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THE HONG KONG
POLYTECHNIC UNIVERSITY
香港理工大學

Department of Applied Physics

Final Year Project Report

Project Title:

**Photocatalytic Ag@TiO₂ nanoparticle fabrication and its
application in methylene blue degradation**

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Abstract

Photocatalysts are widely used inside the paint to remove dangerous volatile organic compounds (VOCs). In this project, a hybrid material - Ag@TiO₂ was fabricated in order to substitute for conventional pure TiO₂ photocatalysts used in paint. The nanostructure of this new material was examined by transmission electron microscope. The Ag@TiO₂ obtained has a much smaller size than TiO₂ nanoparticles made by same method. Photocatalytic activity of Ag@TiO₂ was also examined, and it was found that this new material can trigger the photocatalysis process under visible light; while conventional TiO₂ cannot. The corresponding catalytic mechanisms are discussed in detail.

Methylene blue, acting as an indicator of amount of VOCs, was added into the Ag@TiO₂, and UV-Vis spectroscopy was used to measure the change of absorbance peak in methylene blue. By comparing the degradation effect on methylene blue between pure TiO₂ and Ag@TiO₂, it turned out that the Ag@TiO₂ has a higher degradation efficiency.

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Chapter 1 Introduction

1.1 Introduction of nanotechnology and photocatalysis

Nanotechnology is the technology for production and application of nanostructured materials. Understanding of the relationships between the material dimensions and its physical properties is one of the major missions for scientists. During the past twenty years, a great deal of research efforts have been put on synthesizing nanostructured materials, investigating properties related to different low dimensional materials, including physical and chemical, and the possible applications in nanomaterials.

Photocatalysis is one of the major applications in nanotechnology. It is widely used inside the paint to remove dangerous volatile organic compounds (VOCs) including formaldehyde, benzenes and radon [1]. These compounds may affect human health. For example, formaldehyde may cause cancer of the blood, throat and nose, which is listed as the human carcinogen inside Fourteenth Report on Carcinogens published by the National Toxicology Program [2].

During manufacturing process, the photocatalysts such as titanium dioxide nanoparticles or zinc oxide nanoparticles are added inside the paint. After shining the paint under UV light, the electrons are excited to produce hydroxyl radicals which can be used to remove formaldehyde inside the paint by secondary reaction.

However, the photocatalysis process mentioned above cannot be done under visible light. This is because the electrons in the valence band of TiO_2 cannot be effectively excited without enough energy [3]. Therefore, paint manufactures must buy UV lamps and use a period of time to finish the photocatalysis process. This raises the manufacturing cost for the investment of equipment, electricity cost for operations and longer working hours.

1.2 Objectives

To reduce the manufacturing cost of the paint, a series of experiments is done to enhance the production and separation of photo-induced electron-hole pairs in the semiconductor the valance band and conduction band of TiO_2 . Theoretically, the photocatalysis reaction can be done under visible light after the formation of plasmonic metal-semiconductor heterostructure.

The main objectives of this project include

- (1) To fabricate the Ag@TiO_2 , which is a hybrid material having a broader absorption wavelength range
- (2) To test the degradation efficiency of methylene blue (Formaldehyde)
- (3) Conclusion drawn - comparison of degradation efficiency between pure TiO_2 and the hybrid Ag@TiO_2 material

1.3 Organization of report

At the beginning of the reports, serval literature reviews were done and grouped in chapter 2. These reviews were done at different period in purpose of background investigations before we conducted the experiment. The reason of analyzing these

reviews will be explained in chapter 3-6.

Next, five different experiments will be introduced in chapter 3-6. The experiment setting up, procedures, analysis, discussions and related literature reviews are provided in each of the chapters.

Finally, the conclusions will be drawn and recommendations for future studies are provided.

The timeline of this project is shown below:

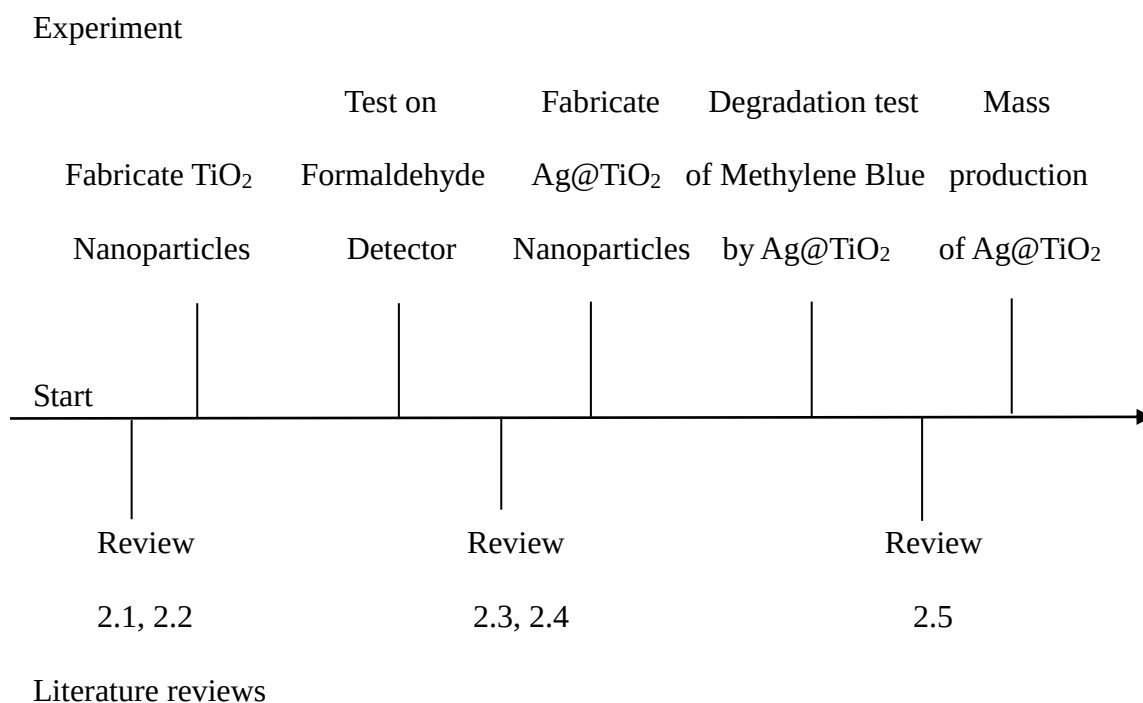


Figure 1. The timeline of the final year project.

Chapter 2 Literature Review

2.1 Material properties of TiO₂

Titanium dioxide (TiO₂) is one of the most commonly used materials for photocatalytic applications, which refers to the usage of light to impact catalytic activity to a chemical compound. Its powder form is largely used as catalysts in the field of detoxification of aqueous effluents by photocatalysis [4]. The wide usage of TiO₂ is because of its high stability, efficient photoactivity and very low cost.

There are three mineral forms of TiO₂ in the nature. They are anatase, rutile and brookite form. Different forms of TiO₂ has different size, shape and structure. They will influence their properties (both optical and catalytical), number of defects and the stability of phase. For anatase form, it crystallizes in tetragonal system. It is kinetically stabilized but not in equilibrium phase. It is photoactive and previous studies have shown that it the most efficient phase to use in photocatalysis [5]. For rutile form, it crystallizes in tetragonal unit cell. It is in equilibrium phase and is the most common form in nature. It is photostable with the highest refractive indices among all crystals. Study has shown that is the most efficient phase to use in sono-catalysis [5], which refers to the effects of sound-generated waves used on catalytic chemistry.

It is found that temperature is one of the major factors to influence the phase of TiO₂ [6]. For amorphous TiO₂, it crystallized into anatase nanophase below 300 °C. When it is heated up to 570 °C - 800 °C, diffuse phase transition occurs and TiO₂ transforms for anatase form to rutile form [6].

To enhance the photocatalytic efficiency, factors such as electron-hole recombination rate, crystallinity and particle interconnection should be considered. Although anatase form is the most efficient phase in photocatalysis, it is shown that anatase–rutile mixture is more effective than each phase separately in photocatalysis. One of the most efficient commercial photocatalysts is Degussa P-25 commercial powder which manufactured by flame hydrolysis [7]. It contains 80% of anatase form TiO_2 and 20% of rutile form TiO_2 .

