

# Photo Catalytic Ability of Acicular Shaped TiO<sub>2</sub> Rutile Powder in Aqueous Metal-EDTA Solutions

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Photo catalytic characteristics of nano-sized TiO<sub>2</sub> powder with rutile phase produced using homogeneous precipitation process at low temperatures (HPPLT) were compared with those of commercial P-25 powder by Degussa Co. The TiO<sub>2</sub> powder by HPPLT showed very higher photoactivity in the removal rate, showing lower pH values in the solution, than the P-25 powder when eliminating metal ions such as Pb and Cu from aqueous metal-EDTA solutions. This can be inferred the more rapid photo-oxidation or -reduction of metal ions from the aqueous solution, together with relatively higher efficiencies in the use of electron-hole pair formed on the surface of TiO<sub>2</sub> particle, under UV light irradiation. Also, in the view of the TiO<sub>2</sub> particle morphology, compared to the well-dispersed spherical P-25 particle, the agglomerated TiO<sub>2</sub> particle by HPPLT consists of acicular typed primary particle with the thickness ranged of 3 ~ 7 nm, which would be more effective to the photocatalytic reactions without electron-hole recombination on the surface of the TiO<sub>2</sub> particle under the UV light irradiation. It is, therefore, thought that the higher photo activity of the rutile TiO<sub>2</sub> powder by HPPLT in the aqueous solutions resulted from having its higher specific surface area as well as acicular shape primary particle with very thin thickness.

*KeyWords:* HPPLT, Photocatalytic Effects, Ultrafine TiO<sub>2</sub> Powder, Rutile Phase, Nano-Sized

## 1. INTRODUCTION

Somorjai suggested[1] the reason for lower photo catalytic efficiencies in rutile TiO<sub>2</sub> phase because the recombination of the electron-hole pair produced by UV irradiation occurs more rapidly on the surface of the rutile phase and the amounts of reactants and hydroxides attached to the surface of the rutile phase are smaller

than those of the anatase TiO<sub>2</sub> phase. However, according to Mill's et al's study[2], the decrease in the photo catalytic effect during the transformation from the anatase to rutile TiO<sub>2</sub> phase was not due to the change in the crystalline structure but mainly due to those in the specific surface area and porosity. Also, Serpone[3] reported that although light scattering is higher for

submicron sized secondary particles of  $\text{TiO}_2$  than nanoparticles, the former has a large surface area as nanoparticles and then may yield superior efficiency in photo catalysis. In this study, the nano-structured  $\text{TiO}_2$  rutile phase powder with a high specific surface area was produced by a homogeneous precipitation process at ambient or very low temperatures below  $100^\circ\text{C}$  (HPPLT)[4,5], which had been proposed as being a cost effective and high quality process. The photo catalytic results of the  $\text{TiO}_2$  powder by HPPLT (HPPLTed  $\text{TiO}_2$  powder) were compared with those of commercially used P-25 powder with mainly the anatase phase when removing the heavy metal ions such as Pb and Cu ions from an aqueous solution, and the reason why the HPPLTed  $\text{TiO}_2$  powder shows superior efficiency in the photo catalysis was investigated.

## 2. EXPERIMENTAL PROCEDURE

The preparation procedure of HPPLTed  $\text{TiO}_2$  ultrafine powder directly from aqueous  $\text{TiOCl}_2$  solution has been described in detail elsewhere[4,5]. For photo catalytic reaction of the powder, using a re-circulating cylindrical batch typed reactor, inside which the irradiation source was placed, and a static batch typed reactor having the exterior irradiation source, the photolysis was carried out at ambient temperature in the deaerated conditions. Their photo catalytic properties were examined by comparing their metal ion recovery abilities from the aqueous solutions including Pb and Cu ions. The aqueous solutions of metal ion complexed 1:1 molar with EDTA(2Na) were introduced, in which the reagent grade of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2$  were used. The photolysis was performed after adding 2g/L of  $\text{TiO}_2$  powder by HPPLT or P-25(Degussa Co.) to the aqueous metal-EDTA solutions. After the photolysis, the remaining metal ion concentrations in the aqueous solutions were detected by AA spectrophotometer(Perkin-Elmer 5100 PC). TEM equipped with EDS was also used for analyzing the compositions and shapes of the  $\text{TiO}_2$ -metal complexes containing metal or metal oxides.

## 3. RESULTS AND DISCUSSION

When heating the aqueous  $\text{TiOCl}_2$  solution produced from  $\text{TiCl}_4$  during HPPLT, as crystalline  $\text{TiO}_2$  was directly precipitated and settled down, as previously reported[4,5].

