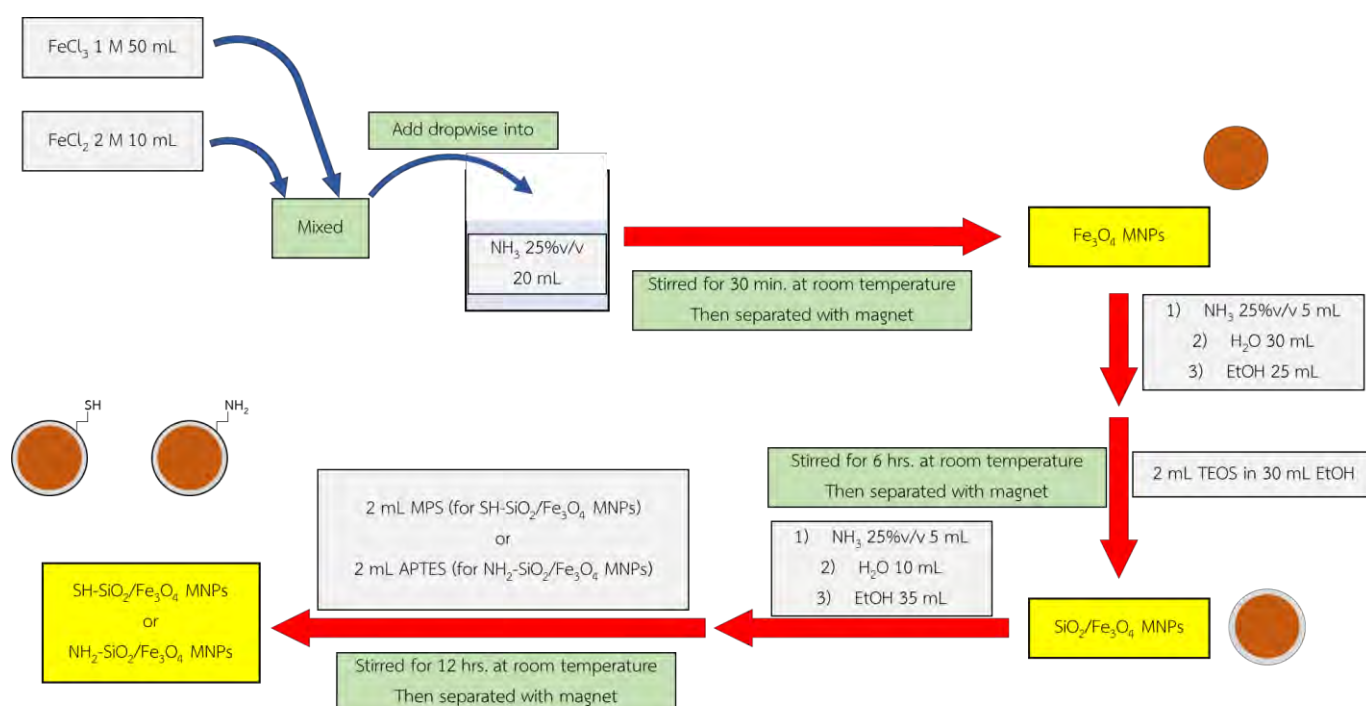


Figure 2.2 : Synthesis path for Fe_3O_4 MNPs, $\text{SiO}_2/\text{Fe}_3\text{O}_4$ MNPs and functionalized $\text{SiO}_2/\text{Fe}_3\text{O}_4$ MNPs

2.3.3 CdS MQDs synthesis

2.3.3.1 Growth of CdS QDs on the surface of Fe₃O₄ MNPs

Adapted from previous work, 0.09 g of CdCl₂ was added into a mixture between 10 mL of Fe₃O₄ MNPs in water and 40 mL of DI water in a 3-neck flask. The mixture was mechanically stirred under N₂ atmosphere in Schlenck line. Then 250 μL of TGA was added and the solution turned white opaque. 1 M NaOH was added dropwise to adjust the pH to 9.0, and then 5.0 mL 0.1 M Na₂S was added slowly to form CdS QDs on the surface of MNPs. The mixture was mechanically stirred and heated at 120°C under N₂ atmosphere for 4 hours. The particles were separated with a magnet and washed with DI water and ethanol. Washed particle was dispersed in DI water.^{7, 19}

