

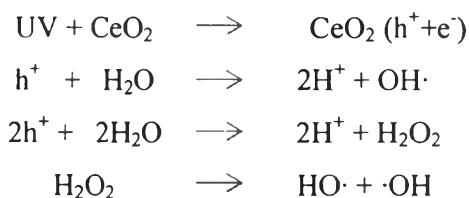
CHAPTER II

LITERATURE REVIEW

2.1 Cerium (Ce)

Cerium an element categorized as a rare earth element. It is found in minerals such as monazite and bastnasite. The cerium is mostly governed by trivalent and tetravalent oxidation states. However, trivalent states of cerium are more stable than tetravalent states. There are a lot of commercial applications of cerium which are addition to fuel to reduce emissions, catalysts, and use in fuel cell, etc.

Typically, Cerium is used in form of cerium oxide. The structure of CeO₂ is a fluorite structure in the space group Fm3m. At high temperature CeO₂ can be reduced to a nonstoichiometric structure. In this work, we will focus at the photo-catalytic application of cerium oxide followed by



The radicals which were generated from the catalyst will react with contaminants in the waste water to produce clean and clear water. The energy band gap of CeO₂ is around 2.7-3.4 eV depending on the preparation method. CeO₂ can absorb energy from the light which has wavelength around 350-400 nm (near visible light) due to low energy band gap. There are various ways to synthesize the CeO₂. The most popular way to synthesize CeO₂ is hydrothermal technique. However, the hydrothermal technique is quite difficult to synthesize due requiring both temperature and high pressure and it is also time consuming. The synthesis technique used in this project is simpler and requires less energy; however, agglomeration occurred which produced slightly larger particles. Here, the CeO₂ nanoparticles were synthesized by precipitation method at room temperature without any pressure.

Antonio de Faria and Transatti (1994) compared the point of zero charge of CeO₂ with different preparation techniques of CeO₂ and found that each technique

has their individual point of zero charge value depending on surface structure or surface pretreatment. To support Antonio and Transatti's discoveries, Park et al. prepared the hydrolysis of CeCl_4 without calcination and have reported the PZC value of 6.75. In addition, Pedio et al. prepared hydrous CeO_2 by hydrolysis of Cerium sulfate with calcination and found that PZC is about 7.6 which was the same as Ray et al.

Nabavi et al. discovered that the PZC value is either 10.5 or 8.6 depending on surface pretreatment. From their experiment, the oxide was obtained from the hydrous precipitate after calcination at $800\text{ }^\circ\text{C}$. Pure CeO_2 showed a PZC of 8.6. By using the thermal decomposition preparation technique, it was found that PZC of CeO_2 is 8.1 ± 0.01 . So, it could be confirmed that the point of zero charge depends on preparation techniques.

Chelliah, Rayappan and Krishnari (2002) studied about synthesis and characterization of cerium oxide nanoparticles. Cerium oxide was synthesized by using cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and sodium hydroxide (NaOH). They found that the polycrystalline nature of cerium is face centered cubic structure and the size of cerium is approximately 9-16 nm. From the SEM images, CeO_2 showed nanosized spherical shaped particles and the size is approximately 550.54 cm^{-1} . Furthermore, the UV-visible absorbance spectrum of cerium nanoparticles is approximately 325 nm.

Bouchaud, Balmain, Bonnet, and Pedraza (2011) studied on relative amount of Ce(III)/Ce(IV) species in aqueous media which can be used to predict precipitation mechanisms. They found that the hydrolysis of Ce^{3+} consist of Ce^{3+} , $\text{Ce}(\text{OH})^{2+}$, $\text{Ce}(\text{OH})_2^{2+}$, $\text{Ce}(\text{OH})_3^+$ and the hydrolysis of Ce^{4+} consist of Ce^{4+} , $\text{Ce}(\text{OH})^{3+}$, $\text{Ce}(\text{OH})_2^{2+}$, $\text{Ce}(\text{OH})_3^+$, and $\text{Ce}(\text{OH})_4$. At low pH, There are a lot of Ce^{3+} species due to the high amount of Ce(IV) species. However, Ce^{4+} and $\text{Ce}(\text{OH})^{3+}$ will convert to Ce^{3+} because they are more stable than others form of cerium ions. At high pH, oxygen will affect the precipitation mechanism that oxidizes Ce^{3+} to Ce^{4+} species mainly in the form of $\text{Ce}(\text{OH})_2^{2+}$, $\text{Ce}(\text{OH})_4$, and $\text{CeO}_2 \cdot x\text{H}_2\text{O}$. $\text{Ce}(\text{OH})_4$ is likely to precipitate at a spontaneous manner at pH higher than 4.