2.2 Review of conventional methods for TiO_2 synthesis

There are different methods for fabricating TiO_2 powers for photocatalytic use. One of the most convenient ways is using the method of hydrolysis. Hydrolysis refers to reactions that involve breaking of a bond in a molecule by using water. For producing TiO_2 powers, titanium tetrachloride (TiCl_4) or tetrabutyl titanate are usually used as the precursor at the beginning of the experiment.

In the review of using titanium tetrachloride as the precursor [8], ammonium sulfate with hydrochloric acid is added into the titanium tetrachloride solution with stirring. Next, the solution is put into the 95-degree oven for an hour. After that, ammonium hydroxide is added to the solution and cools down the solution in the room temperature for precipitation. Finally, TiO_2 powers can be obtained after the washing, filtering and drying process by using the silver nitrate solution which is used to remove the chloride ions. The review results can finally obtain the power size around 7 nanometers.

In the review of using tetrabutyl titanate as the precursor [9], ethanol is added into tetrabutyl titanate. Next, hydrochloric acid is added into the solution to prevent the reaction becomes over-vigorous. After that, adding deionized water into the solution with two hours of magnetic stirring. Finally, the solution is washed and heated up for an hour. The TiO_2 power is observed after the product is grinded and the obtained powder size is around 1 micrometer.

2.3 Material properties of Ag@TiO_2 nanostructures

2.3.1 Introduction of Ag@TiO_2

It is reported that the photocatalytic activity of pure TiO_2 nanoparticles had no significant absorption in the visible light region [10]. The reason of inefficient absorption is because the electrons of TiO_2 cannot be excited from valance band to conduction band. The visible light does not have enough energy ($E_{\text{threshold}} \approx 3.0\text{eV}$) to excited the electrons to produce hydroxyl radicals ($\cdot\text{OH}$).

To improve the absorption under the visible light, scientists have already tried out serval methods. One of the ways is to deposit TiO_2 nanoparticles on the surface of noble metals nanoparticles, forming a core shell structure as shown at Figure 2.

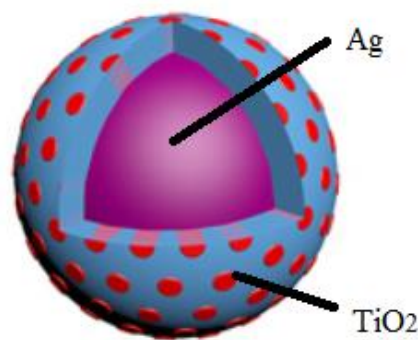


Figure 2. Core-shell structure of Ag@TiO_2 .

The common noble metal nanoparticles examples are silver and gold. They can exhibit catalytic, optical, electrical properties and specific surface plasmon absorption [11]. In the core-shell structure mentioned above, depositing TiO_2 nanoparticles on noble metals surface has several advantages. First, the silver core can capture and trap the photo-induced electrons or holes and decreasing the recombination of electron-hole pairs effectively. Second, it can extend the light absorption of TiO_2 to the visible light region and hence to enhance the photocatalytic activity[12].

2.3.2 Schottky barrier

The reason of light absorption increase by introducing silver core may be related to semiconductor physics. Since the silver metal core is contacted with TiO_2 shell, which is a n-type semiconductor, a Schottky barrier may be formed. Then, a banding occurs at the core-shell interface. The energy bands of the semiconductor and metal in contact are adjusted in order to align both vacuum levels. Due to the re-adjustment of vacuum levels, it was necessary for the Fermi levels to be ‘bent’ to higher (or lower) energy, as shown in figure 3. Therefore, a barrier is formed at the interface. It originates from a space charge layer on the semiconductor surface[13]. When visible light shines on the Ag@TiO_2 , most of the photogenerated electrons might be excited from the surface of the Ag core to the conduction band of the TiO_2 shell because of the surface plasmon resonance[14]. Then the electrons diffuse to the surroundings for reaction.

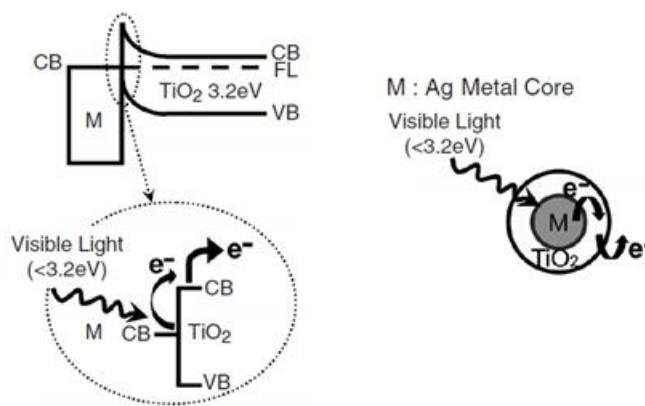


Figure 3. Schottky barrier banding with corresponding photocatalytic mechanism.

[18]

2.3.3 Surface plasmon resonance

Surface plasmon resonance (SPR) is the resonant oscillation of conduction electrons at the interface between negative and positive permittivity material stimulated by incident light [15]. Before understanding this mechanism working in Ag@TiO₂, two terms have to be known first – evanescent wave and plasmon wave.

2.3.3.1 Evanescent wave

In wave optics, when a wave strikes to a medium boundary at an angle larger than the critical angle with respect to the normal to the surface and the refractive index is lower on the other side of the boundary, total internal reflection occurs. The wave cannot pass through and is entirely reflected. However, it is discovered that the reflected light is not directly produced for the total internal reflection light [16]. The light first propagated by around the distance of one wavelength deep in the other side of the boundary. Then the wave move along the surface by around half wavelength long.

Finally, it returns to the originally medium. The wave passing through the other side of the boundary is called evanescent wave.

2.3.3.2 *Plasmon wave*

Plasmon wave generally refers to a gas composed of positive and negative charges with relatively high density [17]. The number of positive and negative charged particles is almost equal. The valence electrons on a metal surface may be considered as the electron gases that move in the background of uniform positive charges, which can be considered as a type of plasma. When the metal is subjected to electromagnetic interference, the electron density distribution inside the metal becomes non-uniform. Because of the Coulomb force, some electrons are attracted to the area with excess positive charge. The electrons do not stop at the equilibrium position because of the momentum gain. They continue to move forward for some distance. After that, the repulsion forces between the electrons force the electron group to leave that area again. This creates a collective oscillation of the entire system. The presence of Coulomb forces causes this collective oscillation to be repeated continuously. This oscillation is called plasma oscillation. The oscillation is expressed in form of waves that called plasma waves [17].

2.3.3.3 *Interaction between evanescent wave and plasmon wave*

When light is totally reflected on the surface of the original boundary by total internal reflection, both evanescent wave and plasma wave exists in the other side of the

boundary. Resonance may occur when the two waves encounter. When the evanescent wave resonates with the surface plasmon wave, the reflected light intensity is greatly reduced. The energy is transferred from the photons to the surface plasmon. Most of the energy of the incident light is absorbed by the surface plasmon waves with the energy of the reflected light drastically reduced [14].

In the Ag@TiO₂ core-shell system, the silver metallic core acts as the plasmon surface with a lower refractive index comparing with TiO₂. When the light is injected to the silver core through the medium of TiO₂, both surface plasmon wave and evanescent wave exist and resonance can occur. The electrons can absorb the energy of light and have enough energy to jump through the Schottky barrier. The electrons in the conduction band can react with the surrounding and hence the photocatalytic efficiency under visible light increases.

2.4 Review of conventional methods for Ag@TiO₂ synthesis

Although there are numerous ways to fabricate Ag@TiO₂, the principle of producing it is the same. Fabrications of Ag@TiO₂ contains three main steps. The first step is to synthesize the silver core by a reduction reaction. In this reaction, silver source, reduction agent and stabilizer are required. The second step is to synthesize the titanium dioxide nanoparticles by using titanium source and ethanol. Finally, titanium dioxide coating is added onto the silver nanoparticles. If powder form of Ag@TiO₂ obtained, heating and grinding are required to increase the yield. From different journals, three different ways of fabricating Ag@TiO₂ are investigated.

The tables below (Figure 4-6) summarized the experimental procedures and required equipment for the experiment by three different methods [18][19][20].

Table 1. Summary of fabrication of Ag@TiO₂ in journal (1).