The precipitation reaction in the aqueous  $\text{TiOCl}_2$  solution was carried out in the temperature ranges of 17 to  $105^\circ\text{C}$ , and the XRD results of the crystalline structure

are shown in Fig.1(A). Because the precipitates consisted of only rutile and anatase  $\text{TiO}_2$  phases, the volume fractional change of rutile  $\text{TiO}_2$  phase with the synthesis temperature was calculated by Kumar's equation[9]. Below  $65^\circ\text{C}$ , rutile  $\text{TiO}_2$  phase was produced regardless of the temperatures, but anatase  $\text{TiO}_2$  phase was first formed at  $70^\circ\text{C}$ , 30% of anatase  $\text{TiO}_2$  at  $80^\circ\text{C}$ , and 100% of anatase  $\text{TiO}_2$  at the temperatures above  $95^\circ\text{C}$ . For example, the HPPLTed  $\text{TiO}_2$  powder formed at  $50^\circ\text{C}$ , as shown in Fig.1(B), shows quite different crystallinity from that of P-25 powder, which consists of mixed rutile and anatase phase. Because the anatase phase in the powders heat-treated below  $650^\circ\text{C}$  was not detected, this HPPLTed  $\text{TiO}_2$  powder was thought to have only pure rutile phase. As reported in ref.(4), the pure anatase  $\text{TiO}_2$  phase formed at  $100^\circ\text{C}$  also showed the stronger crystallinity with the increase in the heat-treated

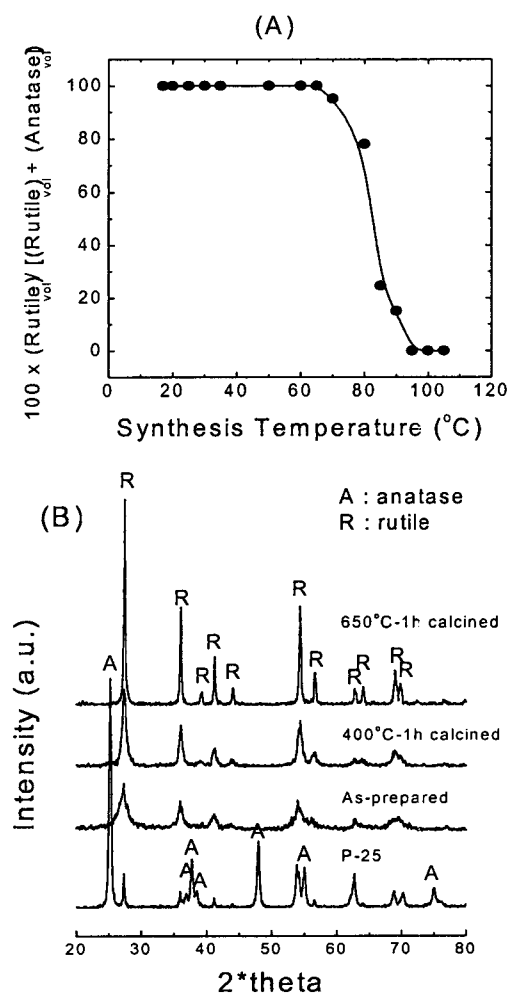


Fig.1. (A) Volume fraction of rutile  $\text{TiO}_2$  phase formed at various synthesis temperatures. (B) XRD patterns for the  $\text{TiO}_2$  powder by HPPLT before and after calcinations in air, and for the P-25 powder.

temperature. Thus, it can be thought that all the as-synthesized TiO<sub>2</sub> powders by HPPLT are very stable crystalline phase even though the formation temperature was very low.

The remaining Pb ion concentration in aqueous Pb-EDTA solution was analyzed after illuminating for 1 hr the solution which had 145 wppm of Pb ions, together with agitating the powders of Fig.1. Fig.2 shows the amount of Pb metal ion recovery, which was converted from the amount of removal by photocatalytic reaction. This photocatalytic reaction was simply conducted in the 50 mL static batch type reactor. Here, the adsorbed concentration was measured right after stirring the solution for 30 min in the dark room. The TiO<sub>2</sub> powders with mainly rutile phase, synthesized at the temperatures below 80°C, had almost the same amounts of adsorbed and finally recovered Pb ions regardless of the synthetic temperatures, whereas those decrease rapidly above 80°C of the synthetic temperature at which the volume fraction of the rutile phase is abruptly lessened. These results are opposite to the previous reports[1,11-12], showing that the anatase phase is more effective in photo catalysis than the rutile phase. In this study, the powders produced below 80°C have 130~200 m<sup>2</sup>/g of specific surface area, and the powders produced above 80°C have 40~70 m<sup>2</sup>/g of specific surface area. It was confirmed that the pure anatase phase synthesized at rapid heating conditions[4], which had about 100 m<sup>2</sup>/g of specific surface area, had almost the same amount of recovery as the rutile phase powder produced at 50°C, when pure anatase phase was specially treated not to agglomerate. Therefore, the reason that the rutile phase produced below 80°C has a