Wu et al. (2002) studied the effect of the pH of the reaction medium on the crystallization of CeO_2 grains under hydrothermal condition without agglomeration. They found that the grain size of CeO_2 powder will increase with increasing reaction temperature and reaction time. Also, the lower the pH in the reaction medium, the lower the moisture content of the sample. The synthesis of the powders under hydrothermal conditions is thought to be the effect of Ostwald ripening where the smaller grain dissolves and larger grains grows. For the precipitated $\text{Ce}(\text{OH})_4$, the solubility product of $\text{Ce}(\text{OH})_4$ is very small when Ostwald ripening occur, the solute will diffuse more quickly, therefore, larger grains grow more quickly. In acidic hydrothermal medium, surfaces of the grain with ion SO_4^{2-} , CO_3^{2-} and OH^- are replaced by water molecules, so the combination of SO_4^{2-} or CO_3^{2-} with Ce^{4+} and hydrogen bonding will decrease. As a result, the agglomeration is reduced and more regular morphologies were obtained than observing the synthesis in neutral or basic medium.

Masui, Hirai, Imanaka, Adachi (2002) have synthesized cerium oxide nanoparticles without agglomeration of the nanoparticles by using citric acid. The size of cerium oxide is approximately 3.9 nm calculated from the BET specific surface area that has the same result as the HREM image. It indicated that the particles have weak agglomeration. They found that citric acid works as a protective agent against particle growth. From FTIR, there is only peak of hydroxyl group and carbonyl group which suggest that cerium nanoparticles were covered by citric acid molecules. Form this work it can said that the size of cerium oxide particles are controlled by the adsorption of citric acid molecules on the surface of the particles due to cerium-citric acid complexes in the solution.

2.2 Silver Nanoparticles

Silver (Ag) is a noble metal which is resistant to corrosion and oxidation in moist air. Silver nanoparticles can be prepared by various ways, but in this work Ag nanoparticles were prepared by wet chemistry. AgNO_3 was reduced by NaBH_4 using

COPSS as a capping agent to control the size of Ag nanoparticles. The size of Ag nanoparticles is approximately 200 nm.

Normally, Ag nanoparticles were used as doping agent on the other metal such as TiO₂, CeO₂ and ZnO₂. However, this work will use Ag nanoparticles to prevent the recombination reaction in the photo-catalytic process and also increase the photon harvestment due to the Surface Plasmon Resonance (SPR) of Ag nanoparticles to increase the photo-catalytic activity of CeO₂.

Roshan Nainan, Pragati Thakur and Manchar Chaskar (2012) studied on synthesis of Silver doped TiO₂ nanoparticles for photo-catalytic degradation of methyl orange. TiO₂ nanoparticles were synthesized by sol-gel method by using hydrolysis and condensation of TTIP. Ag/TiO₂ nanoparticles were synthesized by using photo-deposition of Ag on the surface of TiO₂. They found that the size of pure TiO₂ nanoparticles is smaller than Ag/TiO₂ and specific surface area of pure TiO₂ is higher than Ag/TiO₂. However, the photo-catalytic activity of Ag/TiO₂ is still better than pure TiO₂ because Ag acts as an electron trap and prevents the recombination reaction which is an important factor for photo-catalytic activity. Furthermore, Ag/TiO₂ also can absorb in wider range of UV-visible light due to lowering of band gap.

Thou-Jen Whang et.al (2009) tried to improve the photo-catalytic activity of TiO₂ to be used under visible light. The silver nanoparticles were chosen to dope on the TiO₂ to improve the efficiency of TiO₂. Ag/TiO₂ nanoparticles were produced by laser-liquid interaction of silver nitrate in isopropanol. From their result, it can be seen that Ag can improve the photo-catalytic activity of TiO₂ obviously because Ag can prevent the recombination reaction and improving charge transfer. The best amount of Ag is 2%wt. to get 82.5% degradation of methylene blue in 2 hours under the light.