Title of paper	Fabrication and photocatalytic activities in visible and UV light regions of Ag@ TiO ₂ and NiAg@TiO ₂ nanoparticles
Materials Required	• Silver nitrate solution(AgNO₃) • Hydrazinium hydroxide (N₂H₅OH) • Hexadecyl-trimethylammonium bromide (CTAB) • Titanium(IV) isopropoxide (Ti(OCH(CH₃)₂)₄ (TTIP) • Ethanol (C₂H₅OH)
Equipment Required	• Orbital shaker • Centrifuge • Oven
Steps	1. Synthesis of Ag nanoparticles (a) Hydrazinium hydroxide solution (100 mM, 0.5 ml) and AgNO₃ solution (50 mM,0.5 ml) were added to CTAB solution (1 mM, 20 ml) in sequence (b) Reaction solution was stirred at 30 °C for 10 min to form an Ag nanoparticle dispersion 2. Fabricate the coating of TiO₂ (a) Titanium(IV) isopropoxide (TTIP) was dropped into ethanol first and then the solution was added to the Ag alloy nanoparticle dispersions with the molar ratios 1:1 for Ag@TiO₂ nanoparticles (b) The mixtures were vigorously stirred and then mixed by an orbital shaker at room temperature to yield Ag@TiO₂ nanoparticles (c) The products were recovered by centrifugation, then washed with water to remove residues on the surface, and finally dried

	in an oven at 50 °C.
Estimated time	Until the product is dried

Table 2. Summary of fabrication of Ag@TiO₂ in journal (2).

Title of paper	Preparation and photocatalytic properties of Fe ³⁺ -doped Ag@TiO ₂ core-shell nanoparticles
Materials Required	- Hydrazine solution(N₂H₄) - Hexadecyl-trimethylammonium bromide (CTAB) - Silver nitrate solution(AgNO₃) - Titanium(IV) isopropoxide (Ti(OCH(CH₃)₂)₄ (TTIP) - Ethanol (C₂H₅OH) - Distilled water
Equipment Required	- Rotary evaporator - Oven
Steps	1. Preparation of Ag clusters (a) 3 ml of 1 mM aqueous hydrazine solution was added into 120 mL of 1 mM cetyltrimethylammonium bromide (CTAB) aqueous solution, and the mixture was stirred for 1 min at room temperature. (b) After 3 mL of 50 mM aqueous AgNO₃ solution was added to the above mixture, the resulting solution became dark brown, which means that Ag clusters were formed in a short time. (c) The final composite was stirred for another 10 min to make this redox reaction completed. 2. Preparation of Ag@TiO₂ core-shell-type nanoparticles An adequate amount of 1 mM titanium tetraisopropoxide (TTIP) ethanol solution was added to the highly dispersed Ag solution under vigorously stirring for 10 minutes at ambient temperature to obtain a suspension of Ag@TiO₂ core-shell-type nanoparticles with different Ag

	content. 3. Crystallization of Ag@TiO₂ nanoparticles (a) The excess solvent (ethanol and water) in the Ag@TiO₂ suspension was removed by rotatory evaporation until the Ag@TiO₂ powder was produced. The brown powder was hydrothermally crystallized at 180 °C for 12 hours. (b)The powder was rinsed by distilled water repeatedly and then dried at 80 °C.
Estimated time	1 day

Table 3. Summary of fabrication of Ag@TiO₂ in journal (3).

Title of paper	A highly sensitive ethanol sensor based on Ag@TiO ₂ nanoparticles at room temperature
Materials Required	• Deionized water • Silver nitrate solution (AgNO₃) • Trisodium citrate (C₆H₅Na₃O₇) • Potassium borohydride (NaBH₄) • Tetra-n-butyl titanate (C₁₆H₃₆O₄Ti) • Isopropanol (IPA;(CH₃)₂CHOH) • Distilled water • Ethanol (C₂H₅OH) • Oleic acid(C₁₈H₃₄O₂)
Equipment Required	• Magnetic stirrer • Centrifuge • Oven
Steps	1. Deionized water (47 mL), 0.5 mM silver nitrate solution (10 mL), and 0.5 mM Trisodium citrate (10 mL) were mixed in a beaker. 2. 10 mM Potassium borohydride (0.7 mL) was added to the solution. The solution turned from colorless to yellow as Ag nanoparticles were generated.

	3. The pH of the Ag nanoparticle solution was adjusted with oleic acid, and then 150 mL of IPA was added into the solution. 4. A solution of Tetra-n-butyl titanate (0.71 mL, 0.1 M) in IPA (25 mL) was slowly added drop-wise, with vigorous magnetic stirring, completing the preparation of the core-shell Ag@TiO₂ solution. 5. The core-shell Ag@TiO₂ was then separated through centrifugation, washed with distilled water and ethanol several times, and dried for 2 days at 60°C. 6. Finally, Ag@TiO₂ was calcined at 500°C for 3 h and cooled to room temperature.
Estimated time	3 days

2.5 Toxicology of Ag@TiO₂

One of the project aim is to apply Ag@TiO₂ inside a commercial product. Therefore, the safety of using nanoparticle is important. The literature study is divided into two parts: TiO₂ nanoparticles and Ag nanoparticles.

For TiO₂ nanoparticles, several studies had demonstrated that no penetration or translocation could happen through the skin [21-22]. Different scientists believed that it is safe to use in commercial products. In the market, a wide range of commercial products have already launched such as protection cream, textile fibers and wood preservatives. However, some potential danger may occur under long-term exposure.

Some study shown that titanium dioxide nanoparticles entering our pulmonary route can be very dangerous [22]. Titanium dioxide nanoparticles may then translocate to the brain or the systemic circulation which cause different diseases such as carcinogenesis, genotoxicity and immune disruption.

For silver nanoparticles, several studies shown that skin contact does not result in significant health effects [23]. However, the toxicological studies are largely inconsistent inside human bodies [23-24]. One of the reason is that the silver sample used in different experiment varies. Different particle size and shape are adapted so that the experiment effect on human bodies are inconsistency. Another reason is because there is lack of unified methodology in the planning the related biological experiment [25]. On the other hand, silver nanoparticles may have a negative impact on the environment. By considering only silver nanoparticles, it may be absorbed by some species and bioaccumulates in the food chain. However, silver nanoparticles could be highly dynamic in the environment. Different transformations can be occurred because of its high surface area and surface energy. Examples of transformations are oxidation, sulfurization and chlorination. Until now, no universal conclusion can be drawn about these transformations. Further *vivo* toxicity and transformation of silver nanoparticles investigation can be made in the future.

Chapter 3 TiO₂ powders fabrication procedures and results

3.1 Introduction, aim and related literature reviews

To start the investigation in photocatalytic materials and corresponding mechanisms, literature review 2.1 was done to examine the material properties of one of the most commonly used photocatalysts in water treatment and detoxification – titanium dioxide. It is found that the nanostructure and the size will affect the photocatalytic efficiency, and generally the efficiency can be enhanced by reducing its size. This is because smaller sizes refers to higher surface-to-volume ratio. Therefore, an experiment of fabricating titanium dioxide powders was designed to make sure this catalysis as small as possible. Literature review 2.2 was accomplished as a reference to design and modify this experiment. Two samples of using different titanium source were made by the hydrolysis method. Then the sample nanostructures and sizes were compared by using a transmission electron microscope.

3.2 Experiment setup

3.2.1 Materials and equipment required

3.2.1.1 Method of using titanium tetrachloride (TiCl₄) as Titanium source

Materials:

- Titanium tetrachloride
- Ethanol
- Iced deionized water

Equipment:

- Magnetic stirrer
- Centrifuge
- Oven

3.2.1.2 Method of using tetrabutyl titanate as titanium source

Materials:

- Tetrabutyl titanate
- Ethanol
- Hydrochloric acid
- Iced deionized water

Equipment:

- Magnetic stirrer
- Centrifuge
- Oven

3.3 Experiment procedures

3.3.1 Method of using titanium tetrachloride (TiCl₄) as Titanium source

1. 20 mL of ethanol is added into 1mL of iced deionized water.
2. 100 μ L of TiCl₄ is added into the solution with 15 minutes of stirring.
3. Centrifuge the solution for 15 minutes by 7500 rounds/min.
4. Remove the organics on the top of solution and add 5mL of iced deionized water.
5. Move the solution into a beaker and put it into a 60° C oven for 8 hours.
6. Grind the products into powder form and the product can be observed.