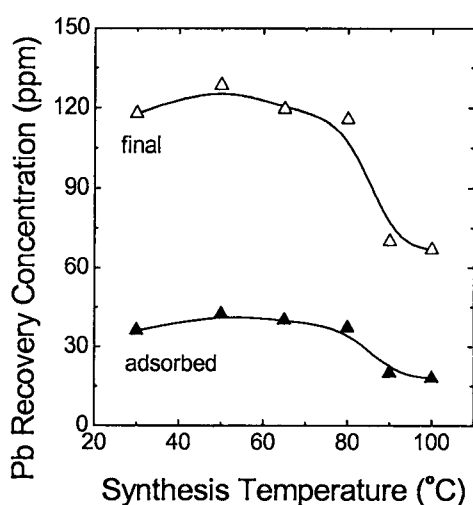


Fig.2. Pb recovery concentration measured from the aqueous Pb-EDTA solutions for the TiO<sub>2</sub> powders with the various synthesis temperatures, after irradiation for 1hr in the static type reactor.

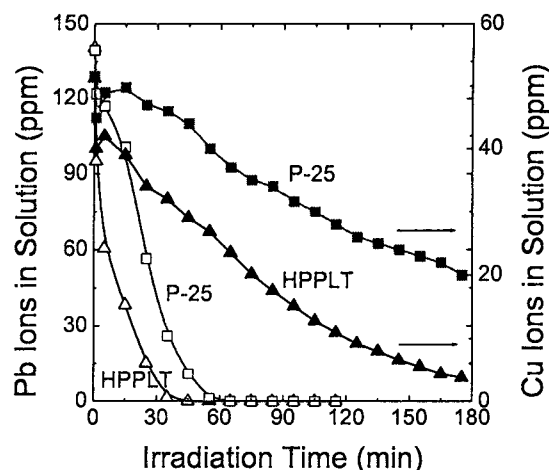


Fig.3. Pb and Cu concentrations remaining in the aqueous Pb- and Cu-EDTA solutions with the irradiation time in the re-circulating type reactor when the HPPLTed and P-25 TiO<sub>2</sub> powders were used as the photocatalyst.

more efficient Pb recovery than the anatase phase can be suggested to relate to the specific surface area rather than the crystal structure itself

In order to compare the HPPLTed TiO<sub>2</sub> powder prepared with an optimized condition with P-25 powder, commercially famous TiO<sub>2</sub> powder in the world, Fig.3 shows the photo catalytic results of the HPPLTed TiO<sub>2</sub> at 50°C and P-25 powders in the 2000 mL re-circulating batch type reactor, using the aqueous metal-EDTA solutions having a 143 wppm Pb ion and a 52 wppm Cu ion concentration. Here, the concentrations at 0 min and 1 min of irradiation time indicate for convenience the initially added concentration of metal ions and the adsorbed metal concentration in the dark room for 30 min, respectively. It is shown that the initial metal adsorption and removal rate of the HPPLTed powder is larger and faster than those of the P-25 powder. The complete removal of Pb ions by the HPPLTed powder was 1.5 times higher than the P-25 powder, showing that it takes about 35 min and 55 min to remove Pb ions completely by the HPPLTed and P-25 powder, respectively. In the removal of Cu ions from the aqueous Cu-EDTA solution having a 52 wppm Cu ion, the complete removal did not happen in a 3 hrs reaction time by the both powders. The fact that the initial concentration of Cu ions decreases again after slightly increasing the Cu ion concentration can be explained as the Cu ions were dissolved again in this solution, in which the photo catalytic reaction preferentially occurred on EDTA rather than on Cu ions that were adsorbed on

the  $\text{TiO}_2$  powder surfaces as being Cu-EDTA status formed by the EDTA ligand. While the reaction by the P-25 powder continues slowly until 180 min, the reaction by the HPPLTed  $\text{TiO}_2$  powder increases abruptly after 60min. From the result that 90% and 62% 52 wppm of Cu ion concentration was taken by the HPPLTed powder and P-25 powder, respectively, it can be concluded that the photo catalytic ability of the HPPLTed  $\text{TiO}_2$  powder is 1.5 times greater than that of the P-25 powder. It was confirmed from TEM analysis that Pb ions were recovered with the form of both Pb and PbO lumps simultaneously by the oxidation and reduction processes, whereas Cu ions were recovered with the form of a Cu lump by only the reduction process, in our experiments.

