CHAPTER III
EXPERIMENTAL

Materials and Equipment

3.1 Equipment:

1. Field emission scanning electron microscope (FE-SEM), Hitachi S4800
2. UV-Visible spectropy, Avaspec-2048
3. X-Ray Diffraction (XRD), Rikagu
4. UV reactor

3.2 Chemicals and Solvents:

1. Poly(diallyldimethylammonium chloride), or PDADMAC, medium molecular weight, 20 wt.% in water, Mw=200,000-350,000, ALDRICH
2. Poly(acrylic acid), PAA, Mw=150,000, SIGMA ALDRICH
3. Poly(styrene sulfonate), PSS, ALDRICH, Mw=70,000
4. Poly(styrene sulfonate-co-maleic acid), COPSS, typical Mw=20,000, ALDRICH
5. Sodium chloride, NaCl, CARLO ERBA, 99.5%
6. Ammonia, NH_4, APPLICHEM PANREAC, 30%
7. Hydrogen peroxide, H_2O_2, aqueous solution, CHEM-SUPPLY, 35%
8. Ethanol, EtOH, LAB SCAN
9. Cerium(III) nitrate hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$, ACROS ORGANICS.
10. Sodium carbonate, Na_2CO_3, CARLO ERBA
11. Silver Nitrate, $AgNO_3$, CARLO ERBA
12. Sodium borohydride, $NaBH_4$, FISHER CHEMICAL
13. Hydrochloric acid, HCl, LAB SCAN, 37%
14. Sodium hydroxide, NaOH, CARLO ERBA
15. Methyl violet dye, MV, Fluka

3.3 Experimental Procedures

3.3.1 Synthesis of Cerium Oxide (CeO_2)

CeO_2 nanoparticles were prepared by precipitation technique using various polyelectrolytes which are PDADMAC, PAA, PSS and COPSS (5, 10, 20, 30, 50 and 100 mM) as capping agents and 0.5 M Na_2CO_3 as precipitant. All chemicals can be dissolved in distilled water. First, dissolve both $Ce(NO_3)_3 \cdot 6H_2O$ and polyelectrolytes then mix it together. After that, adjust the pH to 8.0 by using Na_2CO_3 (drop wise or quick adding) then stir or sonicate for 1 hour then rinse it with water 5 times and heat it in the oven at 100 °C for 24 hours (For synthesized by using temperature, the solution will be heated to 60 °C before adjust the pH). Finally, $Ce(OH)CO_3$ was obtained. Then, take the $Ce(OH)CO_3$, $Ce(OH)CO_3$ with polyelectrolytes into the furnace to calcine for 6 hours at 550 °C. The orange powder of CeO_2 will be obtained.