2.3.3.2 Growth of CdS QDs on the surface of SiO₂/Fe₃O₄ MNPs

Adapted from previous work, 0.09 g of CdCl₂ and 0.15 g of SiO₂/Fe₃O₄ MNPs were added into 50 mL of DI water in a 3-neck flask. The mixture was mechanically stirred under N₂ atmosphere in Schlenck line. Then 250 μL of TGA was added and the solution turned white opaque. 1 M NaOH was added dropwise to adjust the pH to 9.0 then 5.0 mL 0.1 M Na₂S was added slowly to form CdS QDs on the surface of MNPs. The mixture was mechanically stirred and heated at 120°C under N₂ atmosphere for 4 hours. The particle was separated with magnet and washed with DI water and ethanol. Washed particle was dispersed in DI water.^{8, 19}

2.3.3.3 Growth of CdS QDs on the surface of SH-SiO₂/Fe₃O₄ MNPs

Like the growth of QDs on the surface of SiO₂/Fe₃O₄ MNPs, 0.09 g of CdCl₂ was added into a mixture between 10 mL of SH-SiO₂/Fe₃O₄ MNPs in water and 40 mL of DI water in a 3-neck flask. The mixture was mechanically stirred under N₂ atmosphere in Schlenck line. Then 200 μL of TGA was added, and the solution turned white opaque. 1 M NaOH was added dropwise to adjust the pH to 9.0 then 5.0 mL 0.1 M Na₂S was added slowly to form CdS QDs on the surface of MNPs. The mixture was mechanically stirred and heated at 120°C under N₂ atmosphere for 4 hours. The

particle was separated with magnet and washed with DI water and ethanol. Washed particle was dispersed in DI water.

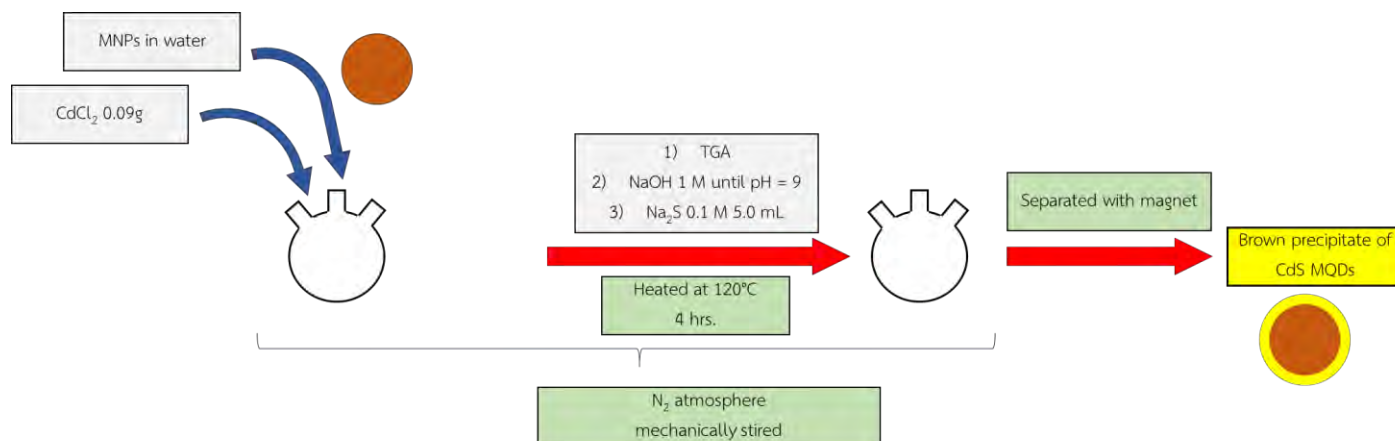


Figure 2.3 : Synthesis scheme summarizing the growth of CdS QDs on the surface of MNPs

2.3.3.4 Formation of disulfide bond between TGA-capped CdS QDs and SH-SiO₂/Fe₃O₄ MNPs

Following Sun's method, 10 mL of CdS QDs in water in 3-neck flask was connected to Schlenk line with N₂ to prevent air agitation. Then 20 mL of SH-SiO₂/Fe₃O₄ MNPs in water was added and the mixture was stirred. 1.0 M NaOH was used to adjust pH to 11.0, and the reaction was done under N₂ atmosphere and room temperature for 6 hours. The particle was separated with a magnet and washed with DI water and ethanol until the pH is 7.0 then dispersed in DI water.⁶