Fig.4 shows TEM photos of the HPPLTed and P-25  $\text{TiO}_2$  powders before and after the photolysis to investigate how the different particle morphologies could affect the reaction. The HPPLTed  $\text{TiO}_2$  powder has a chestnut bur shape with a size of 0.2~0.4  $\mu\text{m}$ (Fig.4(a)), in which the primary acicular particles are coagulated, while the P-25 powder, loosely agglomerated, has a round shape with a size of 20~50 nm (Fig.4(b)). It was confirmed that the HPPLTed powder has a larger specific surface area ( $\sim 180 \text{ m}^2/\text{g}$ ) than the P-25 powder has ( $\sim 55 \text{ m}^2/\text{g}$ ), which is important to the photoactivity. Fig.4(c, d) show the shape of the reduced Cu lumps in the solution with the same Cu ion concentration after the photolysis. A lot of the reductive process for Cu ions seemed to occur on the surface edge of the HPPLTed powder because many of the Cu metal lumps were detected around  $\text{TiO}_2$  secondary particles of the HPPLTed powder of Fig.4(c), whereas they were presented sparsely in the agglomerated P-25  $\text{TiO}_2$  powder of Fig.4(d). From the above results, the acicular shape of the primary particles with a thin thickness of 3~7 nm in the agglomerated shape of the HPPLTed powder, rather than the easily dispersed P-25 powder, seem to have greatly affected to the photo catalytic reaction together with a higher specific surface area.

#### 4. SUMMARY

The rutile phase  $\text{TiO}_2$  powder having nano-sized acicular primary particles and  $180 \text{ m}^2/\text{g}$  of specific surface area was prepared by patented HPPLT. Comparing the photo catalytic characteristics of both the HPPLTed and P-25  $\text{TiO}_2$  powders, the following results are obtained. The HPPLTed  $\text{TiO}_2$  powder, in spite of its rutile phase, has a higher photo catalytic reaction rate than the P-25 powder in the metal removal from the aqueous metal-EDTA solutions. The reason for the higher photo catalytic reaction of the HPPLTed  $\text{TiO}_2$  powder may be

suggested that the nano-structured HPPLTed powder has a larger specific surface area as well as very thin thickness in the acicular primary particles.

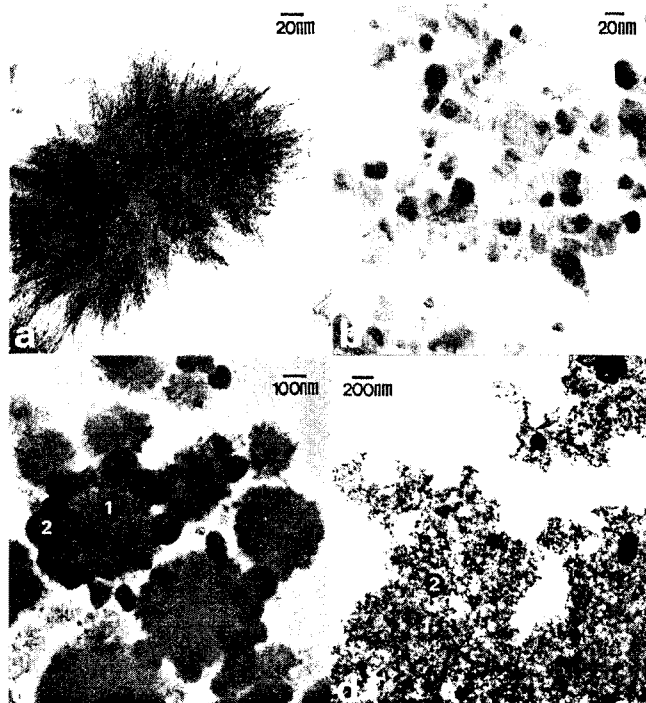


Fig.4. TEM photos for the HPPLTed (a and c) and P-25  $\text{TiO}_2$  (b and d) powders before (a and b) and after (c and d) the photocatalytic reaction, where the numbers 1 and 2 in (c and d) indicate  $\text{TiO}_2$  particle and Cu lump, respectively.

#### ACKNOWLEDGMENTS

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