Wuwarnkar et.al (2013) studied on Ag doped TiO₂ nanoparticles synthesized by a microwave assisted method to improve the photo-catalytic activity of TiO₂ under UV irradiation. The dye used is methyl orange. In their work, they varied the concentration of silver ions, amount of photo-catalyst, reusability of photo-catalyst and pH of dye solution. They found that the optimum concentration of Ag for doped

TiO₂ is 0.25 %mol because at higher concentration, the active site of TiO₂ will decrease because Ag can cover the surface of TiO₂ and also can increase the particles size of TiO₂. The amount of Ag doped TiO₂ was varied. The optimum powder used is 100 mg/100 mL (1g/L) in the presence of 20 ppm methyl orange because the large amount of photo-catalyst can lead to agglomeration of photo-catalyst which results in decreasing in number of active sites. The surface charge of TiO₂ depends on the pH of the medium where TiO₂ will be positively charged when the medium is acidic and vice versa. The optimum pH for dye solution is 3.0 because the dye used is an anionic dye which can be attracted to the positively surface of TiO₂ by electrostatic interaction in acidic medium. In addition, Ag/TiO₂ can be reused five times.

2.3 Photo-catalyst

Photo-catalysis is the acceleration of photo reaction by using catalyst. When the catalyst receives enough energy from the light, electron from valence band will be excited to the conduction band which produces a positively charged holes and negatively charged electrons. Both charges can produce radicals which can react with contaminants in the waste water or used in the process of water splitting as shown in Fig.1.

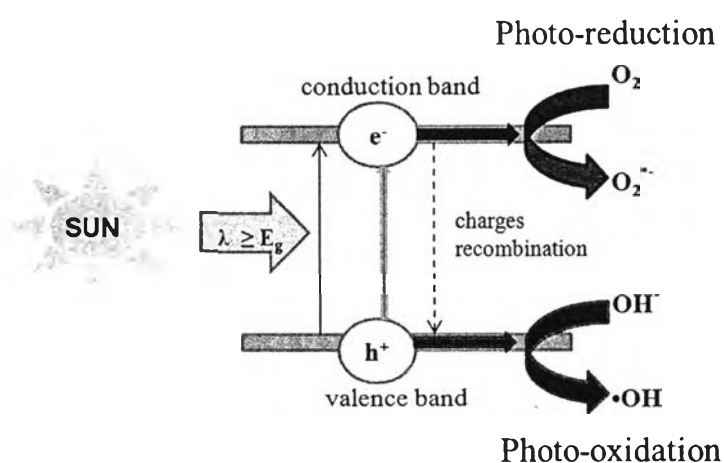


Figure 2.1 Schematic diagram of photo-catalytic.

Photo-catalysts can be divided into two types depending on the phase between reactant and catalyst.

1. Homogeneous photo-catalyst
2. Heterogeneous photo-catalyst

The homogeneous photo-catalyst is when the catalyst and reactant are in the same phase. However, in heterogeneous photo-catalyst is when the catalyst and reactant are in the different phase. This work will focus on the heterogeneous photo-catalyst because homogeneous photo-catalysts are harder to separate from the reactant.

Faisal et al. (2011) studied on ZnO-CeO₂ nanostructures for photo-catalyst. ZnO-CeO₂ nanostructures were synthesized by a simple and a method that requires low temperatures. They found that size of CeO₂ nanoparticles are approximately 40-90 nm distributed on the surface of ZnO with diameters approximately 50-200 nm as shown from XRD and FESEM. Additionally, the photo-catalytic activity of CeO₂-ZnO nanostructure showed the degradation of acridine orange and methylene blue which degraded 84.55% and 48.65% after 170 minutes under UV irradiation.

Yongqing Zhai, Shaoyang Zhang and Hui Pang (2006) studied on the synthesis of CeO₂ for photo-catalyst. CeO₂ nanocrystalline was obtained by the decomposition of hydrated cerium carbonate using ammonium bicarbonate as the precipitant. They found that CeO₂ nanostructure has formed at 300 °C but the crystalline has not grown completely supported from the result of XRD and also the crystalline size increases with the increasing calcination temperature. The dispersity of CeO₂ could be improved by adding the poly(ethylene glycol) (PEG) because PEG can form a protective film around the particle and PEG can be removed by calcination. As-synthesized CeO₂ nanocrystalline used as the photo-catalyst for the degradation of dye Acidic Black 10B under UV irradiation degrades the dye up to 77%.