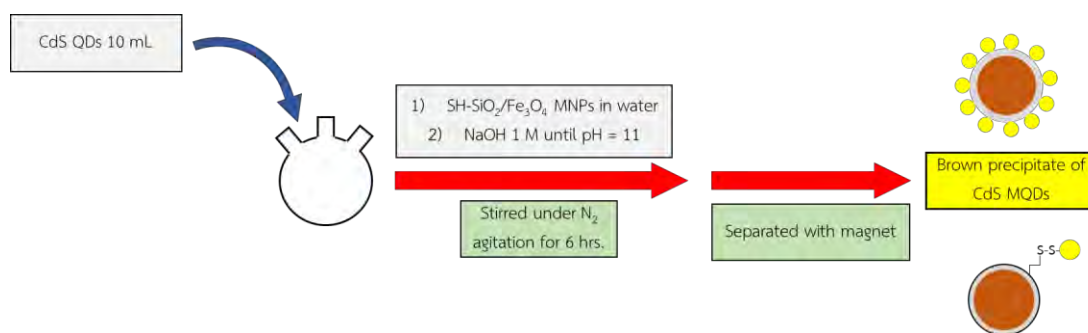


Figure 2.4 : Synthesis of CdS MQDs through the formation of disulfide bond

2.3.3.5 Formation of amide bond between TGA-capped CdS QDs and NH_2 - $\text{SiO}_2/\text{Fe}_3\text{O}_4$ MNPs

Adapted from Sun's method, 5 mL of CdS QDs in water was mixed with 5 mL of NH_2 - $\text{SiO}_2/\text{Fe}_3\text{O}_4$ MNPs. The mixture was stirred at 60°C and under normal pressure for 6 hours. The particles were separated with a magnet and washed with DI water then dispersed in DI water.⁶

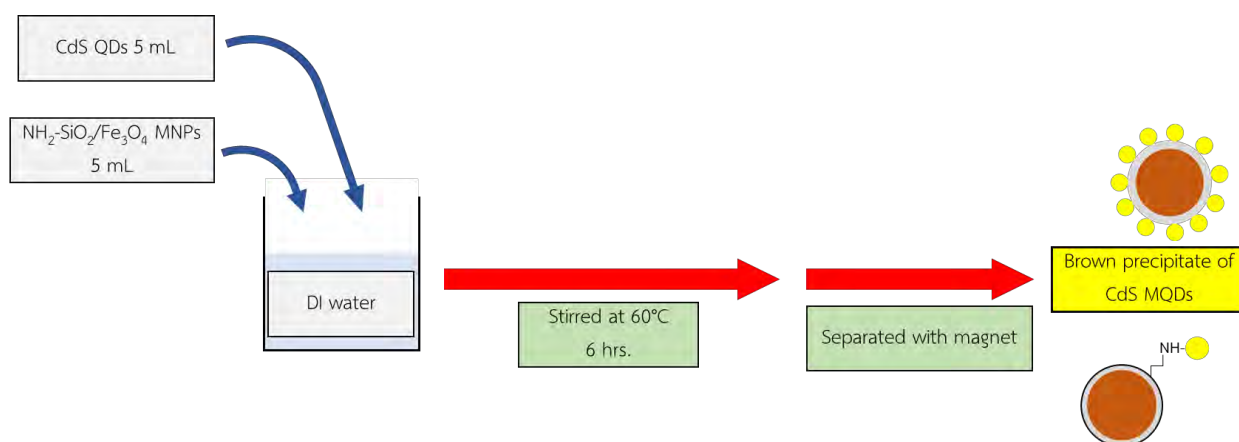


Figure 2.5 : Synthesis of CdS MQDs through the formation of amide bond

2.3.4 Morphological study

Morphology of the synthesized CdS QDs and CdS MQDs was studied using Transmission electron microscope (TEM)

2.3.5 Photoluminescence study

UV/vis spectrophotometer was used to study absorption wavelengths of synthesized particles, and fluorescence spectrophotometer was used to study the fluorescence of the particle when excited by single-wavelength light.

2.3.6 Catalytic study

Adapted from S. Das' experiment, the reaction between potassium thioacetate and *p*-anisidine to yield *N*-(4-methoxyphenyl)acetamide was utilized to determine photocatalytic property of CdS QDs and CdS MQDs. 1 mmol of *p*-anisidine and 1.2 mmol of potassium thioacetate were reacted together with 5 mL of CdS QDs or CdS MQDs as a photocatalyst under 19 W LED light.⁵ The reaction was quenched after 3 hours. The particles were separated by filtration, and the product was separated using column chromatography and measured using gravitometry.

