

CHAPTER IV

RESULTS AND DISCUSSION

CeO₂ nanoparticles are metal oxides which can be used in various applications, and is commonly used in catalytic converters. This project will emphasize on using CeO₂ as a photo-catalyst for waste water treatment. However, to further improve CeO₂ for photo-catalytic activity, materials such as polyelectrolytes and Ag nanoparticles were used to enhance the photo-catalytic activity. This work consists of three parts. First, is the synthesis of cerium oxide which involves the study of the best conditions to synthesize CeO₂. Second, Ag nanoparticles were incorporated with CeO₂. Ag nanoparticles were added to prevent the recombination reaction and enhanced photon harvest of CeO₂. Finally, the CeO₂ was synthesized with polyelectrolytes. The addition of polyelectrolytes will help control the size of CeO₂ by electrostatic interaction between polyelectrolyte and the cerium ions; since it can prevent the agglomeration between cerium ions via Van der Waals interaction.

4.1 Synthesis of Cerium Oxide (CeO₂)

CeO₂ can be synthesized by 3 techniques i.e. hydrothermal, sol-gel, and precipitation technique. In this work, CeO₂ nanoparticles were prepared by precipitation technique by using Ce(NO₃)₃·6H₂O as precursor. Na₂CO₃ was added into Ce(NO₃)₃·6H₂O to adjust the pH to 8.0 and induces precipitation of Ce(NO₃)₃·6H₂O to Ce(OH)CO₃ while stirring. Then, Ce(OH)CO₃ powder was calcined at 550 °C for 6 hours to convert it into CeO₂ nanoparticles.

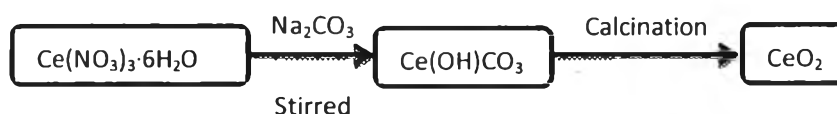


Figure 4.1 Flow chart of the synthesis of CeO₂ nanoparticles.

4.1.1 Find the Best Condition to Synthesize CeO₂ for Photo-catalytic Application

There are various conditions to synthesize CeO₂ but the parameters studied in this research are aging temperature (at 60 °C and at room temperature), speed of adding Na₂CO₃ (quickly and slowly) and mixing method (stirred and sonication). The best conditions will be chosen from the product that produces the most efficient photo-catalytic activity. The photo-catalytic activity was studied by mixing 5 ppm methyl violet dye (MV) and 0.1 g CeO₂ then put it under UV irradiation for 5 hours. Photo-catalysis is when CeO₂ received enough energy from the UV light, the electrons from the valence band will be excited to the conduction band which produces positively charged holes and negatively charged electrons. Both charges can produce radicals which can react with double bond in the MV structure dye into smaller molecules. Therefore, the absorbance intensity of MV will be decreased with time.

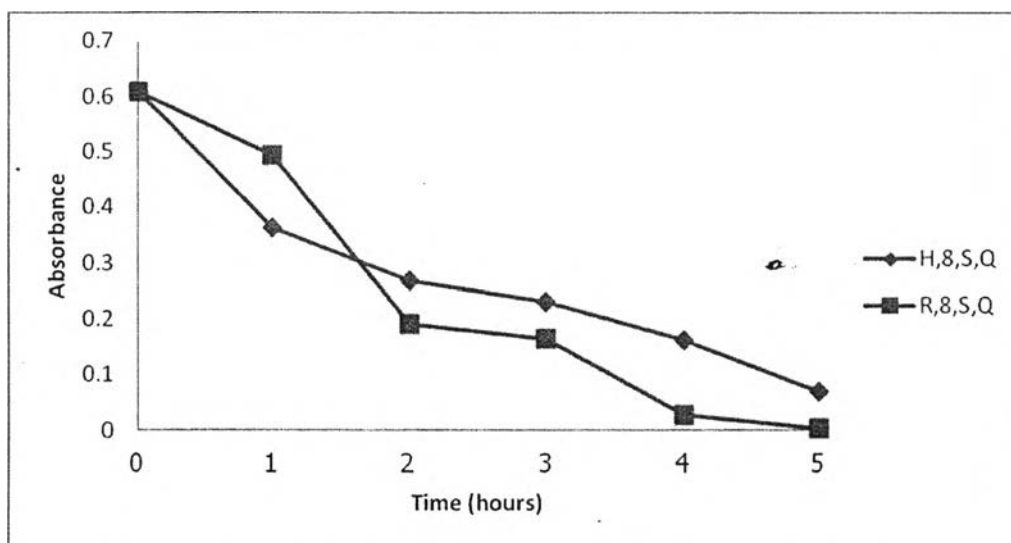


Figure 4.2 Compare the photo-catalytic activity between CeO₂ synthesized at room temperature and heated at 60 °C (H=heat, R=room temperature, 8=pH, S=stirred and Q=adding Na₂CO₃ quickly).

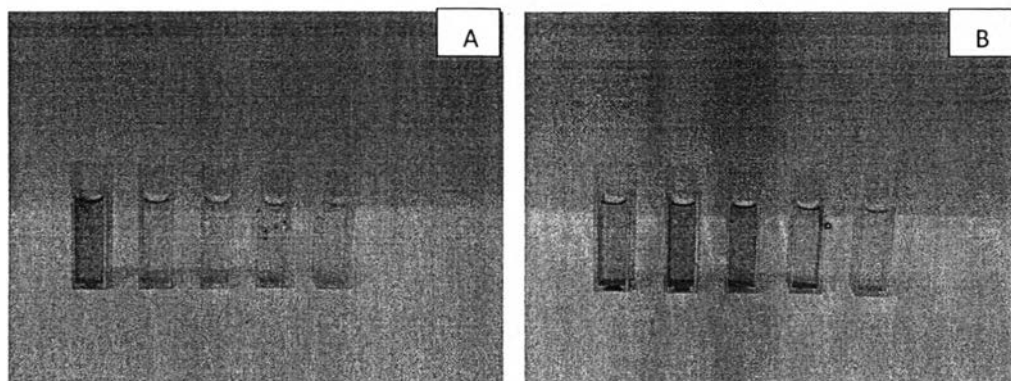


Figure 4.3 Compare the photo-catalytic activity of CeO_2 which synthesized at 60 °C and room temperature; (A) R, 8, S, Q (B) H, 8, S, Q.

The result from Fig.4.2-4.3 was showed the comparison between photo-catalytic activities of CeO_2 between CeO_2 synthesized at room temperature and at 60 °C. It is shown that CeO_2 synthesized at room temperature is slightly better than that at 60 °C due to higher photo-catalytic activity because at 60 °C heating does not produce enough energy to separate the $\text{Ce}(\text{OH})\text{CO}_3$ which can agglomerate by Van der Waals force. Also, the heat energy at 60 °C caused the $\text{Ce}(\text{OH})\text{CO}_3$ particles to move faster which increase the opportunity to be in contact with other $\text{Ce}(\text{OH})\text{CO}_3$ and induce the agglomeration. Therefore, after calcination of $\text{Ce}(\text{OH})\text{CO}_3$, CeO_2 nanoparticles will be bigger. Thus, reduces specific surface area which decreases the photo-catalytic activity of CeO_2 .

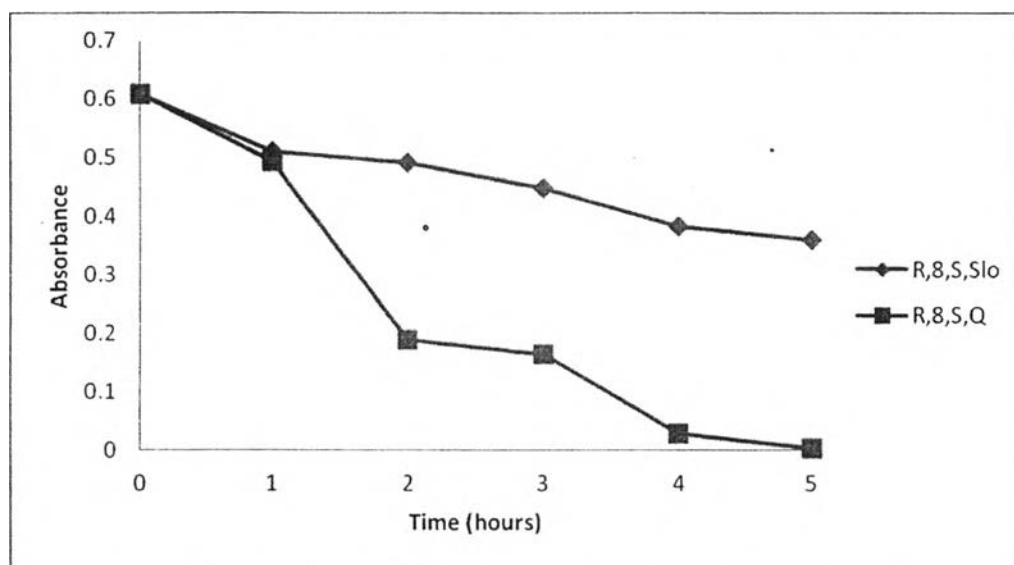


Figure 4.4 Compare the photo-catalytic activity between CeO₂ synthesized by adding Na₂CO₃ slowly and quickly (R=room temperature, 8=pH, S=stirred, Slo=adding Na₂CO₃ slowly and Q=adding Na₂CO₃ quickly).