3.3.2 Method of using tetrabutyl titanate as titanium source

1. 0.68 mL of tetrabutyl titanate is added into 20 mL of ethanol.
2. 1 mL of hydrochloric acid is added into the solution as a stabilizer.
3. 0.2 mL of deionized water is added into the solution and stirred for 2 hours.
4. Centrifuge the solution for 15 minutes by 7500 rounds/min.
5. Remove the organics on the top of solution and add 5mL of iced deionized water.
6. Move the solution into a beaker and put it into a 90°C oven for 1 hours.
7. Grind the products into powder form and the product can be observed.

Take small amount of both powders and dissolve them into 1 mL of deionized water.

Drop a drop of both samples to the TEM support grids respectively for TEM analysis.

3.4 Results and discussions

The TEM results are as followed:

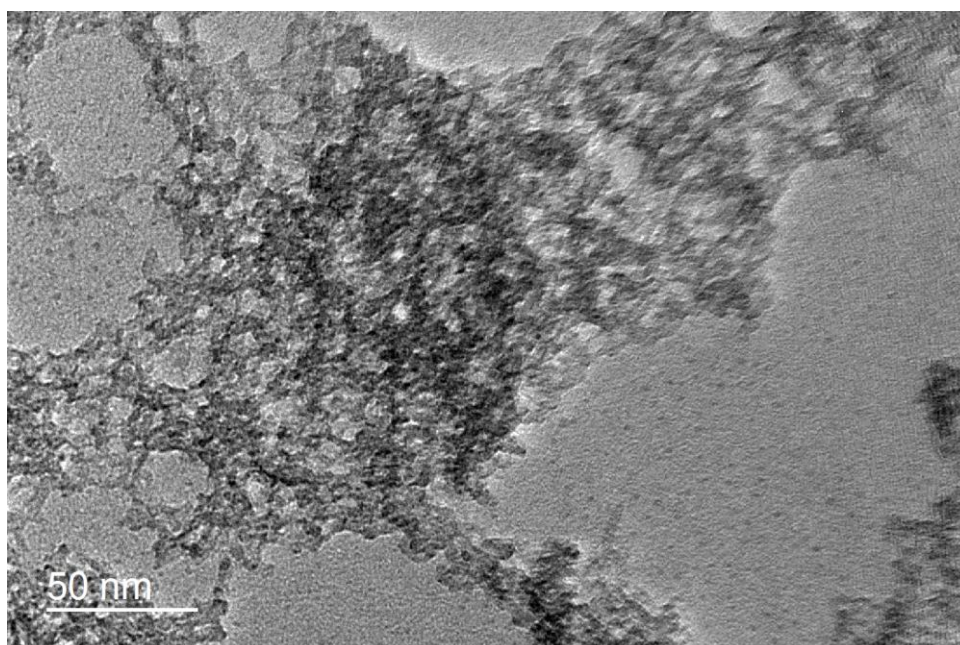


Figure 7. TEM result of TiO₂ particles fabricated by using Titanium tetrachloride.

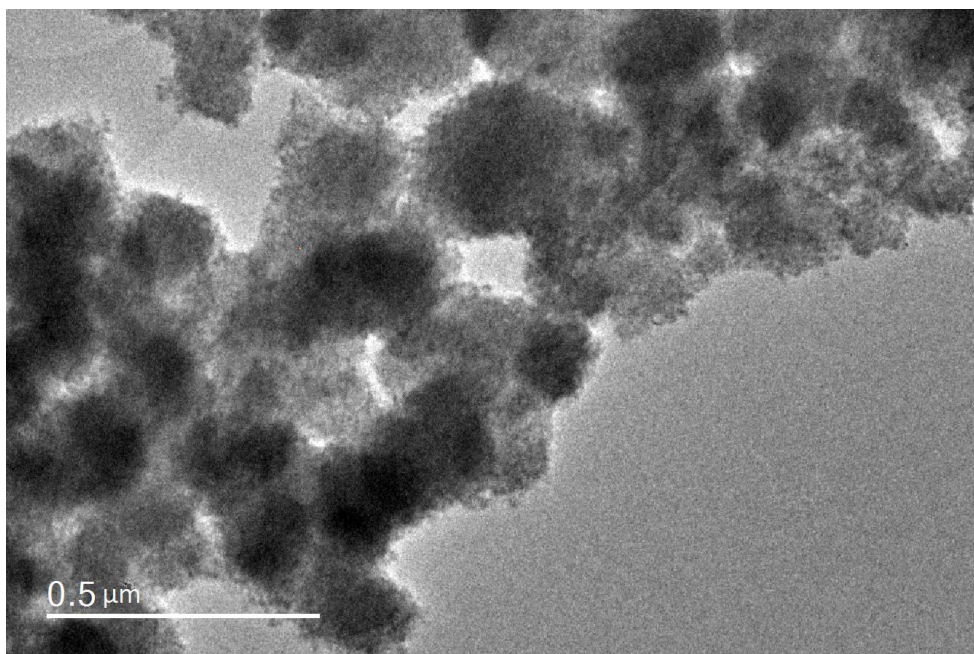


Figure 8. TEM result of TiO₂ particles fabricated by using tetrabutyl titanate.

Discussion:

Both samples do not show the characteristics of a great catalyst. First, both samples have a relatively large size in terms of few hundred nanometers. An ideal catalyst should have a diameter of 1 to 100 nanometers in order to have a huge surface-to-volume ratio. Second, no obvious crystalline structure can be obtained from both samples. This implies that the reaction is not perfectly completed. This implies that some of the titanium atom cannot react with the oxygen atom and different by-product can be obtained. Both characteristics are negatives for the photocatalytic reaction of methylene blue (Formaldehyde) degradation. Other methods of fabricating TiO₂ should be found to improve the photocatalytic efficiency.

Chapter 4 Formaldehyde test by using photo-ionization detector

4.1 Introduction

In order to detect the efficiency of the photocatalysts, experiments have to be done to measure the amount of formaldehyde decomposition before and after the use of photocatalysts. Therefore, an photo-ionization detector (formaldehyde detector) was bought for this purpose. Before any experiment started, a simple test was done to test the accuracy of the photo-ionization detector. Ball samples that claimed to use anti-formaldehyde technology to purify the indoor air were put near the formaldehyde solution. The change of formaldehyde amount was measured through the detector to test whether the detector can work normally or not.

4.2 Experiment setup

4.2.1 Materials and equipment required

Materials required:

- Formaldehyde solution
- Ball samples (bought in Okamoto)
- Formaldehyde detector

Equipment required:

- Fume hood
- Beaker

4.2.2 Photo-ionization detector set up

Before using the formaldehyde detector, it should be put under sunlight for 30 minutes at outer. This step is used to calibrate the detector for better accuracy. Then the formaldehyde detector is ready to use.

4.3 Experiment procedures

1. Wear a mask since formaldehyde solution is harmful to human body.
2. Formaldehyde detector is put into the fume hood. Record the initial reading of formaldehyde amount.
3. Formaldehyde solution is put into the fume hood for 15 second. Observe the reading of formaldehyde amount.
4. After 15 second, remove the formaldehyde solution. Then put the ball sample inside the fume hood for five minutes. Measure the reading of formaldehyde amount.

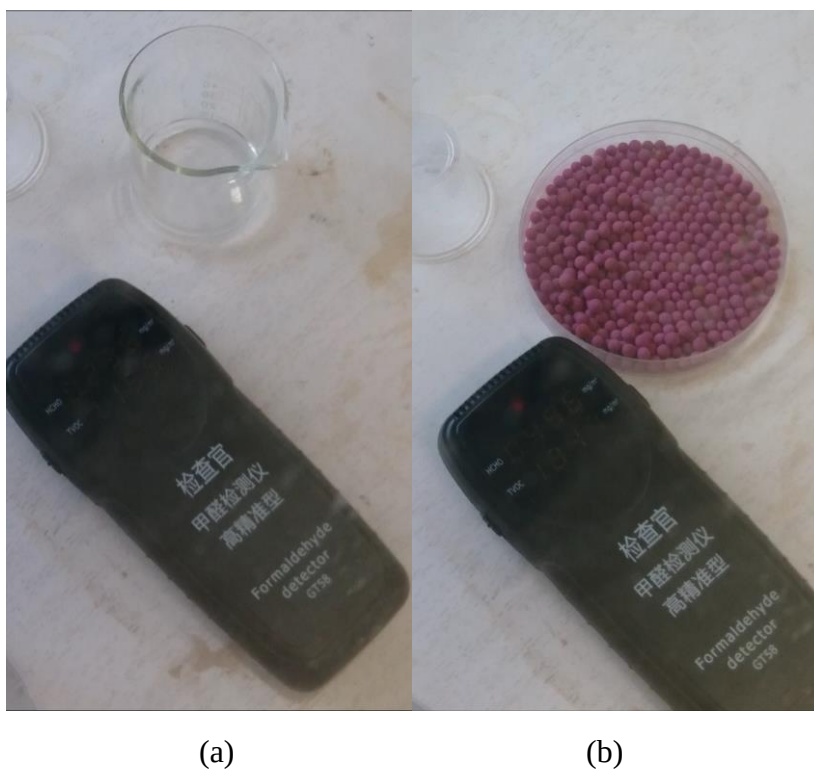


Figure 9. (a) Detector record after the formaldehyde detector just put inside the fume hood. (b) Detector record after the ball samples put in the fume hood for three minutes.