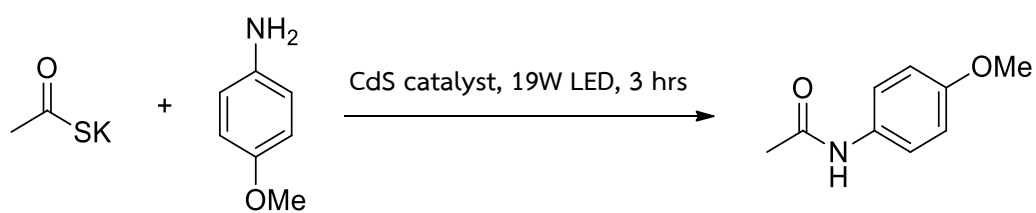


Figure 2.6 : Reaction scheme for catalytic study

Chapter 3

Results and Discussion

3.1 Morphological study

By using TEM, the morphology of CdS, Fe₃O₄ MNPs and CdS grown on the surface of Fe₃O₄ MNPs is shown in Fig.3.1. Although we might not be able to measure the size and indicate the shape of the synthesized particles, some information is acquired by these images. CdS QDs (Figure 3.1A) have diameter of around 10 nm and show some level of aggregation. This uncommonly large size and aggregation is probably due to CdS QDs were kept for long time (more than 3 weeks), leading to degradation of surface stabilizer and merging of 2 or more particles together. For Fe₃O₄ MNPs (Figure 3.1B), the particles appeared to be various in shapes and sizes, ranging from 10 nm to 20 nm, while some degree of agglomeration was observed. The variation in size and shape is the result from the synthesis method of Fe₃O₄ MNPs, where there is no size controlling stabilizer (e.g. PEG) in the reaction. Moreover, the mixture of FeCl₃ and FeCl₂ was dropped into ammonia solution by hand without any dropping rate controller. As dropping rate is a parameter that affects the size as well, particle size/shape were very inconsistent.²¹ Lastly, CdS grown on Fe₃O₄ MNPs (Figure 3.1C-D) showed nanosponge-like structure, as CdS grew on Fe₃O₄ and connected many Fe₃O₄ particles into nanonetworks.⁷ However, we cannot determine the size of this composite structure because their shape was very varied. However, the structure of the network seems not fully optimized and can be improved with more experiments on varying the ratio of CdS and Fe₃O₄. The results here indicated that CdS ODs were successfully grown on Fe₃O₄ MNPs, creating CdS-Fe₃O₄ MQDs, but the morphology of CdS MQDs was changed greatly compared to bare CdS QDs.