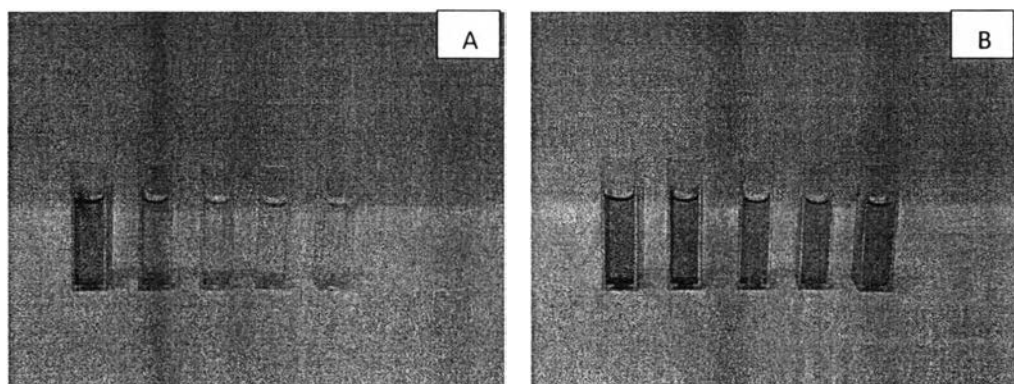


Figure 4.5 Picture of methyl violet in the presence of CeO₂ which synthesized by quickly and slowly added Na₂CO₃ at 0 to 5 hours; (A) R, 8, S, Q (B) R, 8, S, Slo.

Fig.4.4-4.5 shows the comparison between the photo-catalytic activities of CeO₂ synthesized by adding Na₂CO₃ slowly and adding Na₂CO₃ quickly. The photo-catalytic of CeO₂ synthesized by adding Na₂CO₃ quickly is

better than CeO_2 synthesized by adding Na_2CO_3 slowly due to the different between sizes of CeO_2 nanoparticles. Furthermore, CeO_2 synthesized by adding Na_2CO_3 slowly are bigger than CeO_2 synthesized by adding Na_2CO_3 quickly because it has more time for $\text{Ce}(\text{OH})\text{CO}_3$ to grow.

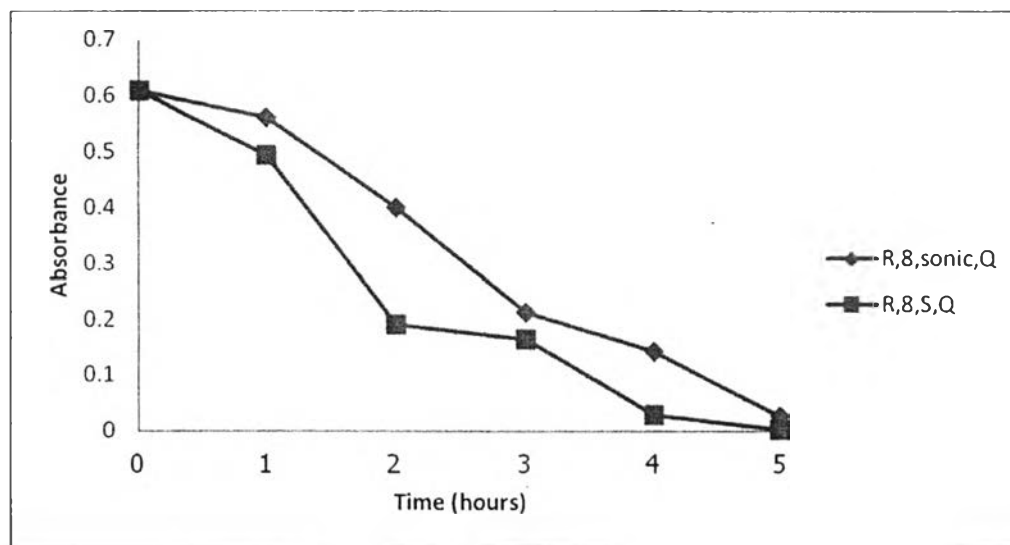


Figure 4.6 Compare the photo-catalytic activity between CeO_2 synthesized by sonication and stirring (R=room temperature, 8=pH, S=stirred, sonic=sonication and Q=adding Na_2CO_3 quickly).

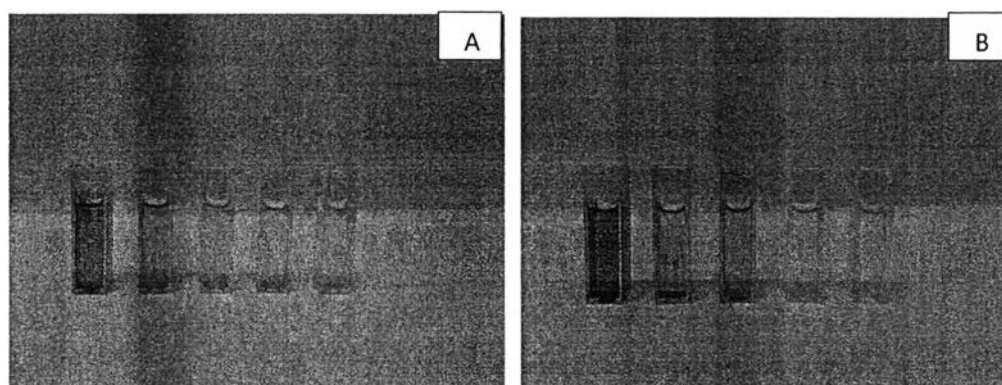


Figure 4.7 Compare the photo-catalytic activity of CeO_2 which synthesized by sonicated and stirred condition; (A) R, 8, S, Q (B) R, 8, sonic, Q.

Results from Fig.4.6-4.7 show the comparison of the photo-catalytic activities between stirring and sonication of CeO_2 during synthesis. It can be seen that the photo-catalytic activity of both condition are alike. However, this research will use stirring condition to synthesize CeO_2 due to using less energy. From the result of various conditions, CeO_2 synthesized at room temperature by adding Na_2CO_3 quickly while stirring is the best condition due to the highest in photo-catalytic activity.

4.1.2 The Morphology of $\text{Ce}(\text{OH})\text{CO}_3$ and CeO_2 Nanoparticles

The morphology and size of $\text{Ce}(\text{OH})\text{CO}_3$ and CeO_2 nanoparticles was investigated by using FE-SEM.

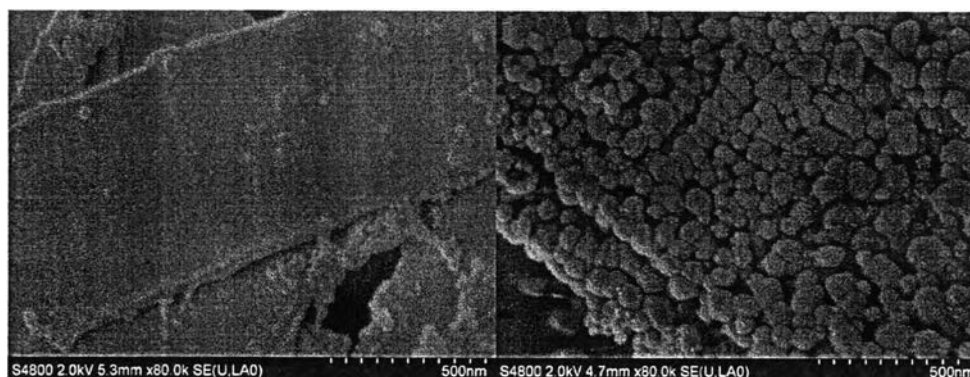


Figure 4.8 Show FE-SEM image of; (A) $\text{Ce}(\text{OH})\text{CO}_3$ and (B) CeO_2 nanoparticles.

Fig. 4.8(A) shows that $\text{Ce}(\text{OH})\text{CO}_3$ has a flake-like morphology and has smooth surface. The CeO_2 nanoparticles agglomerates and have smooth surface with average size 84.7 nm as shown in Fig. 4.8(B).

4.1.3 Study the Charges on the Surface of $\text{Ce}(\text{OH})\text{CO}_3$ for Synthesis of CeO_2

4.1.3.1 Effect of pH on Cerium Hydroxy Carbonate ($Ce(OH)CO_3$)

Charges on the surface of $Ce(OH)CO_3$ was studied using thin film coated glass-slides (primer) by the layer-by-layer deposition. The number of layers on primer which used in this experiment is 5 and 6 layers (5 and 6 layers of primer is positive charge on top and negative charge on top, respectively). $Ce(OH)CO_3$ was dispersed in distilled water by sonication. Afterwards, the pH was adjusted using HCl and NaOH to pH 7 to 10. Then, dip 5 and 6 layers of primer into $Ce(OH)CO_3$ solution. The amount of $Ce(OH)CO_3$ which can attach with primer was measured by UV-visible spectroscopy.

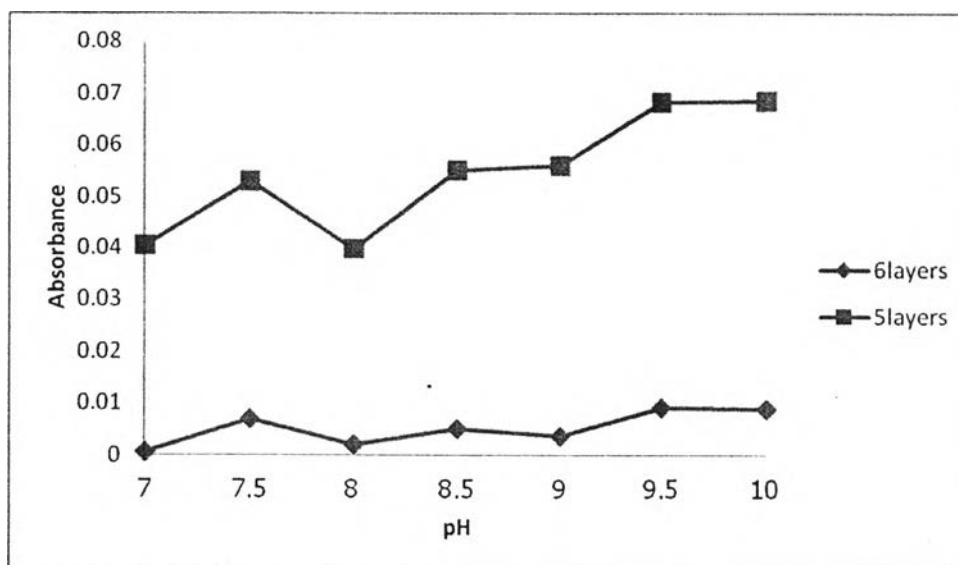


Figure 4.9 Comparison the absorbance between 5 and 6 layers of primer after dipped into $Ce(OH)CO_3$ solution in varying pH solution.