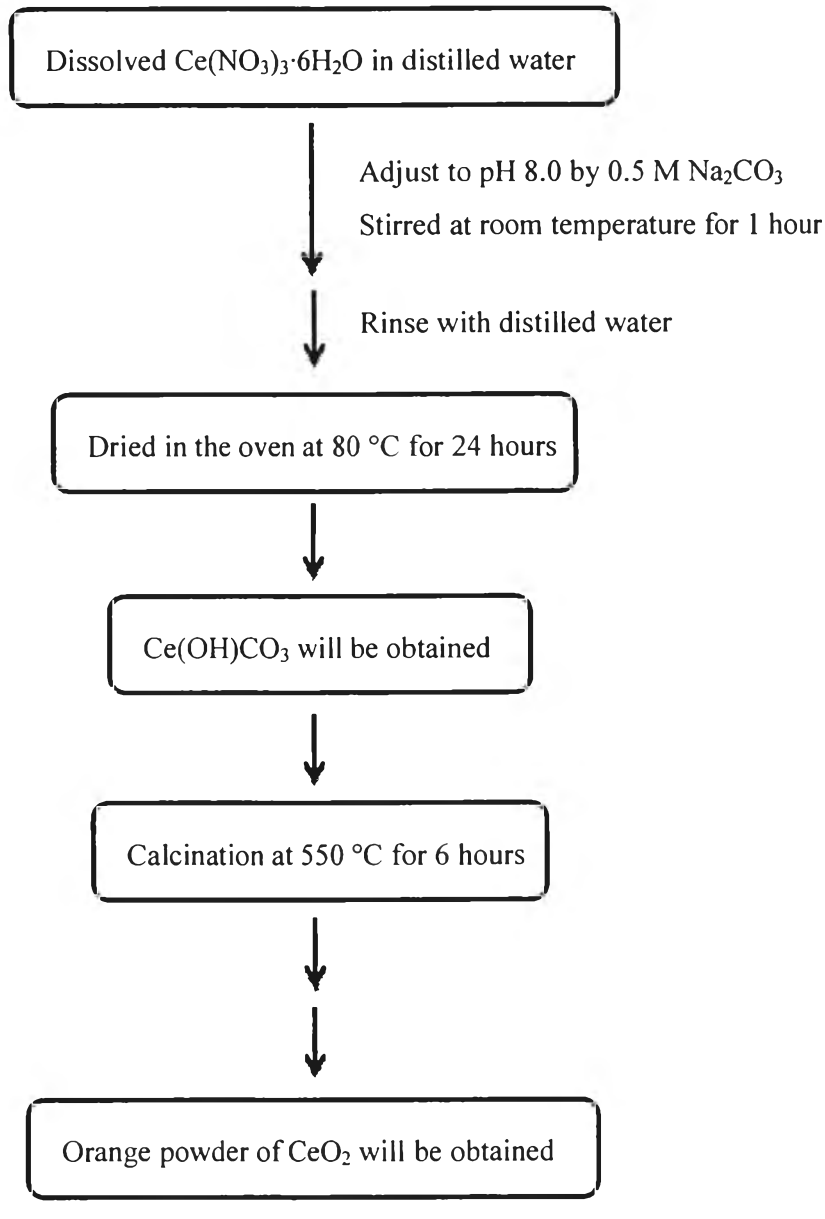

Figure 3.1 Flow chart for synthesis of CeO_2.

3.3.2 Synthesis of Cerium Oxide with Ag Nanoparticles

3.3.2.1 Synthesis of Ag nanoparticles

Ag nanoparticles were prepared by chemical reduction of $AgNO_3$ using COPSS and $NaBH_4$ as capping agent and reduced agent,

respectively. All chemicals can be dissolved in distilled water. First, mixed the $AgNO_3$ (1, 2, 5, and 10 mM) with COPSS (0.001, 0.005, 0.01, and 0.05 mM) then add 5 mM $NaBH_4$. The yellowish solution of Ag nanoparticles will be got after 2 hours.

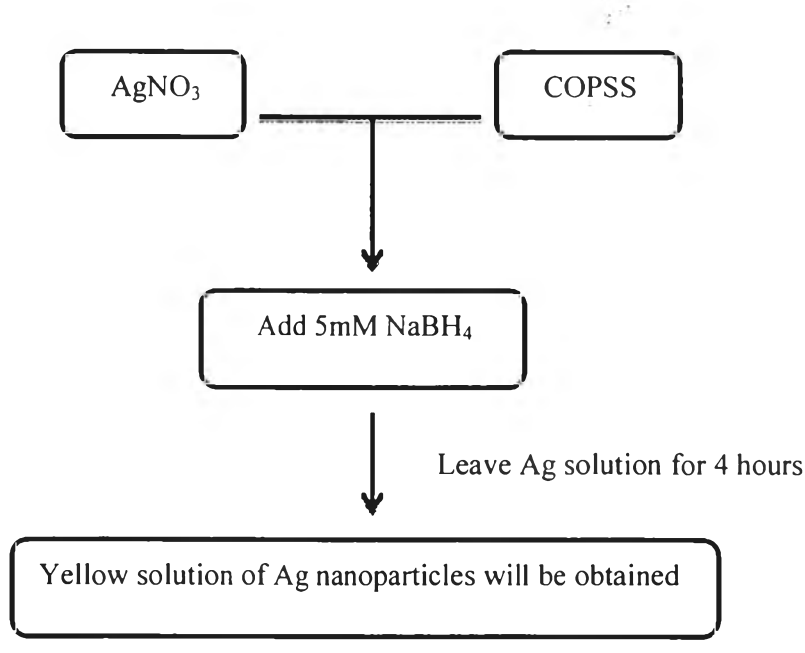

Figure 3.2 Flow chart for synthesis of Ag nanoparticles.

3.3.2.2 Synthesis of CeO_2 on Ag nanoparticles

CeO_2 will be synthesized on the surface of Ag nanoparticles previously prepared. 20 mM $Ce(NO)_3{\cdot}6H_2O$ was added into the Ag nanoparticles solution. The pH of solution was adjusted to 8.0 by using 0.5 M Na_2CO_3 while stirring for 1 hour. Rinse the precipitate with distilled water for 3 times and dry it in the oven 80 °C for 24 hours. The powder of $Ce(OH)CO_3$ with Ag nanoparticles will be obtained. Then, powder undergoes calcination at 550 °C for 6 hours to convert to CeO_2.