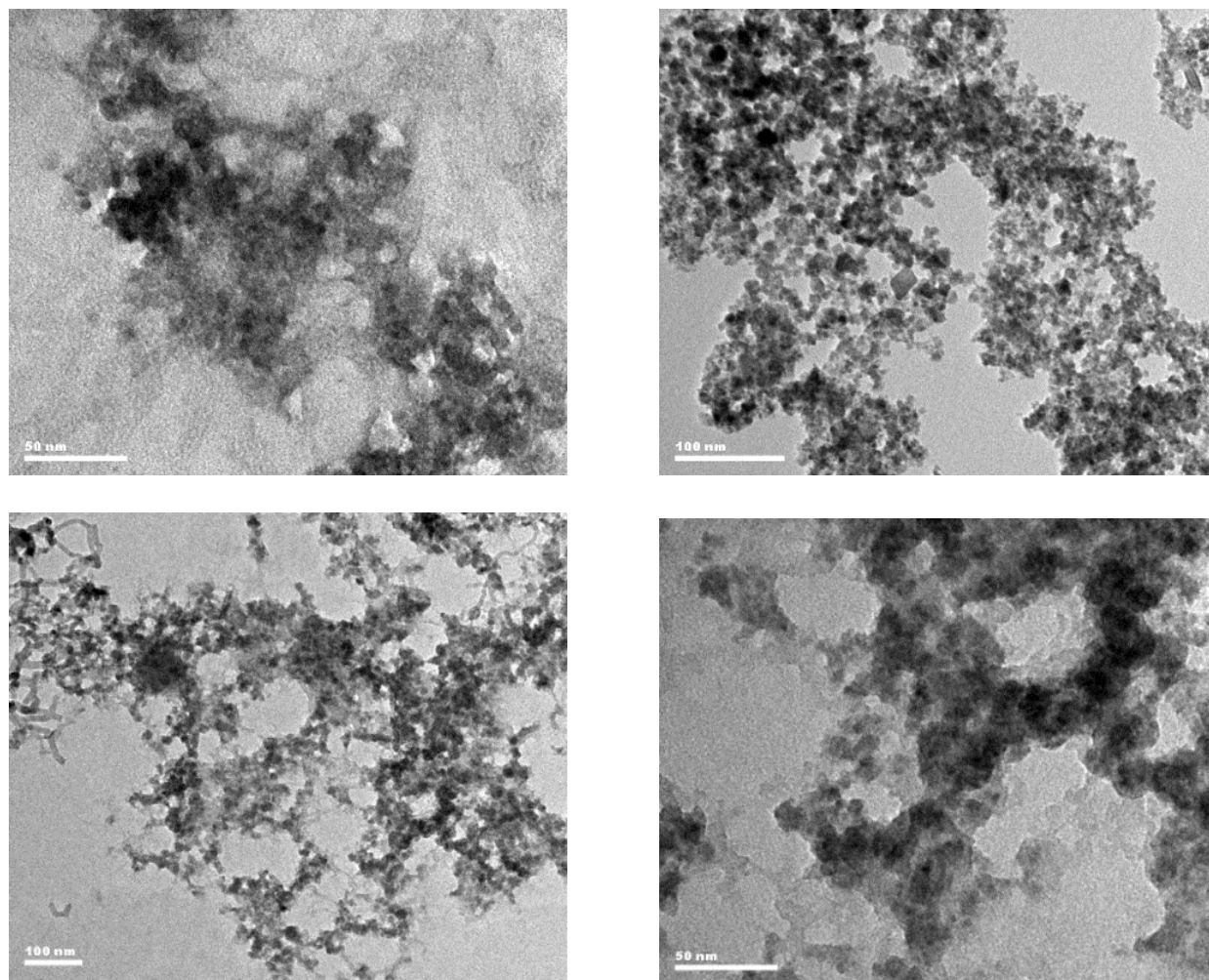


Figure 3.1 : TEM images of (A) CdS QDs, (B) Fe₃O₄ MNPs, (C&D) CdS-Fe₃O₄ MQDs

3.2 Photoluminescence properties

UV/vis spectrophotometer was used to study the absorption wavelength of synthesized particles and determined the excitation wavelength for fluorescence study. UV/vis absorption spectrum of CdS QDs is shown in Fig.3.2 Synthesized CdS QDs have broad absorption band at low wavelength (less than 380 nm), which is characteristic to quantum dots, and showed distinct peak at 440 nm. This peak may come from structural defect of the QDs that lead to energy states forming between actual band gap and absorption of longer wavelength light. Because of the high absorption intensity and prevention of overtone signal, the excitation wavelength of 440 nm was used in fluorescence study.

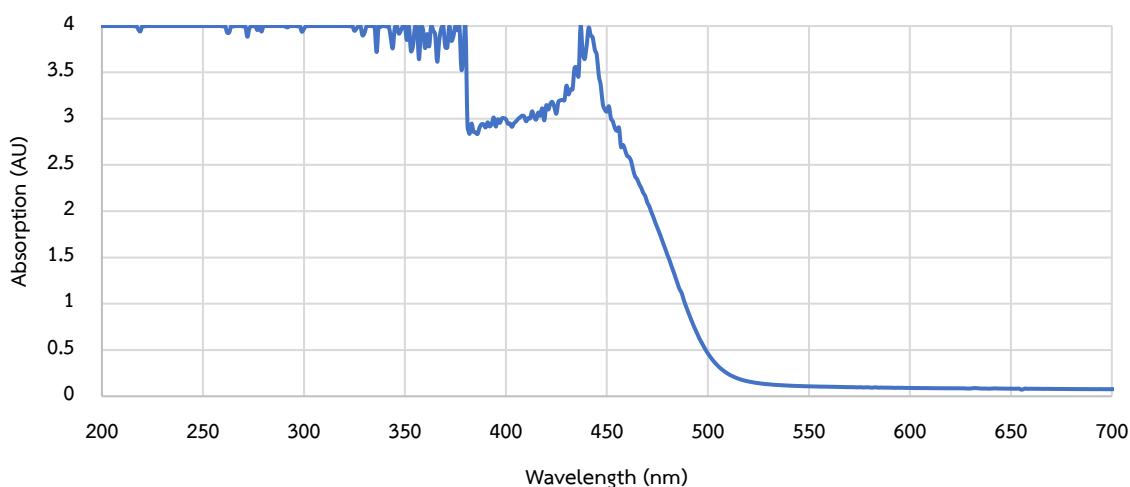


Figure 3.2 : UV/vis absorption spectrum of synthesized CdS QDs

On the other hand, the absorption spectrum of CdS MQDs show no absorption peak nor band, as in Fig.3.3 showing the absorption spectrum of CdS-SiO₂/Fe₃O₄ MQDs. This phenomenon could be originated from the fact that the mixtures of MNPs or MQDs in water were turbid. The particles block and scatter large portion of the incident light. Therefore, the absorption wavelength of CdS MQDs cannot be directly measured by current equipment and will be assumed that they have absorption wavelength similar to bare CdS QDs. Thus, 440 nm was chosen as excitation wavelength for fluorescence study.