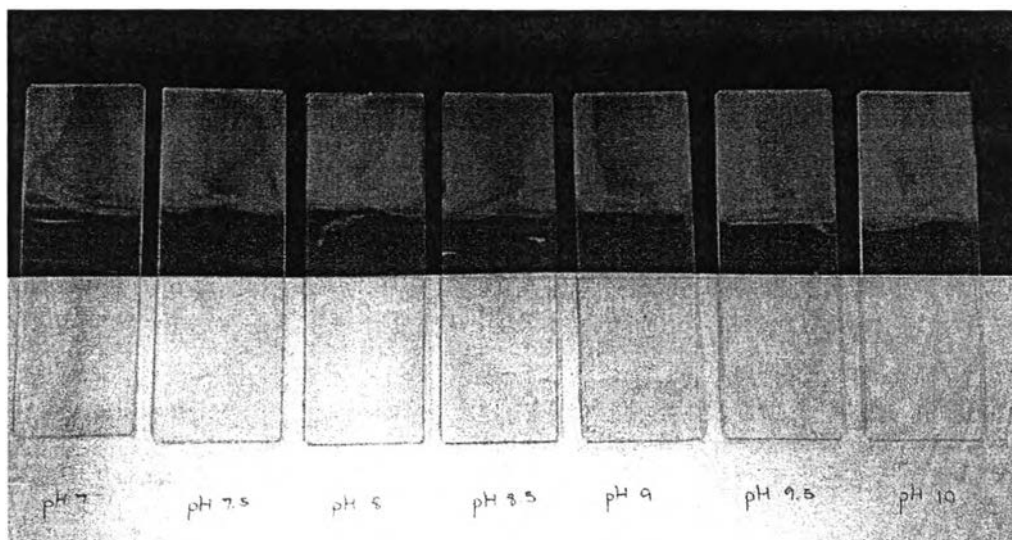


Figure 4.10 Show the picture of monolayer of Ce(OH)CO_3 deposit on 5 layers of primers.

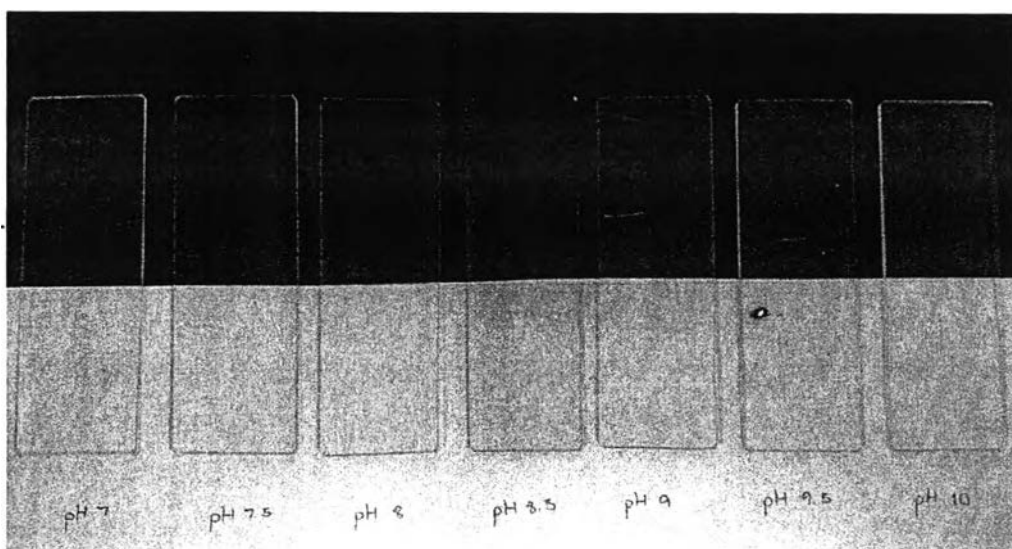


Figure 4.11 Show the picture of monolayer of Ce(OH)CO_3 deposit on 6 layers of primers.

Fig 4.9-4.11 shows that more Ce(OH)CO_3 can be deposited on 5 layers of primer more than 6 layers of primers which indicated that

$\text{Ce}(\text{OH})\text{CO}_3$ has negative charges on the surface. Therefore, it can electrostatically interact with the positively charged PDADMAC.

4.1.3.2 Effect of PDADMAC on $\text{Ce}(\text{OH})\text{CO}_3$

As mentioned previously, $\text{Ce}(\text{OH})\text{CO}_3$ has negative charges on the surface; accordingly, $\text{Ce}(\text{OH})\text{CO}_3$ can be attached with positive charges. In this research, poly(diallyl dimethyl ammonium chloride) (PDADMAC) was used to encapsulate $\text{Ce}(\text{OH})\text{CO}_3$ particles for synthesis of CeO_2 , since PDADMAC is a polycation. In this experiment, $\text{Ce}(\text{OH})\text{CO}_3$ was dispersed in distilled water PDADMAC added and the pH of the solution was adjusted by using HCl and NaOH to pH 5 to 10. After that, 5 and 6 layers of primers were dipped into the solution. The results are showed in Fig.4.12-4.14.

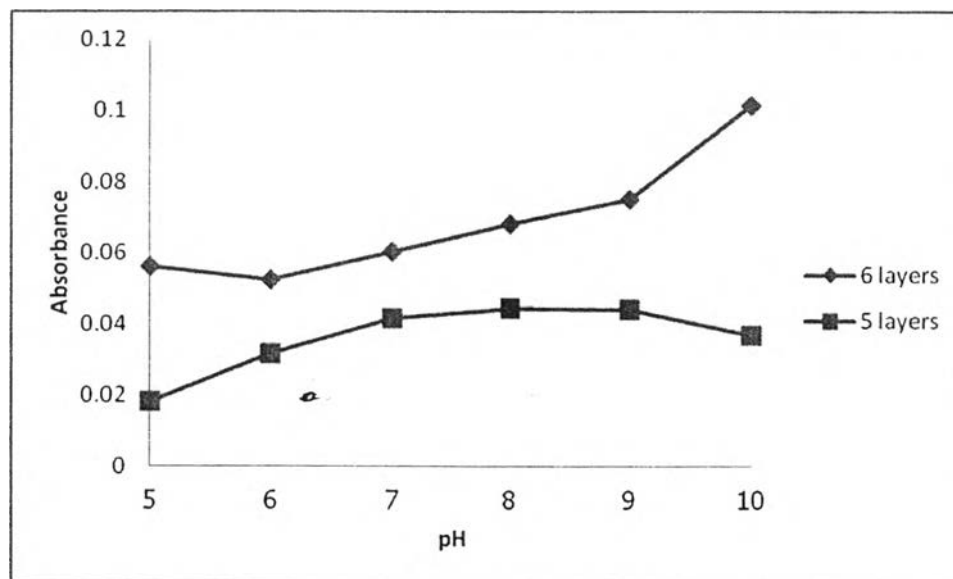


Figure 4.12 Effect of PDADMAC on $\text{Ce}(\text{OH})\text{CO}_3$ with 5 and 6 layers of primer by varing pH.

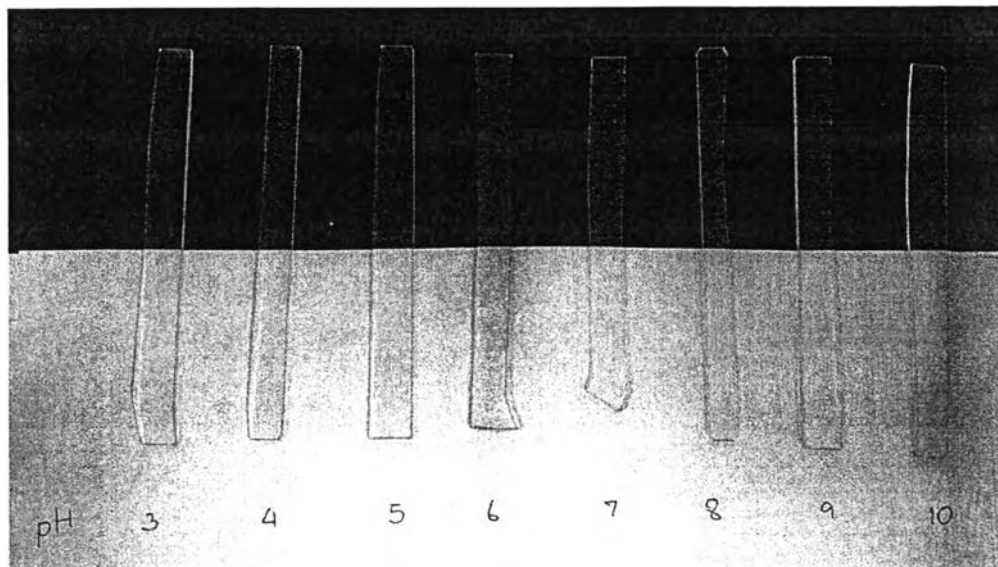


Figure 4.13 Show the monolayer of Ce(OH)CO_3 mixed with PDADMAC deposit on 5 layers of primers.