5. Ventilate the fume hood and repeat the experiment step 1-3.

4.4 Results and discussions

Detector errors were obtained in this experiment for two times. After the formaldehyde solution is put inside the fume hood, the record “8.888” was displayed for more than two minutes. This may be caused by the sudden increase of formaldehyde amount. Also, the reading fluctuation is huge in a short period (two minutes). Both observations show that the detector cannot function normally and is not very reliable.

Besides the inaccuracy of the detector, there are several disadvantages of using formaldehyde as a medium to test the efficiency of the photodetector. First, the experiment is difficult to control. The photodetector can only detect the formaldehyde amount in the air. The formaldehyde molecule in air can easily diffuse to any place irregularly but the detector and ball sample can only be put at one specific position only. Second, the formaldehyde amount indoors may vary during different times when performing the experiment. This may affect the experiment result.

*Remark: This project was named “Photocatalytic TiO₂ nanoparticle fabrication” at the early state of the project (In period of Chapter 3-4). The name was changed to “Photocatalytic Ag@TiO₂ nanoparticle fabrication and its application in methylene blue degradation” based on the experimental result and further investigations.

Chapter 5 Ag@TiO₂ nanoparticles fabrication with corresponding degradation test with methylene blue

5.1 Introduction, Aim and Related literature reviews

After discovering the problems found in chapter 3 and 4, literature reviews were done in order to improve and re-design the experiment. First, to improve the size distribution and photocatalytic efficiency of TiO₂ nanoparticles, it is found that depositing TiO₂ nanoparticles onto the surface of noble metals nanoparticles can improve the photocatalytic activity of TiO₂ under the visible light irradiation, as introduced in literature review 2.3. Second, to enhance the accuracy of detecting photocatalysts efficiency, it was found that the degradation of methylene blue shares the same mechanism as the degradation of formaldehyde [26]. Therefore, the degradation test of methylene blue can act as an indicator of photocatalytic activity of the TiO₂ sample.

This experiment is divided into two sections. The first section is to produce Ag@TiO₂ by using different titanium source. The second section is to characterize the samples made in the first section by TEM and UV spectrum. After that, data are analyzed to examine: (a) Whether Ag@TiO₂ sample is successful made and blind together (b) Size of the samples (c) Degradation effect in methylene blue with different wavelength of light irradiation (d) Comparing the degradation effect of methylene blue between Ag@TiO₂ and TiO₂.

5.2 Experiment setup

5.2.1 Materials and equipment required for fabricating Ag@TiO₂

Materials required:

- Silver nitrate powder
- Sodium borohydride
- Titanium(IV) isopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ (TTIP)
- Tetra-n-butyl Titanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$)
- Poly-ethylene glycol (PEG)
- Ethanol ($\text{C}_2\text{H}_5\text{OH}$)
- Deionized water

Equipment used:

- Magnetic stirrer
- Mortar and pestle
- Centrifuge
- Oven

5.2.2 Materials and equipment required for samples characterization

Equipment required:

- TEM support grids
- Cuvette
- UV spectrometer
- Transmission electron microscope

5.3 Experiment procedures

5.3.1 Fabrication of Ag@TiO₂ nanoparticles

Synthesizing Ag@TiO₂ consists of four main steps. They are preparing of the silver nanoparticles, preparing of titanium oxide coating, adding titanium oxide coating to silver nanoparticles and developing Ag@TiO₂ powder. Three samples are made by using different Titanium source: Titanium(IV) isopropoxide (Ti(OCH(CH₃)₂)₄ (TTIP) and Tetra-n-butyl Titanate (C₁₆H₃₆O₄Ti).

Step 1. Preparation of the silver nanoparticles

	First and Second Trial
Chemicals used	• Silver nitrate powder (Silver Source) • Sodium borohydride (Reduction agent) • Poly-ethylene glycol (PEG) (Surfactant, stabilizer)
Steps	(a) Silver nitrate (17 mg) and Sodium borohydride (15 mg) were separately dissolved in 90mL ice chilled nanopore water. Then mix the two solutions and stir for 5 min. (b) Add 10 mL of solution containing 500 mg of PEG and stir for three minutes (c) Heat the solution at 90-95 °C for 30 minutes



Figure 7. Silver nanoparticles fabricates in the first (left) and second (right) trial.

Step 2. Preparation of Titanium dioxide coating

	First Trial	Second Trial
Chemical used	- Titanium(IV) isopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ (TTIP) - Ethanol ($\text{C}_2\text{H}_5\text{OH}$)	- Tetra-n-butyl Titanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) - Ethanol ($\text{C}_2\text{H}_5\text{OH}$)
TTIP:Ethanol ratio	40 μL :10mL	Two samples (i) 20 μL :10mL (ii) 40 μL :10mL

Step 3. Adding Titanium dioxide coating to silver nanoparticles

	First and Second trial
Steps	(a) Deionized water is added to 1mL Ag solution till 10mL (b) Centrifuged the sample at 6000 rpm for 15 min (c) Remove the organic chemicals on the top and add 200 μL of ionized water (d) Add the TTIP sample to the Ag solution and have a 15 min magnetic stirring (repeat 3 times)

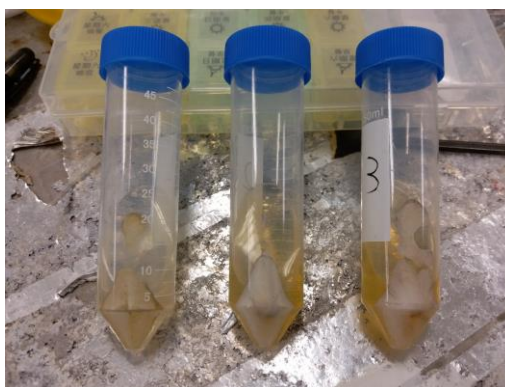


Figure 8. Silver nanoparticles after centrifuged.

Step 4. Develop Ag@TiO₂ powder to increase the yield

	First and Second trial
Steps	(a) Put the solution inside the oven for 12 hours (b) Grind the products into powder (c) Dissolve the powder into 2mL of water for further test

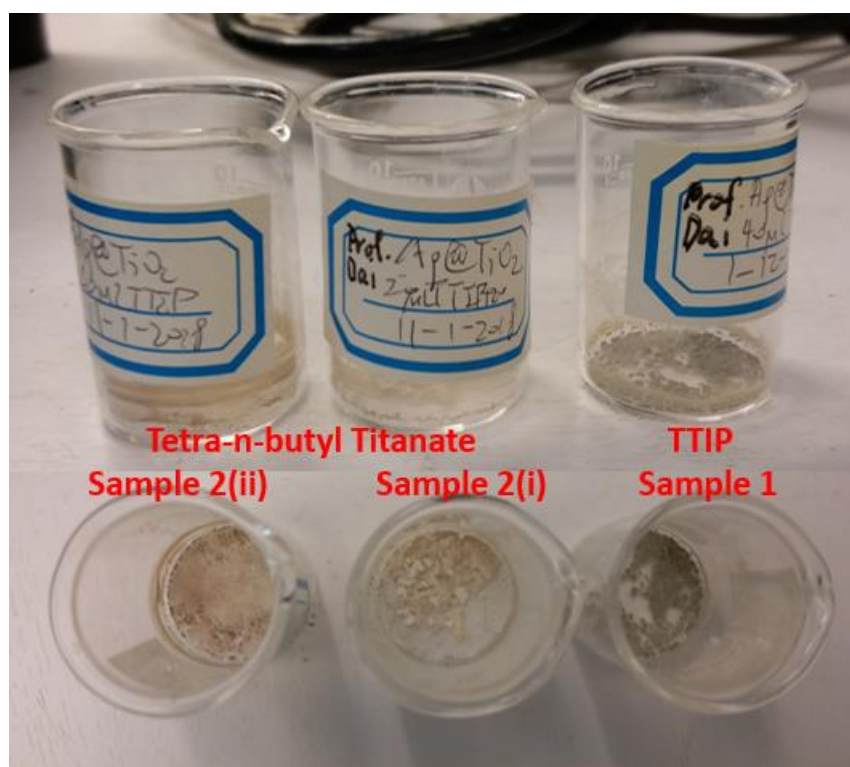


Figure 9. Ag@TiO₂ powders developed after heating in the oven.