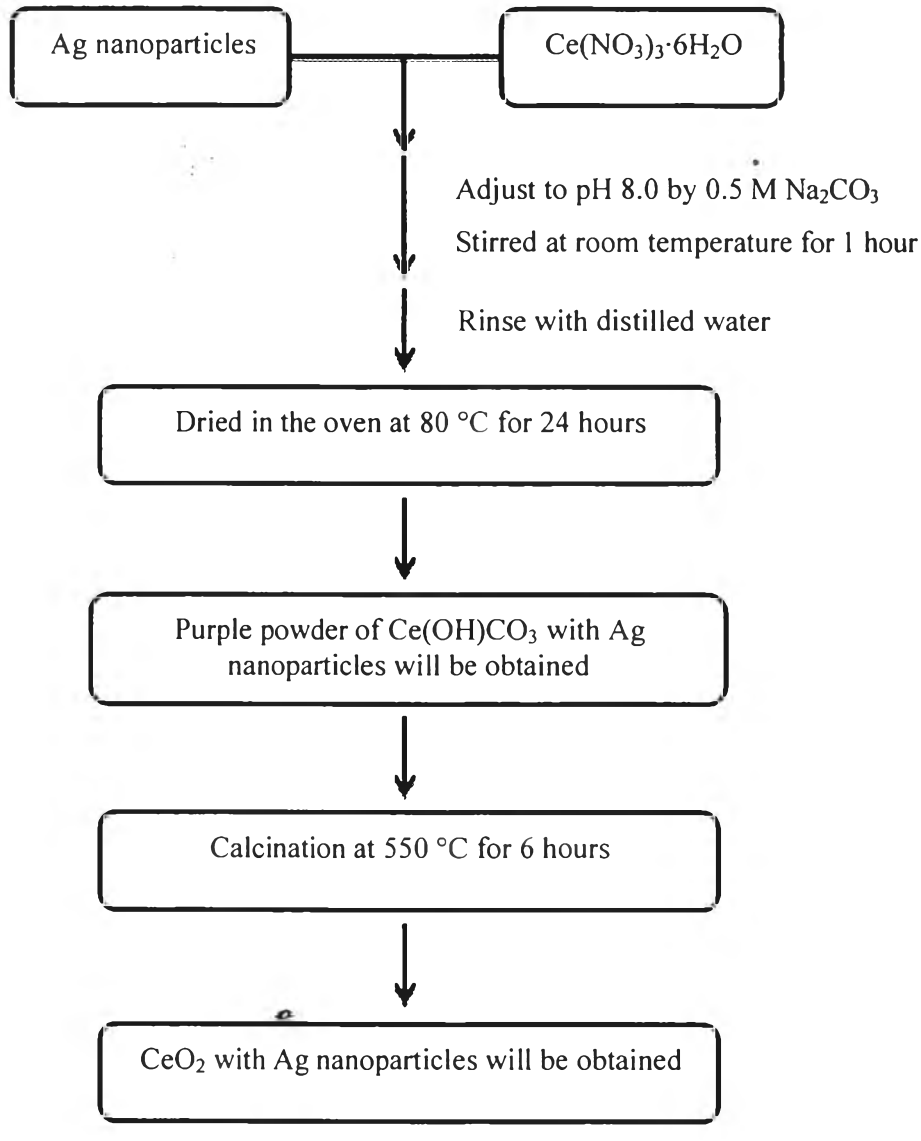

Figure 3.3 Flow chart for synthesis of CeO_2 with Ag nanoparticles.

3.3.3 Photo-catalytic Experiment

Pure CeO_2 and CeO_2 with Ag nanoparticles 0.1 g were mixed with 5, 10, 25, 50 mg/L Methyl violet (MV). Then, sonicate for 5 minutes to disperse the catalyst in MV solution which will be placed later under UV irradiation (16 W, ~350

nm). The degradation of dye was measured by using UV-spectroscopy at 3, 5, 10, 20, 30, 60 and 120 minutes.

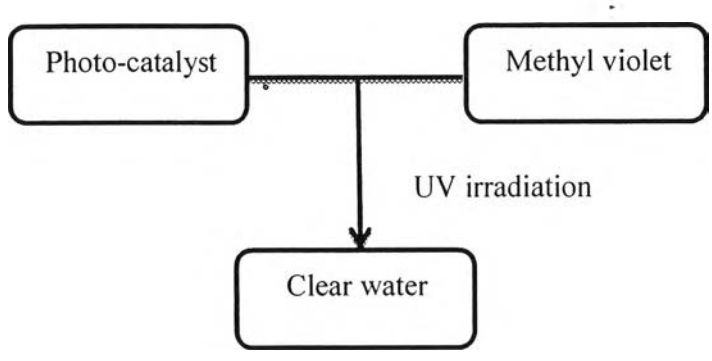

Figure 3.4 Flow chart for Photo-catalytic experiment.