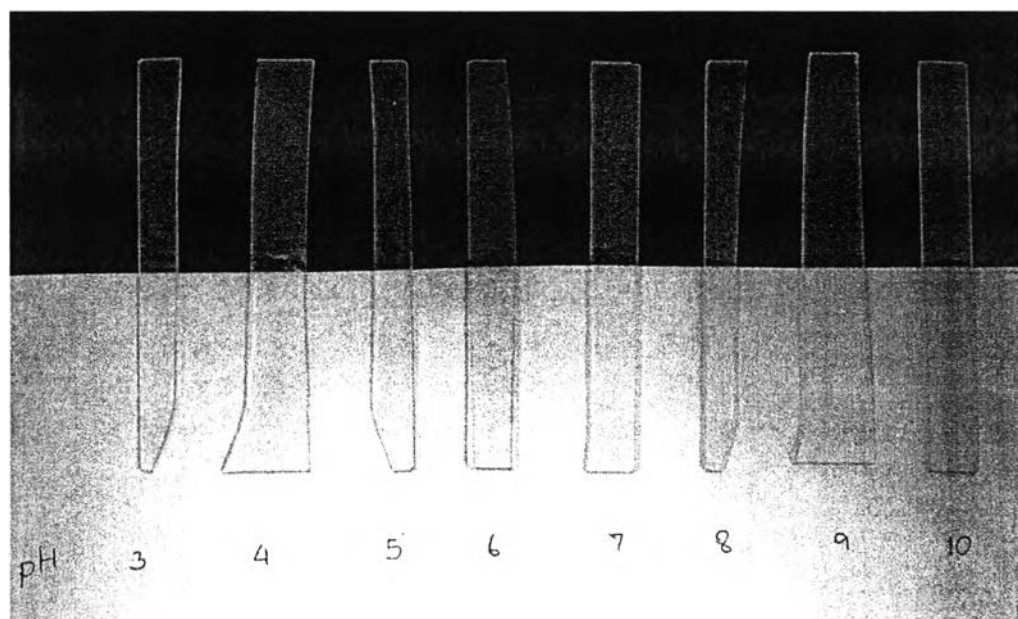


Figure 4.14 Show the monolayer of Ce(OH)CO_3 mixed with PDADMAC deposit on 6 layers of primers.

To prove that the negatively charged $\text{Ce}(\text{OH})\text{CO}_3$ can be encapsulated by the positively PDADMAC, PDADMAC was added during the synthesis. Later, the primers were immersed in the $\text{Ce}(\text{OH})\text{CO}_3$ produced to observe the charge effect. It is shown in Fig 4.12-4.14 that, unlike Fig 4.9-4.11, the $\text{Ce}(\text{OH})\text{CO}_3$ are deposited on the 6 layered primers. This confirms that $\text{Ce}(\text{OH})\text{CO}_3$ is negative which can be encapsulated with PDADMAC to alter the charge surface.

4.1.3.3 The Effect of pH on the Surface's Charge of CeO_2

Every metal oxide has ions on the surface. The type of ion on the surface of metal oxide is depends on the pH of solution. However, the pH which has equal in amount of positive charges and negative charges called point of zero charges (PZC). At the PZC, the surface of metal oxide will be neutral. When the pH of solution is higher than PZC point, the surface of metal oxide will be negative. Conversely, below PZC point the surface is positively charges. Additionally, the PZC value of same metal oxide is different depending on the synthesis technique. In this research, the PZC value of CeO_2 was measured through layer-by-layer technique. CeO_2 nanoparticles were dispersed into distilled water then adjust the pH from 3 to 10 by using HCl and NaOH. The 5 and 6 layers of primer (positive charges and negative charge on top, respectively) were dipped into the solution.

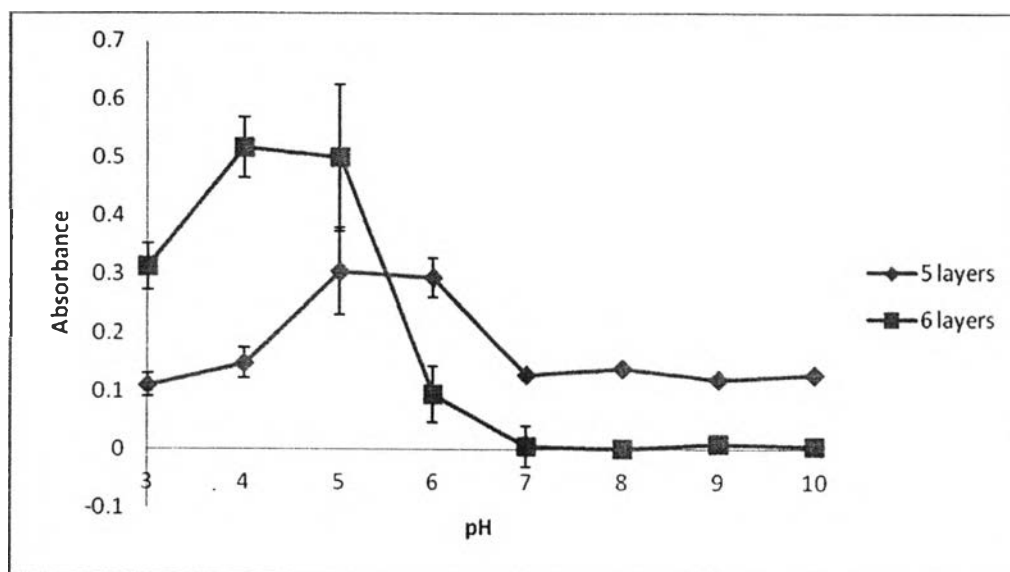


Figure 4.15 Show the effect of pH on the surface's charges of CeO₂.

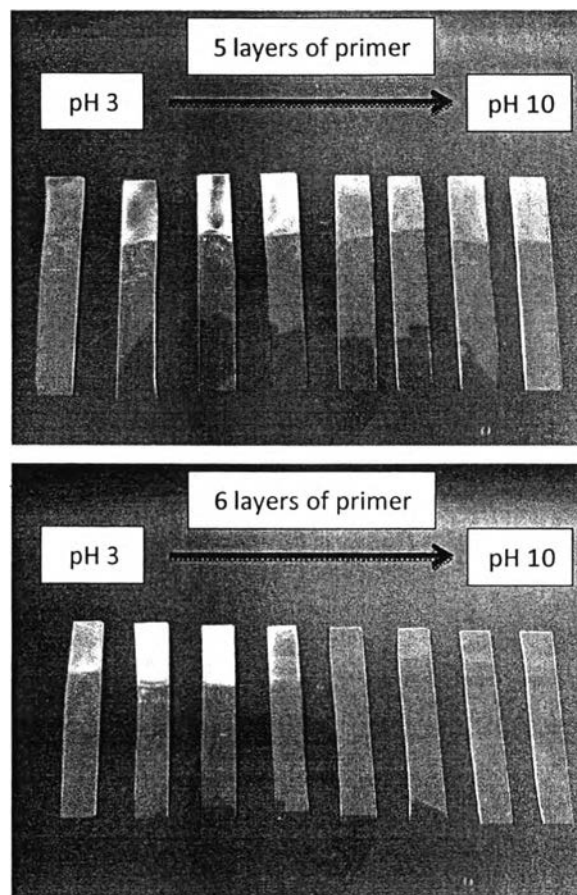


Figure 4.16 Show the picture of 5 and 6 layers of primer dipped into CeO_2 at pH 3-10.

Fig.4.15-4.16 shows the effect of pH on the charge on the surface of CeO_2 . It can be seen that CeO_2 can attach with 5 and 6 layers of primer at different pH, since the charges on the surface of CeO_2 can be change with the varying pH. For this research the PZC point is approximately 5.5 because CeO_2 can deposit on 6 layers better than 5 layers of primer at pH 3-5.5 which indicated that the charge on the surface of CeO_2 is positive. Additionally, at pH 5.5-10 the charge on the surface of CeO_2 is negative because it can deposit on 5 layers of primer which has positive charges on the surface.

4.1.4 Compare the Photo-catalytic Activity between Ce(OH)CO_3 and CeO_2

Ce(OH)CO_3 and CeO_2 nanoparticles were dispersed into 5 ppm methyl violet dye by sonication for 5 minutes. Then, methyl violet in the presence of Ce(OH)CO_3 and CeO_2 nanoparticles and pure methyl violet were exposed with UV light for 5 hours.

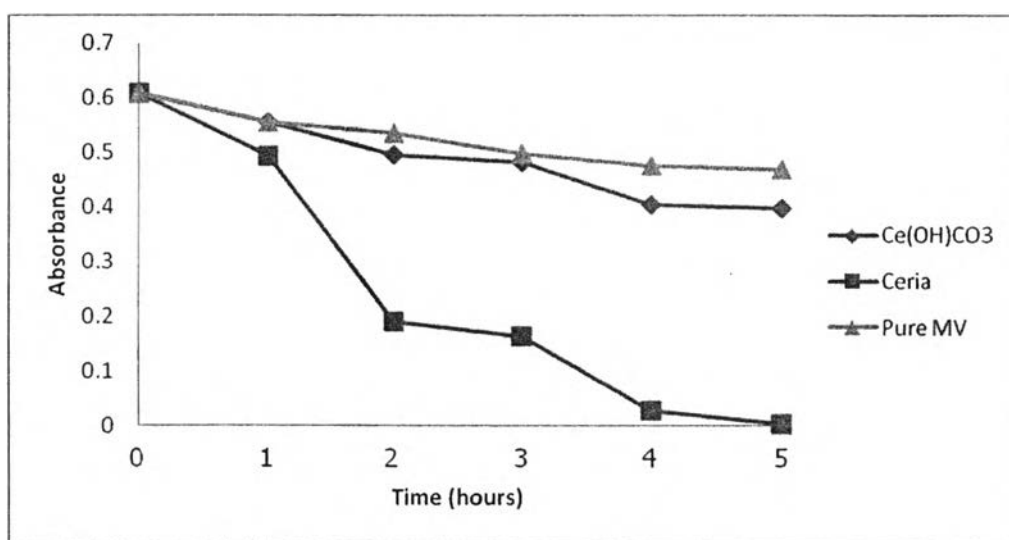
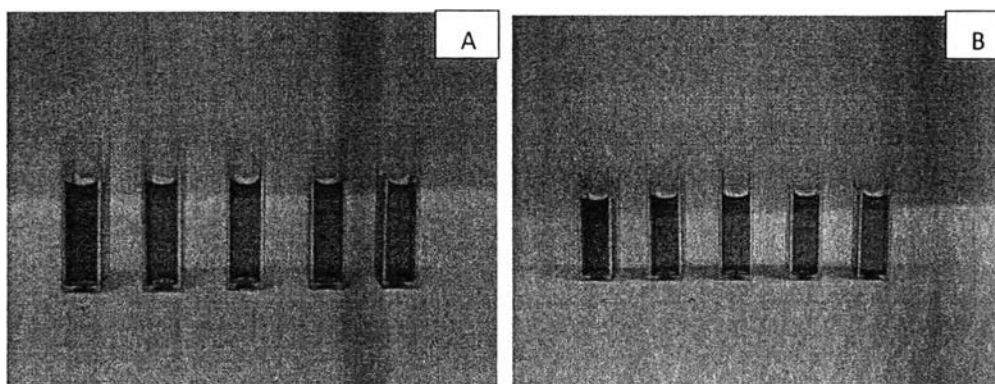


Figure 4.17 Compare the photo-catalytic activity between Ce(OH)CO_3 (before calcination) and CeO_2 (after calcination).