5.3.2 Degradation test of methylene blue by using Ag@TiO₂

Step 1. Drop the Ag@TiO₂ solution to fill up the cuvette.

Step 2. Put the cuvette into the UV spectrometer.

Step 3. Start the detection by selecting the detecting wavelength of 200-900 nm.

Step 4. Save the spectrum graph.

Step 5. Clean the cuvette by deionized water and repeat step 1-4 for the other two samples.

Step 6. Put three samples under the UV light for 5 minutes for investigating the UV influence to the degradation effect in the samples.

Step 7. Repeat step 1-5 by using the samples that shining under UV for 5 minutes.

Step 8. Put three samples under the UV light for 5 minutes more.

Step 9. Repeat step 1-5 by using the samples that shining under UV for 10 minutes.

5.4 Results and discussions

5.4.1 TEM characterization

The TEM results are as following:

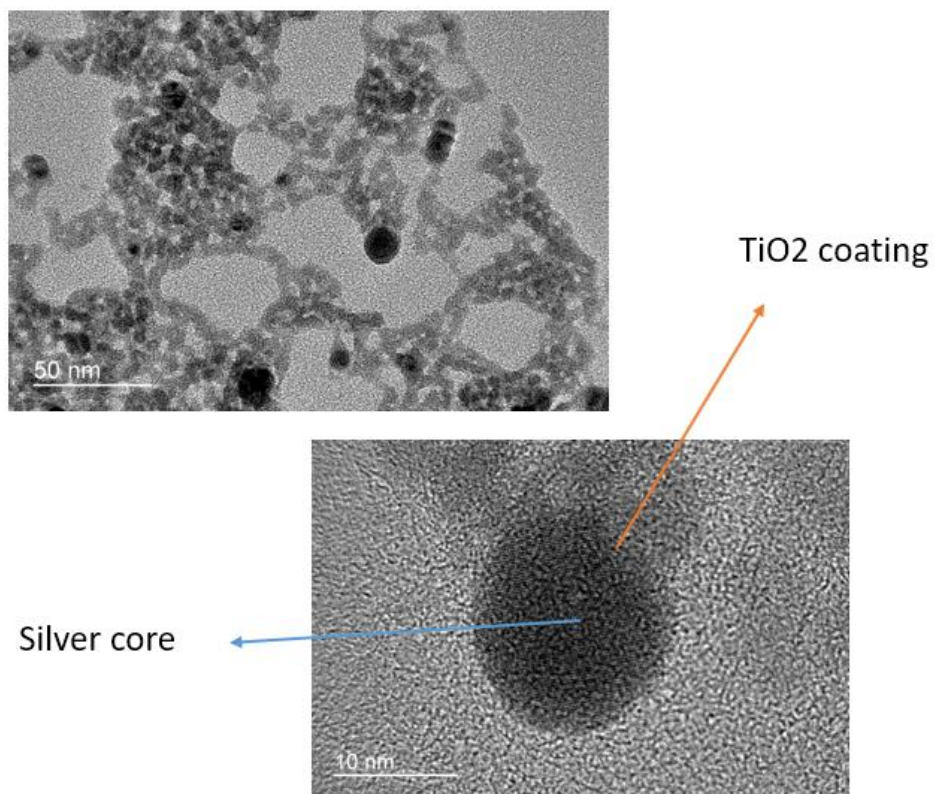


Figure 10. TEM image of Ag@TiO₂ by using Titanium(IV) isopropoxide as Ti source.

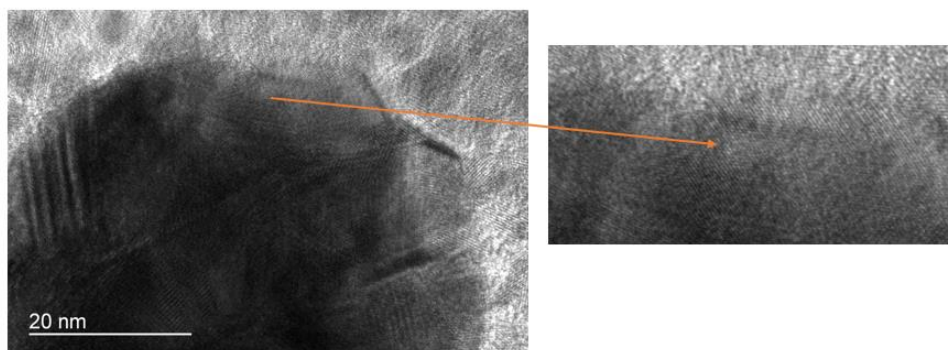
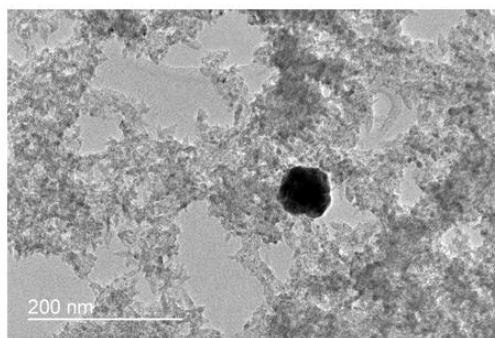


Figure 11. TEM image of Ag@TiO₂ by using Tetra-n-butyl titanate as Ti source.

From the TEM measurement, Ag@TiO₂ by using Titanium(IV) isopropoxide has a diameter of 13 nm while the one using Tetra-n-butyl titanate has a diameter of 60 nm. Both samples fall in the nanotechnology range of 1-100 nm. This refers to larger surface area and hence owns a better photocatalytic activity.

Both TEM images show that the titanium coating and the silver core forms a heterojunction structure. Although no core-shell structure forming as expected, heterojunction structure may also show a good photocatalytic property. This means that the silver and TiO₂ are successfully blend together. Furthermore, Ag@TiO₂ using tetra-n-butyl titanate even shows crystalline structure after calcination, which is shown in the lower part of figure 11. Both observations show that Ag@TiO₂ is an excellent photocatalyst.

5.4.2 UV spectrum characterization

5.4.2.1 UV spectrum results of Ag@TiO₂

The UV spectrum results of Ag@TiO₂ are as followed:

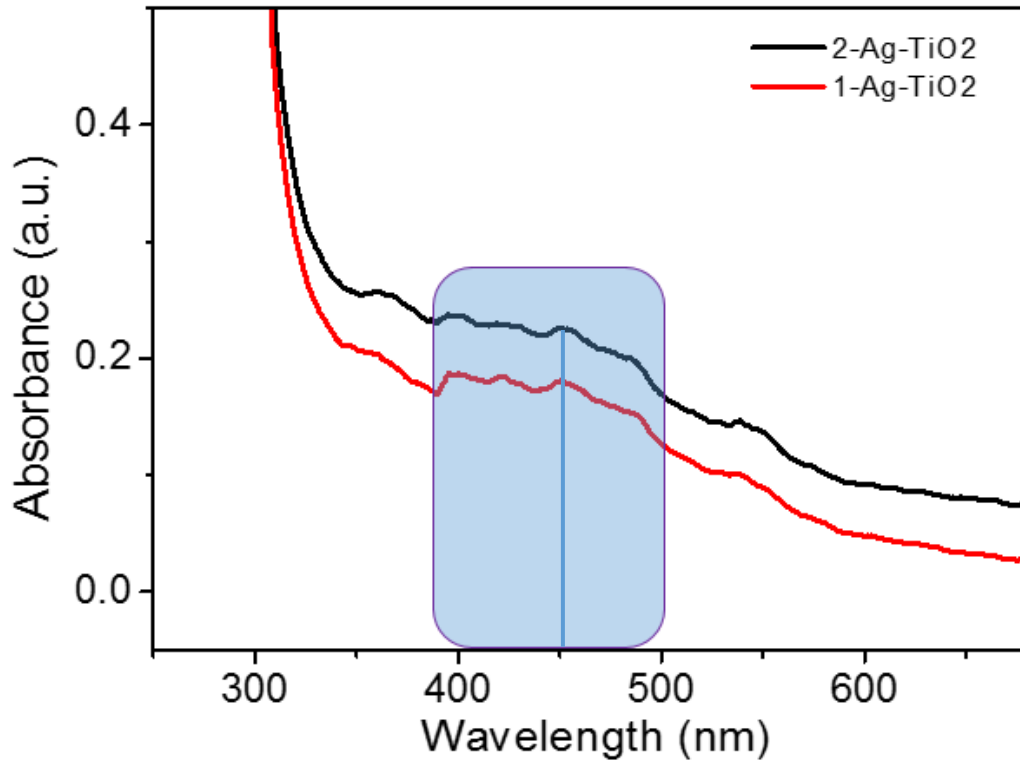


Figure 12. UV spectrum of Ag@TiO₂ sample 1 and sample 2(ii).