Sadia Ameen, M.Shaheer Akhtar, Hyung-Kee Seo and Hyung-Shik Shin studied on CeO₂/TiO₂ for the degradation of bromophenol dye under visible light. CeO₂/TiO₂ was synthesized by mixing both CeO₂ and TiO₂ solution then the solution was adjusted to pH 10. After that kept it with autoclave at 120 °C for 48

hours and calcined at 450 °C with the ramp rate of 5 °C/min. FESEM and TEM showed that TiO₂ nanoparticles has spherical shape and average particle size around 20 nm. The large CeO₂ particles are uniformly embedded into TiO₂ nanoparticles. The XRD graphs showed both peaks of TiO₂ and CeO₂ to confirm that the product consists of CeO₂ and TiO₂. And they also found that bromophenol dye degraded under visible light in the presence of TiO₂/CeO₂ after 3 hours.

2.4 Polyelectrolyte Multilayers

2.4.1 Polyelectrolyte

Polyelectrolyte is a polymer which has electrolyte groups in the repeating unit. It can dissociate in aqueous solution to produce a charged polymer and its counter ions. Polyelectrolyte can be either positive (polycation) or negative (polyanion) which could later be combined as polyelectrolyte multilayers via electrostatic interaction using the layer by layer deposition.

Detsri and Dubas (2013) improved electrical properties of carbon nanotube (CNTs) using Layer-by-layer technique. The CNTs were modified by using either polyaniline blend poly(sodium-4-styrenesulfonate) (PANI-PSS), a polyanion solution or poly(diallyldimethyl ammonium chloride) (PDADMAC), a polycation solution to create negatives charged CNTs and positively charged CNTs, respectively. The three types of layer by layer combinations were prepared, which are PDADMAC/CNT⁻, PANI-PSS/CNT⁺ and CNT⁻/CNT⁺. They reported that the thickness of film will increase linearly with number of layer deposited. Although, CNT⁻/CNT⁺ showed slow growth but it has the highest electrical conductivity.

Kumlangdudsada, Tuantranont and Dubas (2012) were successful in depositing gold nanoparticle on the substrate by using flow layer-by-layer technique. They found that the electrical properties of the film will changed from an insulator to a conductor as the concentration of citrate which is used to synthesize the gold nanoparticles were reduced.

Dubas et al. (2011) also studied the antimicrobial activity of surgical sutures by using layer-by-layer technique. The silver nanoparticles were capped by

sodium alginate (5 mM to 0.1 mM). They reported that the antimicrobial efficiency will increase when decrease the alginate capping due to higher amount of silver ion.

Kumlangdudsada, Tuantranont and Dubas (2011) achieved to protect poly(methyl methacralate) (PMMA) and poly(dimethylsiloxane) (PDMS) substrate from organic solvent by using layer by layer technique. They used poly(diallyldimethyl ammonium chloride) and poly(styrene sulfonate) (PDADAMAC/PSS) or chitosan/alginate to coat on the substrate's surface. They found that chitosan/alginate and PDADMAC/PSS can prevent PMMA and PDMS from organic solvent due to decrease in penetration of organic solvent into the substrate. However, chitosan/alginate is more effective in protecting PMMA and PDMS surfaces than PDADMAC and PSS.

Limsavarn, Sritaveesinsub, and Dubas (2006) studied on synthesis of Ag nanoparticles by using polyelectrolyte and layer-by-layer technique. Silver nanoparticles were prepared by using sodium borohydride and capped with copolymer of styrene sulfonate and maleic monomers. The layer-by-layer was created from poly(diallyldimethyl ammonium chloride) (PDADMAC) and silver nanoparticles with PSS-CO-MA. They found that by increasing the concentration ratio between co-polyelectrolyte and silver nitrate increases the size distribution of nanoparticles. The resulting film will increase the intensity of absorbance peak as number of deposited layers increases. Furthermore, the resulting film can be used in a broad range of conditions since it is stable in both acidic and basic conditions.

Sehgal, Lalatonne, Berret and Morvan (2005) studied the precipitation-redispersion of Cerium oxide nanoparticle with poly(acrylic acid) (PAA). They separated the processes into two-steps. First, the precipitation step mixing cerium oxide with PAA at the same concentration and at pH 1.4. The solution becomes turbid then the solution was centrifuged into two phases. Second, is the redispersion step; they found that above pH 7.5, the solutions will obtain rapid redispersion and complete precipitation. With increasing pH, the hydrodynamic radius will decrease but the later value is still larger than diameter of bulk particles, indicating that nanoceria are coated by PAA. By decreasing the pH from pH 10 to pH 6, the CeO₂-PAA sols remained due to stabilization of CeO₂-PAA. The critical volume fraction

between CeO_2 and PAA is approximately 2, and the solution will get complete redispersion and becomes fully transparent. The conformation of the absorbed polyelectrolyte, which is a part of the monomer, is absorbed on the nanoparticles and the remaining part acts as solvated polyelectrolyte brush.