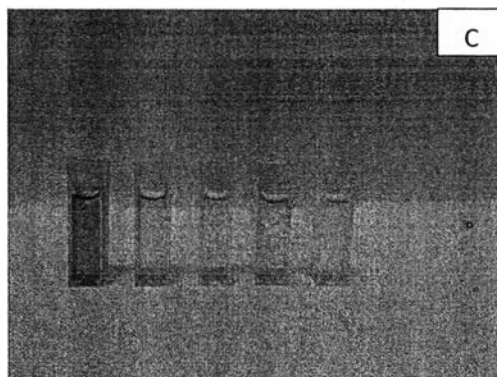


Figure 4.18 Images of methyl violet in the presence; (A) pure MV (B) Ce(OH)CO_3 (C) CeO_2 .

From Fig.4.17-4.18, the photo-catalytic activity of CeO_2 is higher than Ce(OH)CO_3 . Pure methyl violet (MV) can slightly degraded by itself under UV irradiation.

4.2 Effect of Ag Nanoparticle on the Synthesis of CeO_2

Ag nanoparticles were prepared by chemical reduction of AgNO_3 using COPSS as stabilizer to produce negative charges on the surface of Ag nanoparticles. Ag nanoparticles were used to prevent the recombination reaction and also enhance photon harvest of CeO_2 due to the lower in energy band gap and surface plasmon resonance (SPR) properties. CeO_2 nanoparticles were synthesized at the surface of Ag nanoparticles.

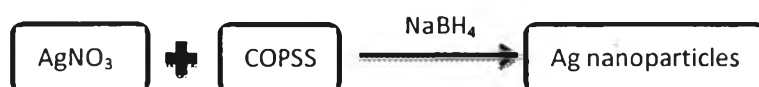


Figure 4.19 Diagram for Ag nanoparticle synthesis.

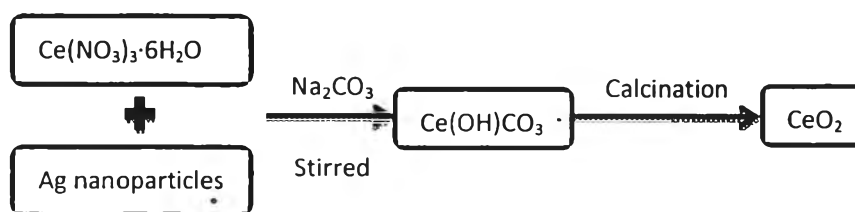


Figure 4.20 Diagram for the synthesis CeO₂ with Ag nanoparticles.

Since cerium ions have positive charges which can attach with the negatively charged Ag nanoparticles, CeO₂ can be synthesized at the surface of Ag nanoparticles.

4.2.1 Effect of AgNO₃ Concentration on Synthesis of CeO₂ with Ag Nanoparticles for Photo-catalytic Application

Ag nanoparticles were synthesized by using 1, 5 and 10 mM AgNO₃. Then, CeO₂ nanoparticles were synthesized at the surface of Ag nanoparticles. The morphology and size of CeO₂ on Ag nanoparticles were investigated by FESEM as shown in Fig. 4.21(B-D).

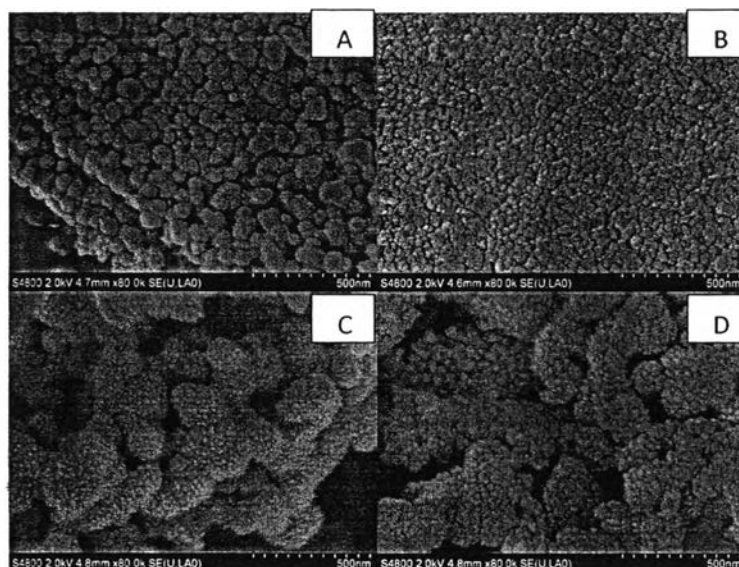


Figure 4.21 FESEM images of CeO₂ at various conditions: (A) Pure CeO₂ (B)-(D) CeO₂ with Ag nanoparticles by using 1, 5 and 10 mM of AgNO₃.

The particles of CeO₂ with Ag nanoparticle are more homogenous and smaller than that of pure CeO₂ as shown in Fig. 4.21 because the surface of Ag nanoparticles has negative charges of COPSS which can cap Ce³⁺ to prevent agglomeration; therefore, controls the size of CeO₂. The size of Ag nanoparticles varies with the concentration of AgNO₃ due to the agglomeration of Ag nanoparticles at higher concentration of AgNO₃ as shown in Fig. 4.21(B-D). The average size of CeO₂ with Ag nanoparticles increases with increasing the concentration of AgNO₃.

4.2.2 Photo-catalytic Activity of CeO₂ with Ag Nanoparticles

CeO₂ and CeO₂ with Ag nanoparticles were dispersed into 10 ppm MV solution by sonication for 5 minutes. The MV solution in the presence of CeO₂ and CeO₂ with Ag nanoparticles was exposed to UV light for 2 hours. The photo-catalytic activity was measured by using UV-visible spectroscopy. The result was showed in Fig.4.22-23.

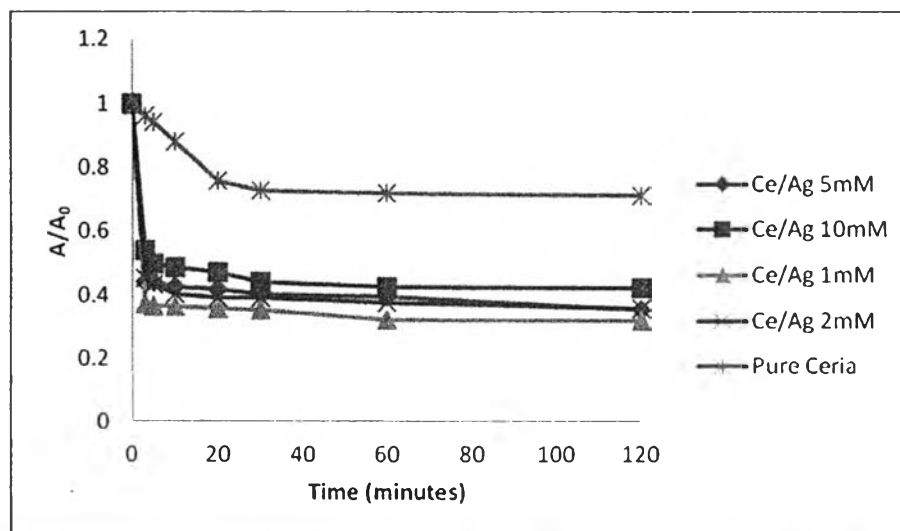


Figure 4.22 Plot comparing the change in methyl violet absorbance at wavelength 577.97 cm^{-1} (absorbance after exposure to UV as A /absorbance before exposure to UV as A_0) and exposure time of Methyl violet in the presence of CeO_2 , and CeO_2 with Ag nanoparticles by varying AgNO_3 concentration.

Fig.4.22, shows the degradation 10 ppm methyl violet in the presence of CeO_2 and CeO_2 with Ag nanoparticles synthesized by using 1, 2, 5 and 10 mM AgNO_3 at 3, 5, 10, 20, 30, 60 and 120 minutes. The graph shows that the photo-catalytic activity of CeO_2 with Ag nanoparticles is higher than pure CeO_2 because Ag nanoparticles can prevent the recombination reaction of electrons from conduction band to valence band and also enhances the photon harvest (Benxia.et al., 2014). Moreover, the photo-catalytic activity of CeO_2 with Ag nanoparticles synthesized by using high concentration AgNO_3 is less than that of low concentration AgNO_3 because the particles size of Ag nanoparticles increases with the increasing of AgNO_3 concentration; therefore, the specific surface area of CeO_2 with Ag nanoparticles at low concentration of AgNO_3 is higher than high concentration of AgNO_3 . It can be concluded that Ag nanoparticles improves the photo-catalytic activity of CeO_2 .