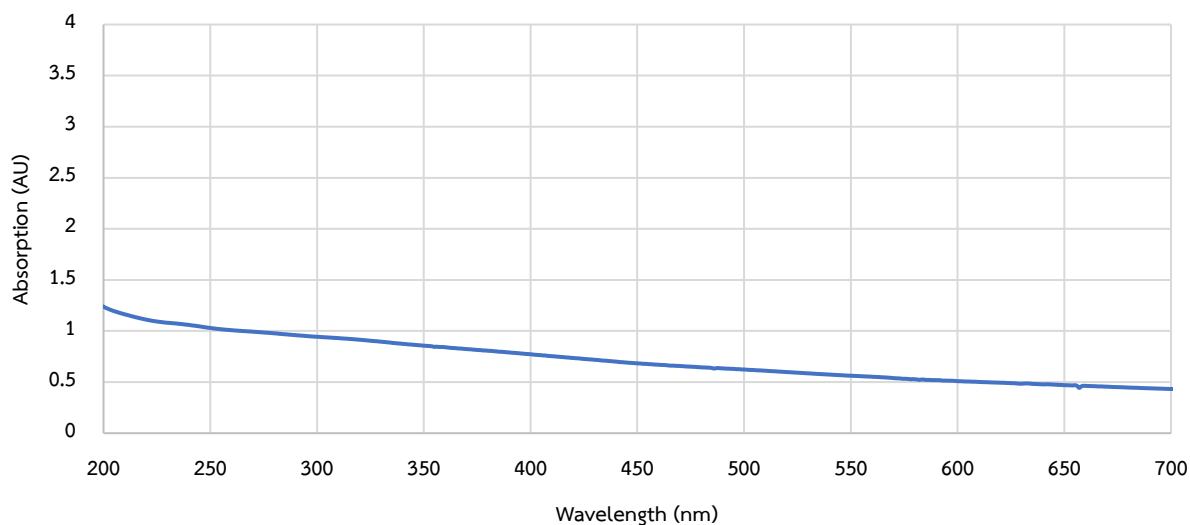


Figure 3.3 : UV/vis absorption spectrum of synthesized CdS MQDs

Fluorescence spectrum of CdS QDs is shown in Fig.3.4. There are four fluorescence bands, one at 450 nm, one at 530 nm, one band at 605 nm and broad band at more than 600 nm. The first peak is contributed to the band edge emission. The second and the third band are caused by surface defects of the particles which lead to various energy levels between the two bands and caused by the Stoke shift. The broad band at more than 600 nm was appeared due to the deformation of the particle due to its being kept for long time (7 days). However, the presence of fluorescence suggests that synthesized CdS QDs can interact with the incident light and generate excited electrons and holes, which are crucial for photocatalysis.

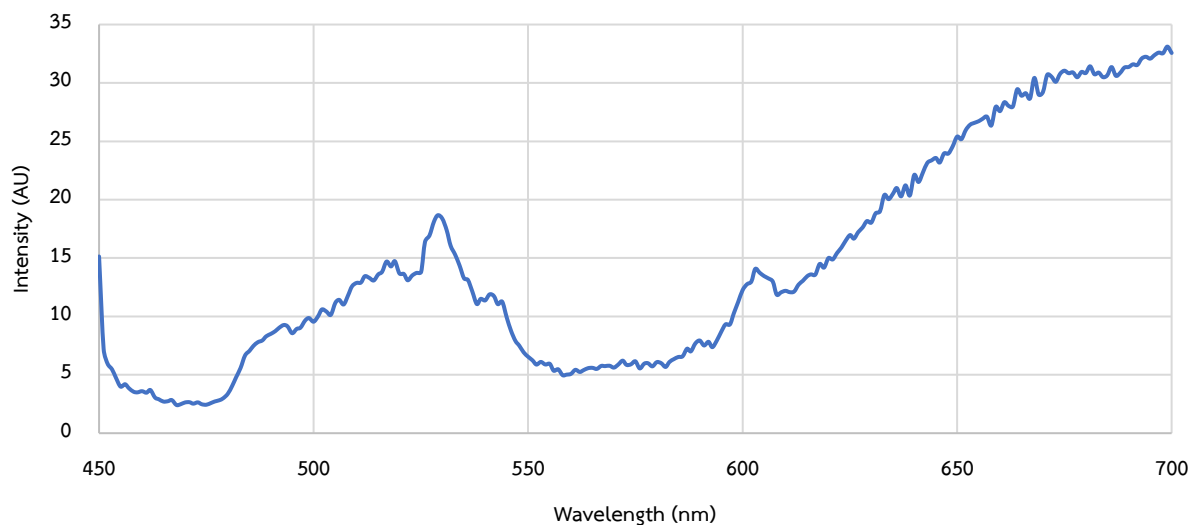


Figure 3.4 : Fluorescence spectrum of synthesized CdS QDs (ex. 440 nm)