From figure 12, the absorbance peak for both Sample 1 and 2(ii) are around 452 nm. This matches the peak of absorbance of Ag@TiO₂ from the reference of around 460 nm [27]. Therefore, this is another evidence that Ag@TiO₂ are successfully fabricated.

5.4.2.2 UV spectrum results of Ag@TiO₂ mixed with methylene blue

The UV spectrum results of Ag@TiO₂ mixed with methylene blue are as followed:

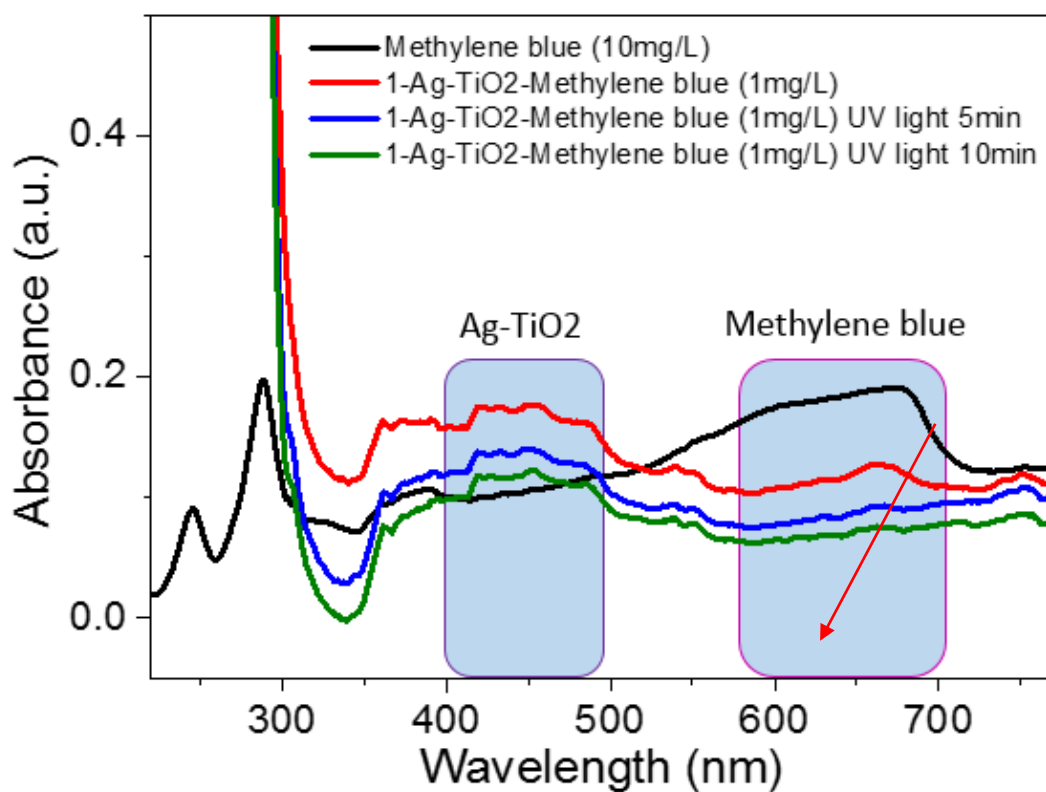


Figure 13. UV spectrum of Ag@TiO₂ sample (made of TTIP) with methylene blue.

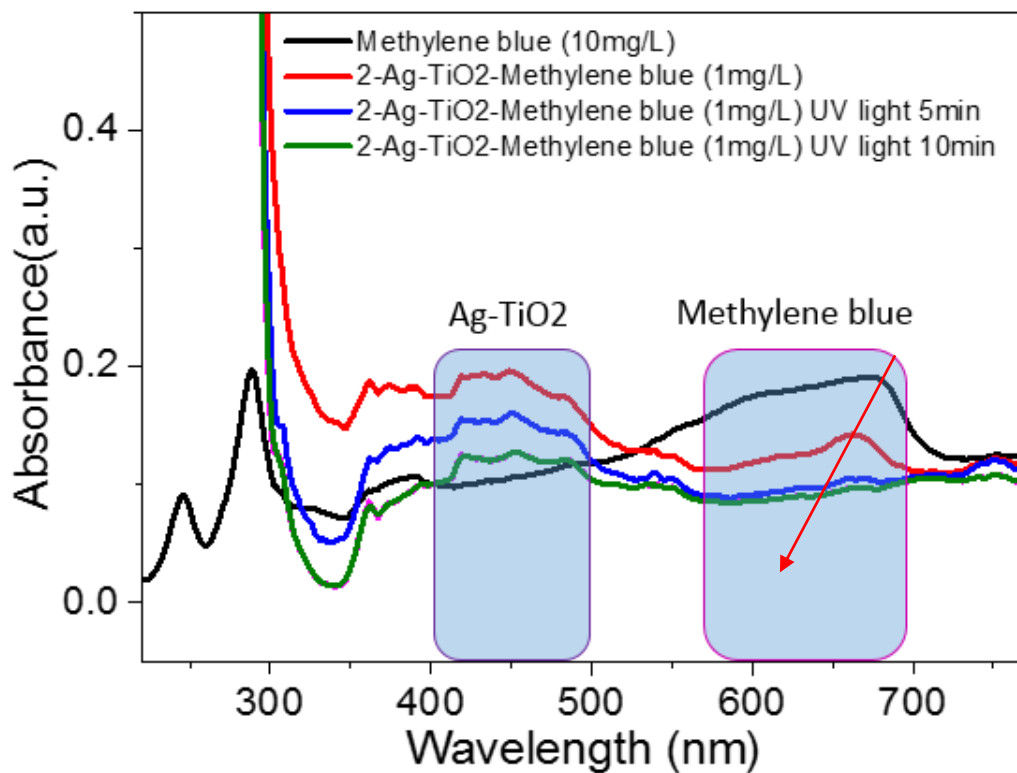


Figure 14. UV spectrum of Ag@TiO₂ sample (made of tetra-n-butyl titanate) with methylene blue.

Methylene blue has two local absorption peaks of 668 nm and 609 nm [28]. If we can detect absorbance of the corresponding peak decrease after adding the photocatalyst into the methylene blue, it implies that Ag@TiO₂ can successfully decompose the amount of methylene blue. From figure 13 to figure 14, both grafts show that the absorption peak near 668 nm has a sharp decline immediately after Ag@TiO₂ samples are added into the methylene blue, regardless of the titanium source. The absorbance peak reduces from 0.18 to 0.12 for Ag@TiO₂ made by TTIP source while the absorbance peak reduces from 0.18 to 0.14 for Ag@TiO₂ made by tetra-n-butyl titanate source. The result shows that using TTIP as titanium source has a better photocatalytic efficiency.

Moreover, both grafts show that the absorbance reduces continuously after putting the sample under UV light for 5 to 10 minutes. This shows that further shining the sample under UV light can enhance the efficiency, although this is not the aim of this project. The peak of the absorbance in the methylene blue experiences a blue shift from 680 nm to 660nm in both figures, which is another evidence of methylene blue degradation. The peak of the absorbance in the Ag@TiO₂ part does not have a shift.