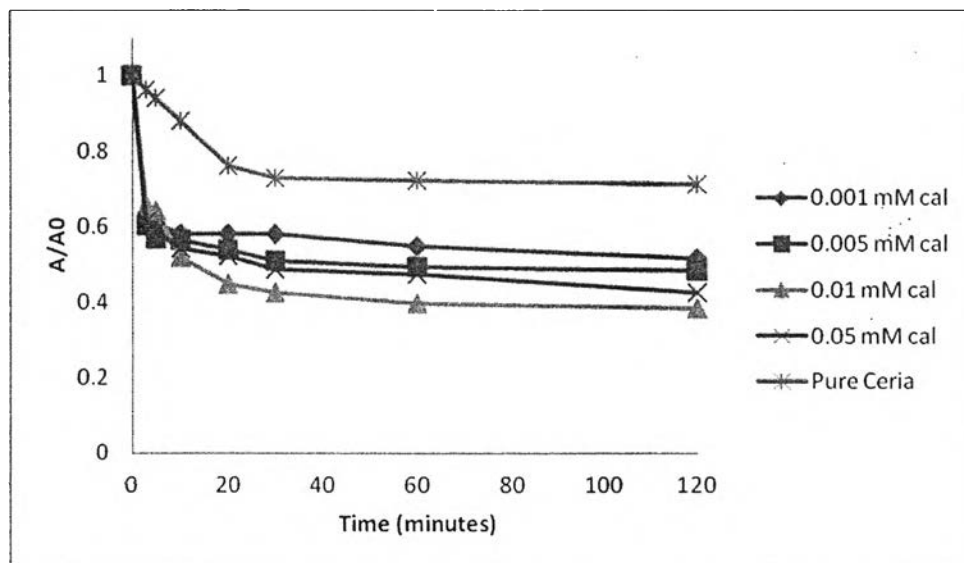


Figure 4.23 Plot comparing the change in methyl violet absorbance at wavelength 577.97 cm^{-1} (absorbance after exposure to UV as A /absorbance before exposure to UV as A_0) and exposure time of Methyl violet in the presence of CeO_2 and CeO_2 with Ag nanoparticles by varying COPSS concentration.

Figure 4.23 describes the photo-catalytic activity of CeO_2 and CeO_2 with Ag nanoparticles. Ag nanoparticles were synthesized by using 1mM of AgNO_3 with varied concentrations of COPSS (0.001, 0.005, 0.01, and 0.05 mM). The photo-catalytic activity of Ag nanoparticles with 0.01 mM COPSS is the highest because there is suitable amount of COPSS to cap Ag ions and prevent agglomeration which results with fine Ag nanoparticles. At low COPSS concentrations which are 0.001 and 0.005 mM, there is insufficient amount of COPSS to cap Ag ions. Additionally, Ag particles have weak negative charges on the surface which allows Ag nanoparticles to agglomerate. At high COPSS concentration (0.05mM) the Ag nanoparticles are large particles because Ag ions were capped by many chains of COPSS which makes the strong negative charge at the surface of Ag nanoparticles that repels one another. Consequently, the photo-catalytic activity of CeO_2 with Ag nanoparticles synthesized by using 0.05 mM

COPSS is higher than CeO_2 with Ag nanoparticles synthesized by using 0.001 and 0.005 mM but lower than 0.01 mM COPSS

4.3 Effect of Polyelectrolyte on Synthesis of CeO_2

The way to improve the photo-catalytic activity is synthesize the CeO_2 as small as possible. This part studies the synthesis of CeO_2 nanoparticles using polyelectrolytes to prevent the agglomeration. Polyelectrolytes were used as capping agent to cap the Cerium ions (Ce^{3+}) before converting it into Ce(OH)CO_3 by Na_2CO_3 . The polyelectrolytes used in this work are PDADMAC, PSS, PAA and COPSS.

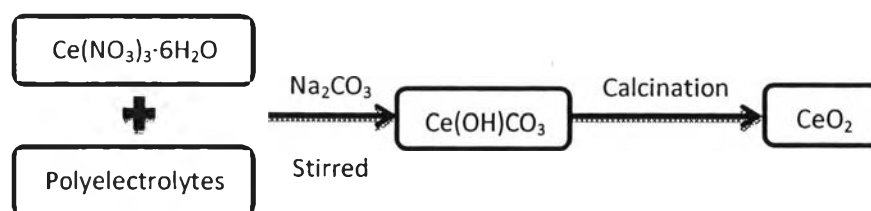


Figure 4.24 Show the diagram to synthesize CeO_2 by using polyelectrolytes.

The morphology and size of CeO_2 nanoparticles synthesized by using polyelectrolytes was investigated by FESEM. The size of CeO_2 nanoparticles synthesized by using polyelectrolytes is smaller than pure CeO_2 as shown in Fig.4.25.

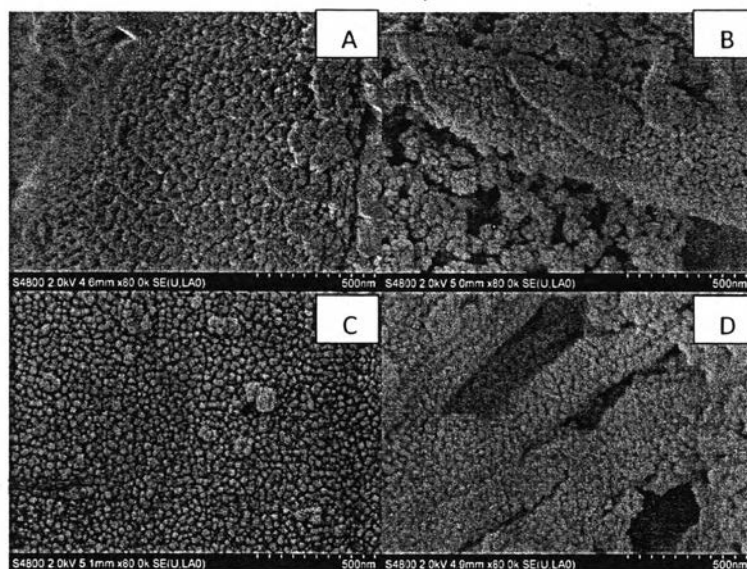


Figure 4.25 Show FESEM image of CeO_2 nanoparticles with polymer: (A) with PDADMAC (B) with COPSS (C) with PSS (D) with PAA.

From Fig.4.25, the average size of CeO_2 nanoparticles with PDADMAC, COPSS, PSS and PAA is 39.72, 33.18, 33.66 and 29.28 nm, respectively. The average size of CeO_2 nanoparticles with PAA is the smallest because PAA has a carboxylic group in the structure which has higher electronegativity; therefore, stronger negative charges to cap Ce^{3+} than the sulfonate group in PSS and COPSS. CeO_2 nanoparticles with PDADMAC produces the largest nanoparticles size because PDADMAC has positive charge which cannot encapsulate Ce^{3+} but the average size of particles still smaller than pure CeO_2 since it can control the size by capping the $\text{Ce}(\text{OH})\text{CO}_3$ which is the intermediate substance before the conversion to CeO_2 .

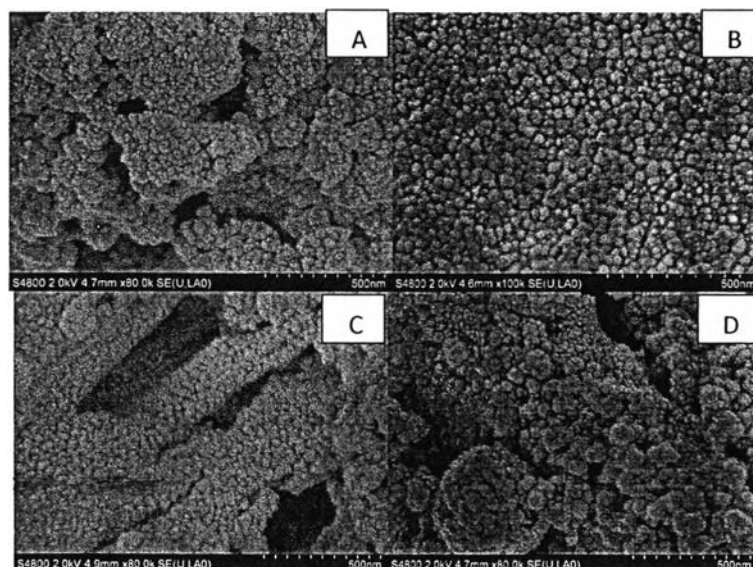


Figure 4.26 Show FE-SEM image of CeO₂ nanoparticles with PAA at varies concentration: (A) 5 mM (B) 10 mM (C) 20 mM (D) 50 mM.

Fig.4.26 shows that the average size of CeO₂ nanoparticles with PAA concentration of 5 mM, 10 mM, 20 mM and 50 mM is 34.4, 33.1, 29.28 and 57.74 nm, respectively. At 20 mM PAA with CeO₂ nanoparticles is the smallest particle because there is suitable amount of PAA and CeO₂ to obtain the smallest particles. For CeO₂ nanoparticles with 5 and 10 mM PAA, the particles are larger than CeO₂ with 20 mM PAA because there is not enough PAA to cap the Ce³⁺ ion to control the size. Additionally, CeO₂ nanoparticles with 50 mM of PAA are bigger than CeO₂ with 20 mM of PAA because Ce³⁺ were capped with many PAA chains.

4.3.1 Photo-catalytic Activity of CeO₂ with Polyelectrolyte

0.1g of CeO₂ nanoparticles was dispersed in 5 ppm methyl violet dye then exposed under UV light for 5 hours. CeO₂ nanoparticles were synthesized by using various types of polyelectrolytes; PDADMAC, COPSS and PAA. Furthermore, each polyelectrolyte concentration will be varied at 5, 10, 20, 30, 50 and 100 mM. The photo-catalytic activity was showed in Fig.4.27.