For CdS MQDs synthesized by growing CdS QDs on the surface of Fe_3O_4 MNPs. The excitation wavelength of 350 is used to increase the fluorescence intensity. There is only one low intensity broad fluorescence band at 600 nm, which is not found in bare CdS QDs. This band might come from the heavily defected structure of CdS being grown onto MNPs, leading to the forming of many defect energies levels and lower fluorescence intensity. The sharp peak at 700 nm was from the fluorescence overtone. The fluorescence spectrum is shown in Fig.3.5

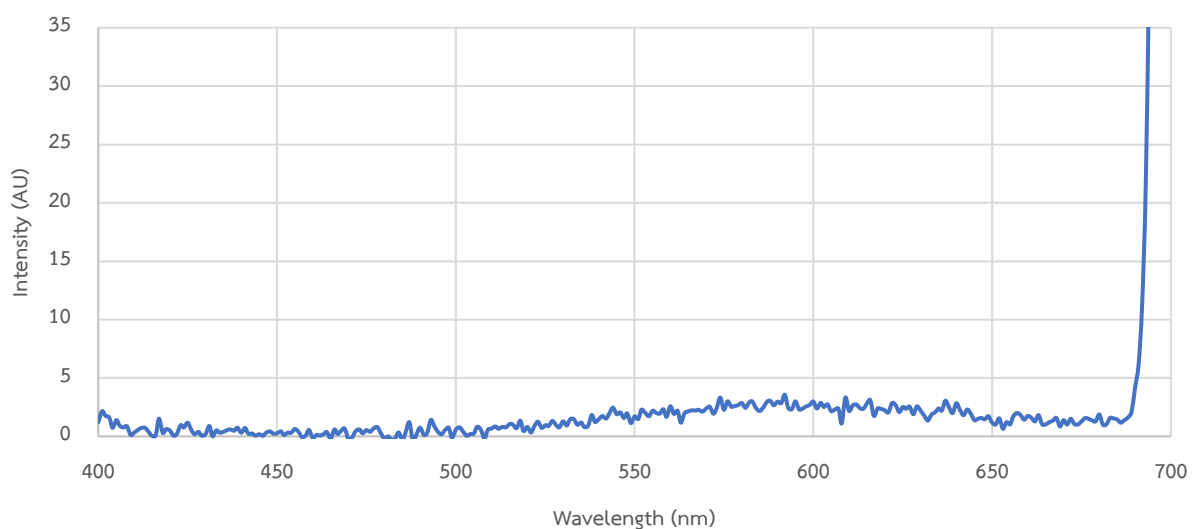


Figure 3.5 : Fluorescence spectrum of synthesized CdS- Fe_3O_4 MQDs (ex. 350 nm)

For CdS MQDs synthesized from Growing CdS QDs on the surface of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ MNPs. The fluorescence spectrum is shown in Fig.3.6 The fluorescence shared some similarity, notably band edge peak at less than 500 nm, one peak at 530 nm and another one at 605 nm, which indicated that the CdS QDs was successfully grown on the surface of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ MNPs and CdS MQDs was yielded. However, there was notable difference to the bare CdS QDs as no deformation