3.3.4 Primer Preparation

The glass slide will be used to study the surface of CeO_2. Glass slides were washed by hot ammonia (NH_3:H_2O_2:H_2O as 5:1:1) for 20 minutes. Then, the glass slides are rinsed with EtOH and dried.

Next, glass slide are dipped into 10 mM of PDADMAC with 1 M NaCl for 1 minute then rinsed with distilled water. Afterwards, the monolayer was dipped into 10 mM of PSS with 1 M NaCl for 1 minute then washed it with distilled water again. The 2 layers of primer are obtained. Primer will be finished with 5 and 6 layers and dried.

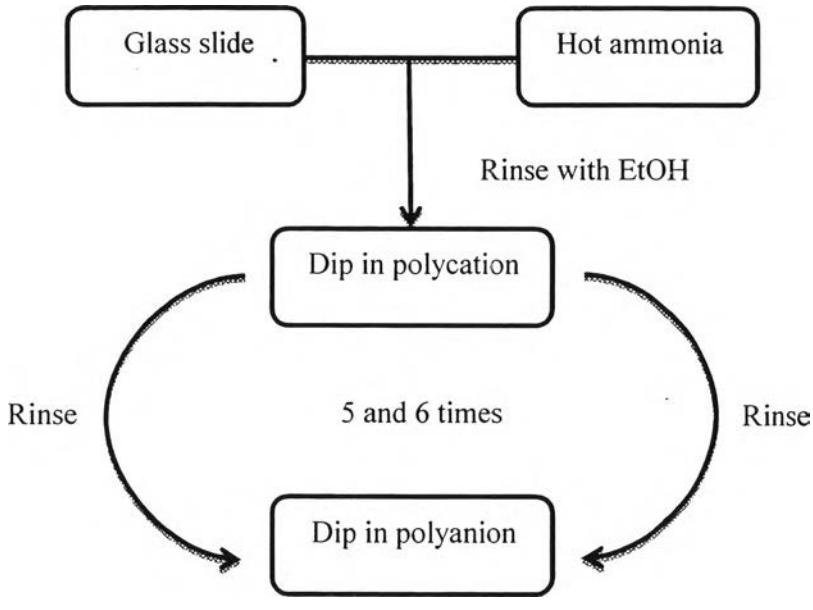

Figure 3.5 Flow chart of primer preparation.

3.3.5 Preparation of CeO_2 Monolayer

0.1 g CeO_2 powders was dispersed in distilled water by sonication it for 5 minutes. The pH of CeO_2 solution was adjusted between 3 to 10 (3, 4, 5, 6, 7, 8, 9 and 10) using HCl and NaOH. Then, the 5 and 6 layers of primer was dipped into the CeO_2 solution for 5 minutes and rinses it with distilled water to remove excess of CeO_2 nanoparticles.

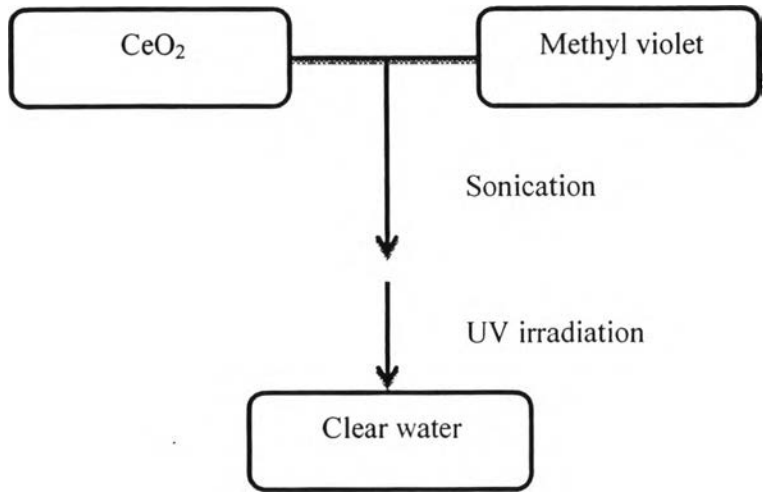

Figure 3.6 Flow chart of CeO_2 monolayer preparation.

3.3.6 Characterization

1. CeO_2 nanoparticles were confirmed by X-ray diffraction

2. The morphology and the size of CeO_2 nanoparticle will be analyzed by Field Emission Scanning Electron Microscope (FE-SEM)

3. The photo-catalytic activity was measured by UV-Visible spectroscopy

4. The attachment efficiency of CeO_2 nanoparticles on glass slide was measured by UV-Visible spectroscopy