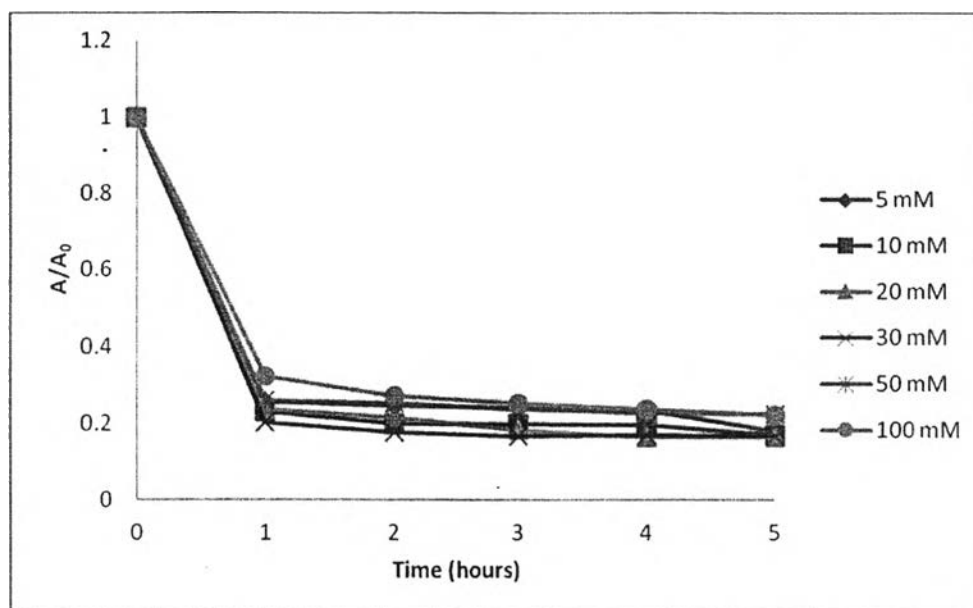


Figure 4.27 Show photo-catalytic activity of CeO_2 synthesized by using PDADMAC as capping agent at various concentrations.

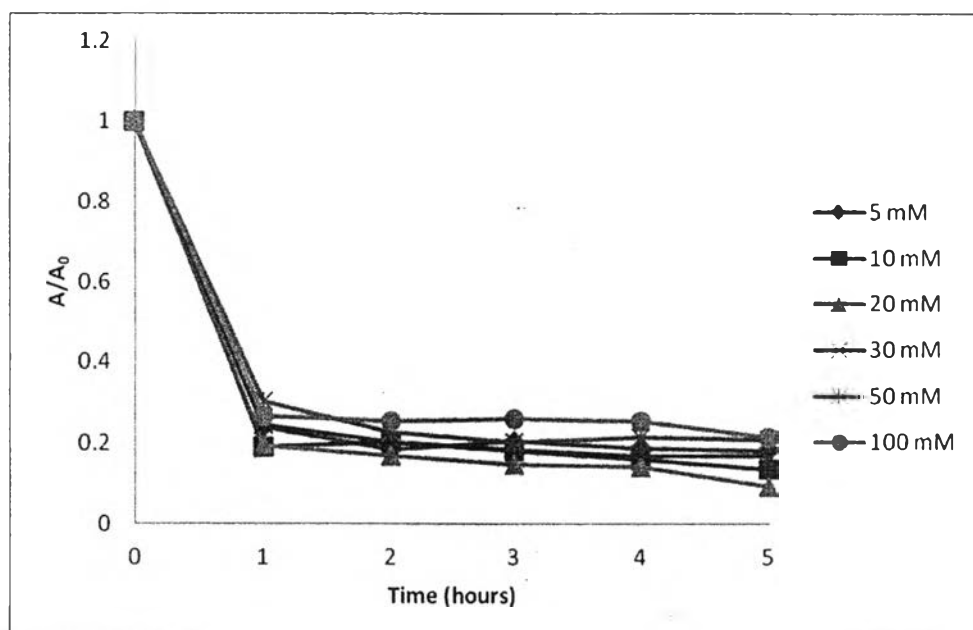


Figure 4.28 Show photo-catalytic activity of CeO_2 synthesized by using COPSS as capping agent at various concentrations.

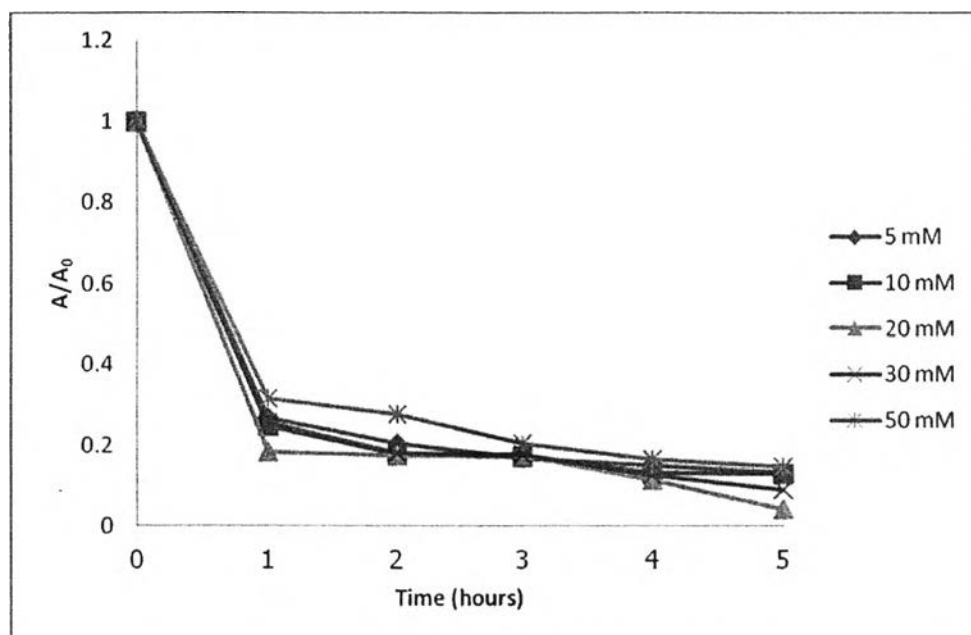


Figure 4.29 Show photo-catalytic activity of CeO_2 synthesized by using PAA as capping agent at various concentrations.

From previous results, the best concentration of all polyelectrolytes for CeO_2 synthesis is 20 and 30 mM. At low concentrations of the negatively charged PAA and COPSS i.e. 5 and 10 mM, there are insufficient amount of polymer to cap Ce^{3+} to control the size of CeO_2 . At 50 and 100 mM PAA and COPSS, there are too much polyelectrolyte cap the Ce^{3+} result in large particles. Moreover, PDADMAC can control the size of CeO_2 even with positive charges because it can encapsulate $\text{Ce}(\text{OH})\text{CO}_3$ which are formed by the reaction between Na_2CO_3 and $\text{Ce}(\text{NO}_3)_3$. The photo-catalytic activity of CeO_2 synthesized with PDADMAC is slightly different in each concentration because the surface of $\text{Ce}(\text{OH})\text{CO}_3$ will have positive charges of PDADMAC on top after encapsulated. Additionally, the $\text{Ce}(\text{OH})\text{CO}_3$ that has not been encapsulated can be attracted towards the positively charged encapsulated $\text{Ce}(\text{OH})\text{CO}_3$; resulting as a large aggregate of CeO_2 at any concentration. The photo-catalytic activity of PDADMAC, COPSS and PAA were showed in Fig.4.27-4.29.

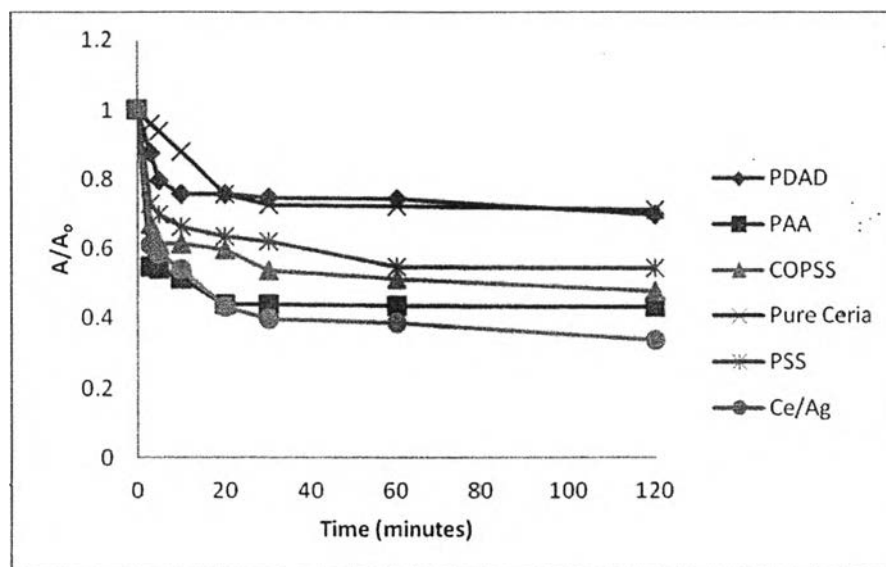


Figure 4.30 Plot comparing the change in methyl violet absorbance at wavelength 577.97 cm^{-1} (absorbance after exposure to UV as A /absorbance before exposure to UV as A_0) and exposure time of Methyl violet in the presence of pure CeO_2 , CeO_2 with varies types of polyelectrolyte and CeO_2 with Ag nanoparticles in the presence of 10 ppm methyl violet dye.