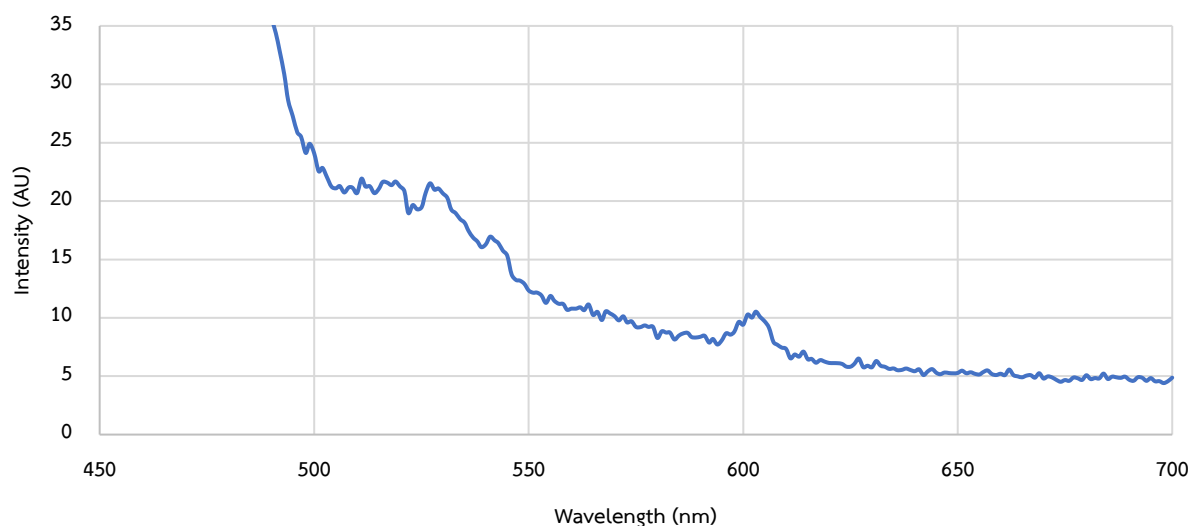


Figure 3.6 : Fluorescence spectrum of synthesized CdS- $\text{SiO}_2/\text{Fe}_3\text{O}_4$ MQDs (ex. 440 nm)



Figure 3.7 : Fluorescence of synthesized CdS QDs under UV light

band was observed in CdS QDs because the particle was kept for much shorter time (less than 1 day)

3.3 Photocatalytic properties

The effort to evaluate the photocatalytic activities of synthesized CdS QDs and CdS MQDs was carried out, the controlled amount of catalyst was used in the amide formation reaction, and the result is shown in Table 3.1. For Entries 1 and 2, CdS QDs was compared with CdS grown on Fe_3O_4 MNPs, and the result showed some notable features. Bare CdS QDs can act as a photocatalyst in the reaction between thioacid salt and amine even at low amount (0.015 wt%) and save the yield of 54%. This result goes along with Das's work in that CdS QDs can be a capable photocatalyst. Moreover, the reaction with CdS- Fe_3O_4 MQDs as photocatalyst showed low but noticeable yield at 10% even with lower amount of catalyst (0.0028 wt%). This result suggests that CdS- Fe_3O_4 MQDs can be potentially used as a photocatalyst in the reaction between thioacid salt and amine to form amide as well; however, controlled experiment with comparable amount of catalyst is needed to evaluate this potential.

Table 3.1 : Photocatalytic study of CdS QDs and MQDs in thioacid mediated amide formation

Entry	Catalyst type	CdS amount (wt%)	solvent	%yield
1	CdS QDs	0.015	water	54
2	CdS- Fe_3O_4 MQDs	0.0028	water	10
3	CdS QDs	0.07	water	24
4	CdS- $\text{SiO}_2/\text{Fe}_3\text{O}_4$ MQDs	0.07	water	70

Comparison between bare CdS QDs and CdS grown on $\text{SiO}_2/\text{Fe}_3\text{O}_4$ MNPs is conducted with Entries 3 and 4, with both having the same amount of CdS in the reaction. CdS- $\text{SiO}_2/\text{Fe}_3\text{O}_4$ MQDs show significantly higher yield than bare CdS QDs. This result is intriguing and suggesting that synthesized CdS- $\text{SiO}_2/\text{Fe}_3\text{O}_4$ MQDs may potentially act better as a photocatalyst in the reaction than bare CdS QDs. However, the yield from Entries 3 and 4 cannot represent the true potential

of both particles because the products from Entries 3 and 4 were kept for long time before separation and characterization, leading to degradation of both product and excessed reagent. The yield shown in Entries 3 and 4 could be lower than the real value; therefore, more experiments must be conducted.

Chapter 4

Conclusion

CdS MQDs were synthesized and their morphology, photoluminescence activities and photocatalytic activity have been evaluated. CdS grown on surface of Fe_3O_4 showed different structure compared to bare CdS QDs in TEM and fluorescence spectrum, showing no significant fluorescence signal, and showed some level of photocatalytic activity in the reaction between potassium thioacetate and *p*-anisidine even at low amount, giving 10% yield of amide when used at 0.0028 wt% compared to bare CdS QDs at 54% when used at 0.015 wt%. CdS grown on surface of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ exhibit more interesting properties in that CdS was able to grow on the surface of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ and preserved fluorescence property, and the reaction of potassium thioacetate and *p*-anisidine with CdS- $\text{SiO}_2/\text{Fe}_3\text{O}_4$ as a photocatalyst gave high yield at 70% compared to CdS QDs at the same amount, 0.07 wt% (24% yield). However, more experiments are required to evaluate the exact photocatalytic property of all synthesized particles. Moreover, photoluminescence and photocatalytic property of other forms of MQDs are required to be studied to identify their potential as photocatalysts.

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Vita

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