2.4.2 Layer by layer Technique

Layer-by-layer is a technique used to fabricate thin layer of film on the surface of material. The films are formed by depositing alternating layers of oppositely charged polyelectrolytes and rinsing in between each step. Typically, the polyelectrolyte multilayers are formed by layer by layer deposition. The layer by layer technique is a simple technique which can be performed in many different ways such as dip coating, spin-coating, spray coating and others. In this work, dip coating is used. The steps to do the layer by layer were described in Fig. 1 (Decher, 1997).

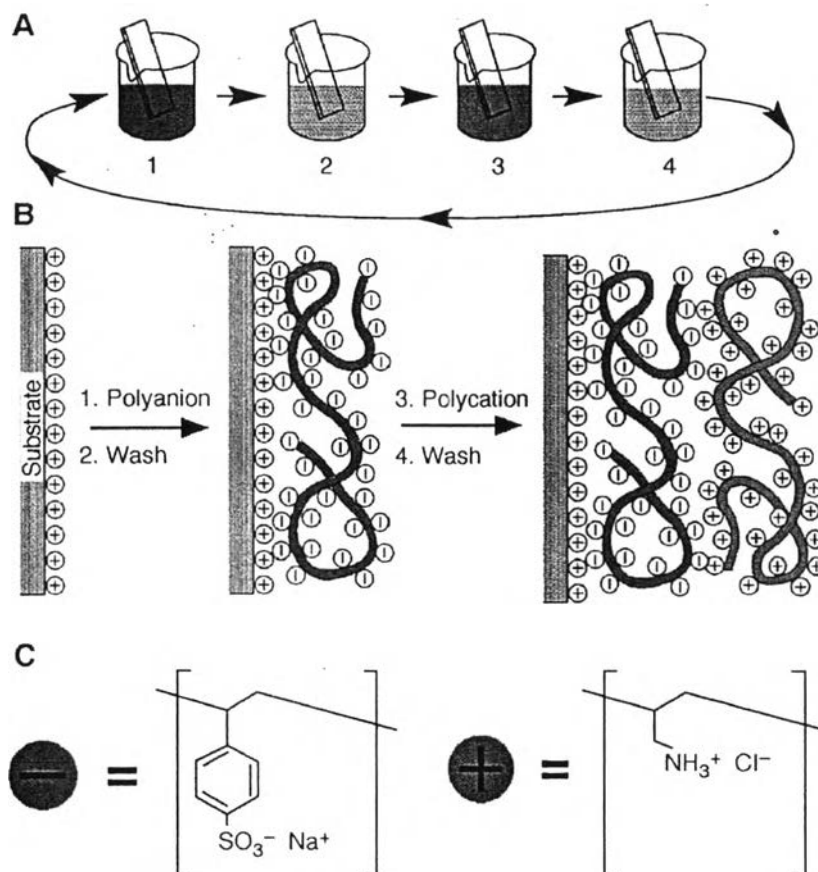


Figure 2.2 An experimental of layer by layer technique.

Before performing the layers by layer, the materials or substrate have to exhibit charges on its surface. Assuming that the material has a positively charged surface, firstly, dip the material into a polyanion solution at a certain time. The polyanion with a negative charge will deposit on the material surface. Then, rinse the material with distilled water. Second step, dip the material into a polycation solution using the same amount of time as the polyanion solution. Then, rinse it with distilled water. Third step, repeat the following steps until the amount of desired layers are achieved.

Dubas, Kumlangdudsana and Potiyaraj (2006) also used the layer-by-layer technique on nylon and silk fibers by using poly(diallyldimethyl ammonium chloride) (PDADMAC) and silver nanoparticles capped with poly(methacrylic acid)

(PMA) for antimicrobial applications. They reported that the antimicrobial activity of PDADMAC/PMA deposition 20 layers onto the silk is 80% bacteria reduction and 50% bacteria reduction for nylon. This technique can be used with other fibers as well.