The photo-catalytic activity of CeO_2 synthesized by using 20 mM of various types of polyelectrolytes, CeO_2 with Ag nanoparticles and pure CeO_2 were shown in Fig.4.30. 0.1 g of the catalysts was dispersed into 10 ppm MV solution. The photo-catalytic activity of PAA has the highest efficiency to decompose the dye molecules compared to other polyelectrolytes because the CeO_2 nanoparticles synthesized by PAA have the smallest particles size. As shown in Fig.4.25, the size of CeO_2 varies with the polyelectrolyte used during synthesis; therefore, affects the photo-catalytic activity of CeO_2 . However, the photo-catalytic activity of CeO_2 synthesized with PDADMAC is similar to that of pure CeO_2 even with difference in size because CeO_2 synthesized by PDADMAC tends to agglomerate with one another. Since, PDADMAC is a polycation, it will interact electrostatically with $\text{Ce}(\text{OH})\text{CO}_3$ which has negative charge. The PDADMAC chain encapsulates $\text{Ce}(\text{OH})\text{CO}_3$; therefore, the $\text{Ce}(\text{OH})\text{CO}_3$ will have positive

charges of PDADMAC on top. Additionally, the $\text{Ce}(\text{OH})\text{CO}_3$ that has not been encapsulated can be attracted towards the positively charged encapsulated $\text{Ce}(\text{OH})\text{CO}_3$; resulting as a large aggregate of CeO_2 . Furthermore, the photo-catalytic activity of CeO_2 with Ag nanoparticles is better than CeO_2 synthesized by polyelectrolyte even the size is slightly different because Ag can prevent recombination reaction and also enhance photon harvest.

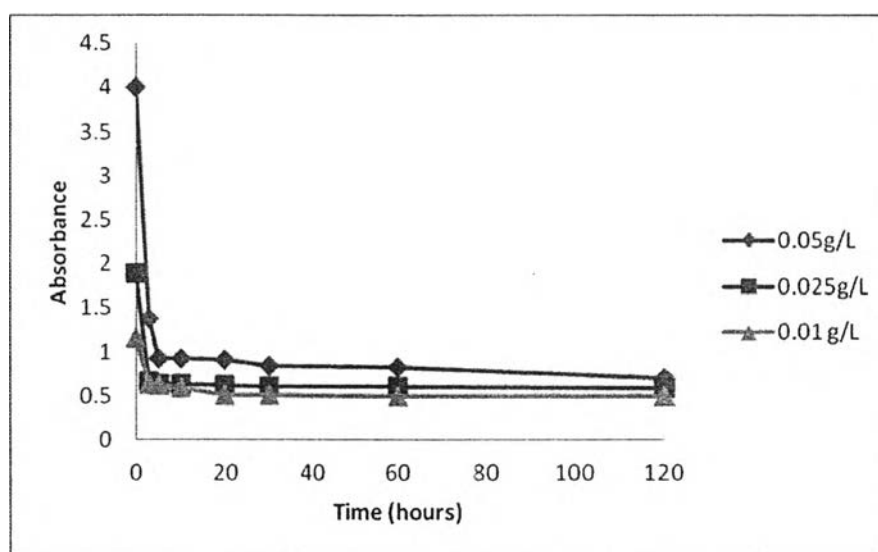


Figure 4.32 Show photo-catalytic activity of CeO_2 with 20 mM of PAA in the presence of MV under UV irradiation at various concentration of MV.

The photo-catalytic activity of the CeO_2 synthesized using PAA at various concentration of MV (0.05, 0.025 and 0.01 g/L) was described in Fig 4.32. It can be seen that the photo-catalytic activity of CeO_2 with 0.01 g/L MV show the lowest absorbance intensity due to less amount of dye molecule. On the contrary, at 0.05 g/L MV in the presence of CeO_2 show the highest absorbance intensity due to much more concentration of dye molecules.

4.4 X-Ray Diffraction (XRD)

The X-ray diffraction spectroscopy was used to identify the synthesized product whether the product is CeO_2 or not. Also, XRD was used to confirm the compositions of CeO_2 with Ag nanoparticles. Additionally, identifies the existence of impurities from polyelectrolytes.

4.4.1 XRD graph of CeO_2 nanoparticles synthesized by using polyelectrolytes and without polyelectrolytes

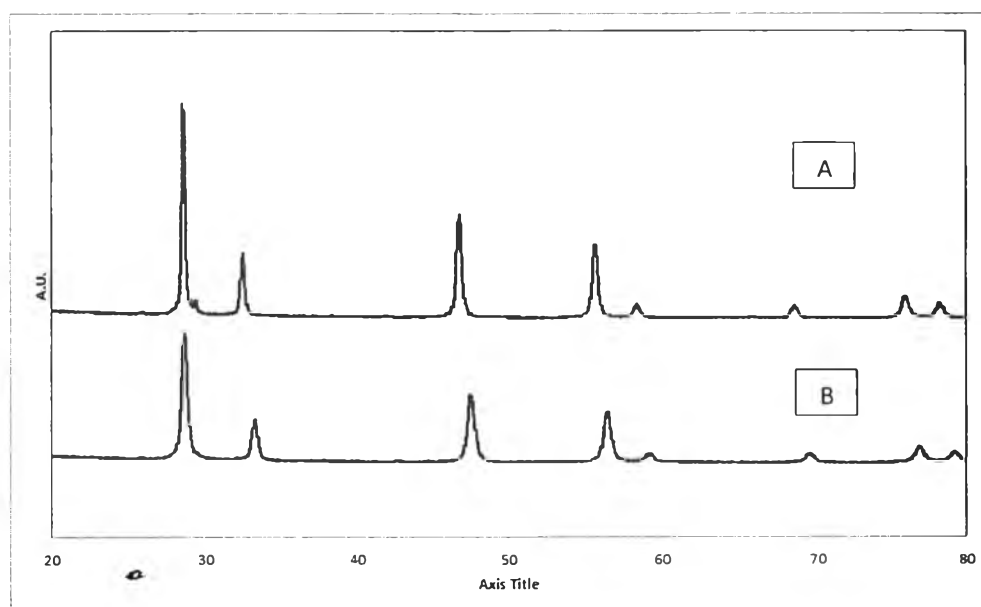


Figure 4.33 XRD graphs of CeO_2 nanoparticles: (A) Pure CeO_2 (B) CeO_2 synthesized by using polyelectrolytes.

Fig.4.33 shows the XRD pattern of the CeO_2 particles over 2θ of 10° - 80° with scan rate $1^\circ/\text{min}$. The peaks at 28.6° , 33.2° , 47.5° , 56.4° , 59.2° , 68.3° , 76.5° and 78.1° of 2θ corresponds to the (111), (200), (311), and (222) planes. As compared to the standard XRD graph of CeO_2 , this sample shows a pure-phase CeO_2 nanoparticle in a cubic fluorite structure (Wong, C.P., 2003). The CeO_2

synthesized with polyelectrolytes has the same XRD graph as that of pure CeO_2 because the polyelectrolyte degrades after calcination at $550\text{ }^\circ\text{C}$, leaving no impurities in the product. The peak from the XRD graph of both CeO_2 and CeO_2 synthesized by using polyelectrolytes are the same because polyelectrolytes were degraded after calcination at $550\text{ }^\circ\text{C}$.

4.4.2 XRD Graph of CeO_2 with Ag Nanoparticles

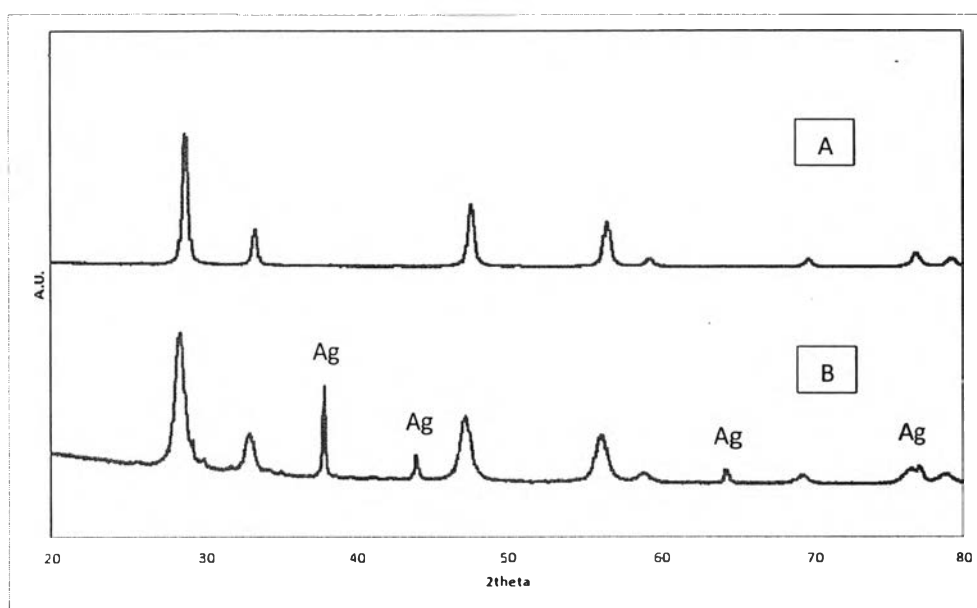


Figure 4.34 Show the XRD peak of; (A) CeO_2 with Ag nanoparticles (2:1) (B) CeO_2 with Ag nanoparticles (1:1).

Fig. 4.34 shows the comparison between XRD graphs of CeO_2 with Ag nanoparticles synthesized at different ratios. The ratio between $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and AgNO_3 is 1:1 and 2:1. At ratio 1:1, XRD can detect both peaks of CeO_2 and Ag nanoparticles but it cannot detect the peak of Ag nanoparticles at ratio 2:1 which indicates that CeO_2 covers the surface of Ag nanoparticles completely. Therefore, XRD cannot detect the peak of Ag nanoparticles (Benxia et al., 2014).