5.4.3 Degradation effect in methylene blue comparison between Ag@TiO₂ and TiO₂

In order to examine whether depositing TiO₂ on the silver can really enhance the efficiency or not, other set of samples were made by using tetra-n-butyl titanate as the titanium source with the same steps shown in section 5.3.1. The only difference is that

extra set of TiO_2 were fabricated at 5.3.1 step 2 as a control sample. Silver nanoparticles were not added to this control sample. UV spectrum characterization were completed and the result is as followed:

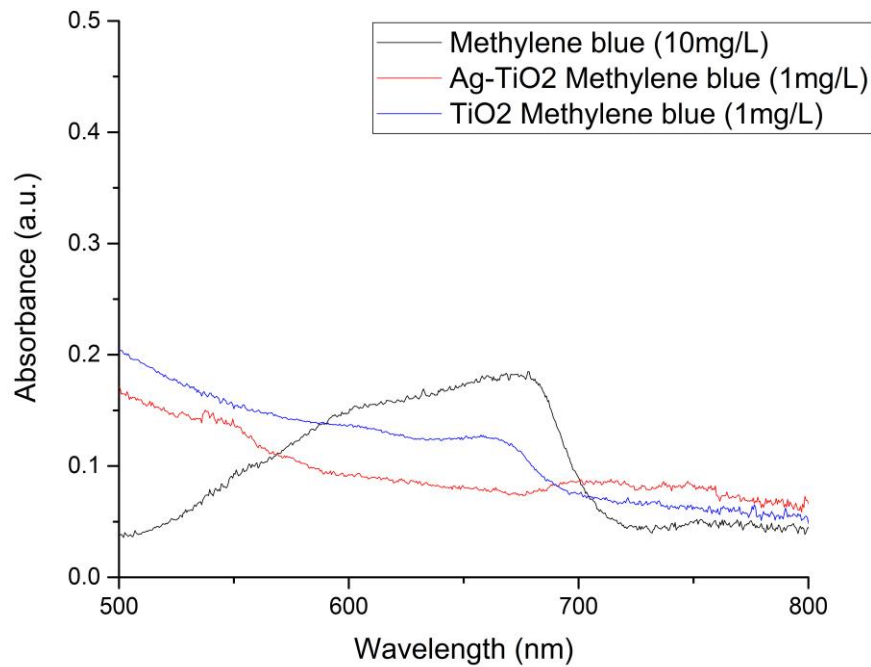


Figure 15. UV spectrum of Ag@TiO_2 (made of tetra-n-butyl titanate) and TiO_2 added with methylene blue

From figure 15, the absorption peak of mixed methylene blue and TiO_2 is 0.13 while that Ag@TiO_2 is lower than 0.1. This shows that Ag@TiO_2 can degrade more methylene blue and have a greater efficiency than the TiO_2 . This result matches the theory shown in literature review 2.3.

Chapter 6 Mass production of Ag@TiO₂

6.1 Introduction, Aim and Related literature reviews

After the successful synthesis of Ag@TiO₂ nanoparticles with satisfying photocatalytic efficiency, we further investigated the possibility of commercializing the product. First, literature review 2.5 was done which related to the safety of using nanoparticle. It is concluded that a wide range of commercial products made of silver and TiO₂ nanoparticles have already launched the market although some potential hazard to human or the environment may exist. After that, we tried to manufacture Ag@TiO₂ in a much greater amount comparing to the amount we fabricated in chapter 5, which is about 1g of Ag@TiO₂ per trial. In this experiment, five grams of Ag@TiO₂ are expected to made. During the mass production process, we tried to observe if any difficulties may occur with a greater portion of products.

6.2 Experiment setup

6.2.1 Materials and equipment required for fabricating Ag@TiO₂

Materials required:

- Silver nitrate powder
- Sodium borohydride
- Tetra-n-butyl Titanate (C₁₆H₃₆O₄Ti)
- Poly-ethylene glycol (PEG)
- Ethanol (C₂H₅OH)

- Deionized water

Equipment used:

- Magnetic stirrer
- Centrifuge
- Oven

6.3 Experiment procedures

Step 1. Preparation of the silver nanoparticles

	Mass production Trial
Chemicals used	• Silver nitrate powder (Silver Source) • Sodium borohydride (Reduction agent) • Poly-ethylene glycol (PEG) (Surfactant, stabilizer)
Steps	(c) Silver nitrate (85 mg) and Sodium borohydride (75 mg) were separately dissolved in 200mL ice chilled nanopore water. Then mix the two solutions and stir for 5 min. (d) Add 100 mL of solution containing 500 mg of PEG and stir for three minutes (c) Heat the solution at 90-95 C for 30 minutes

Step 2. Preparation of Titanium dioxide coating

	Mass production Trial
Chemical used	• Tetra-n-butyl Titanate ($C_{16}H_{36}O_4Ti$) • Ethanol (C_2H_5OH)
TTIP: Ethanol ratio	200μL:50mL (5 bottles Titanium oxide coating required)

Step 3. Adding Titanium dioxide coating to silver nanoparticles

	Mass production trial
Steps	(a) Deionized water is added to 5mL Ag solution till 50mL (b) Centrifuged the sample at 6000 rpm for 15 min (c) Remove the organic chemicals on the top and add 1 mL of ionized water (d) Add the TTIP sample to the Ag solution and have a 15 min magnetic stirring (repeat 3 times)



Figure 16. Adding Titanium dioxide solution into silver nanoparticles solution.

Step 4. Develop Ag@TiO₂ powder to increase the yield

	Mass production trial
Steps	(a) Put the solution inside the oven for 12 hours (b) Grind the products into powder

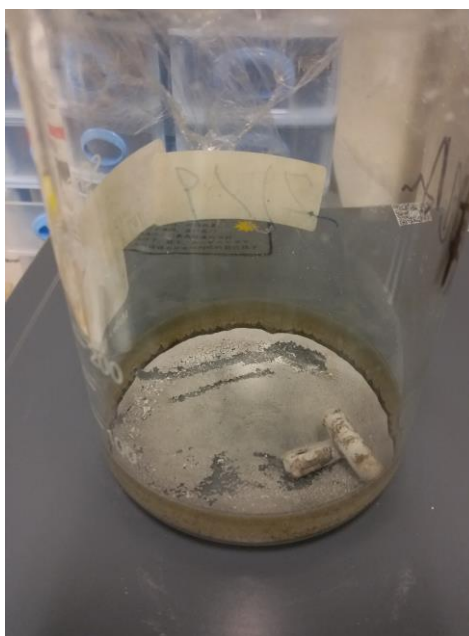


Figure 17. Mass produced Ag@TiO₂ powders developed after heating in the oven.

6.4 Results and discussions

From measurement, 6.3g of Ag@TiO₂ powders were produced which met the anticipation of this experiment. Since five times of titanium source and silver source are used in this experiment, we expect to have the output of about 5 grams. The excess amount of product may be caused by the relatively small percentage of transaction loss when we were shaving out and grinding the powders.

We had found several difficulties when trying the mass production. First, the required amount of iced deionized water (about 1L) and ethanol (about 250mL) is huge comparing with the amount of output (6.3g). It seems that the amount of ethanol and water used can be reduced without affecting the experiment results and corresponding efficiency. This may reduce the manufacturing cost. Second, the silver and TiO₂ tends to form clusters after they sink to the bottom of the beaker when the amount of

corresponding source added increases. This situation drags on the reaction between silver and TiO_2 . Also, the product size seems to be larger since the silver and TiO_2 particles tend to stick together. Further investigations can be done to tackle this type of mass manufacturing issues.

Chapter 7 Conclusions and future recommendation

7.1 Conclusions

In this project, Ag@TiO_2 was successfully fabricated by two different titanium sources with the diameter of 13 nm and 60 nm respectively. From the TEM image, heterojunction structure of Ag@TiO_2 can be obtained which implies that the titanium dioxide nanoparticles can be successfully deposit onto the surface of silver nanoparticles.

From the UV spectrum analysis, the absorption peak of methylene blue reduces after mixing with the Ag@TiO_2 nanoparticles solution. Comparing with the conventional TiO_2 particles, the hybrid Ag@TiO_2 nanostructure has a greater effect on methylene blue degradation. Moreover, the photocatalysis reaction can be done under visible light irradiation by adopting the Ag@TiO_2 . Last but not least, mass production of Ag@TiO_2 was successfully carried out for discovering possible tactical problems.

7.2 Future recommendations

To further enhance the efficiency of this photocatalysts, an optimized structure of Ag@TiO₂ with a controllable thickness of TiO₂ can be fabricated in order to trap more light so that the catalytic efficiency can be further improved. Moreover, other photocatalysts with similar degradation mechanisms such as porous CeO₂ can be further investigated and fabricated as a comparison for choosing photocatalysts with greater efficiency.



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