

## Preparation of Titania Films with Cohered Nanosized Particles Using Improved Liquid Phase Deposition Process

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An improved liquid phase deposition method is proposed for the preparation of titania films with cohered particles. This method involves introducing micro-bubbles into the normal LPD process. The micro-bubble plays a role in the film formation process by not only preventing nucleation in the lateral direction but also creating a hot spot by self-crushing. This results in a rugged surface film with cohered nanosized titania particles possessing anatase crystallinity, even in the as-grown film. The lowering of the transition temperature from the anatase phase to the rutile phase takes place in the films deposited by the improved LPD process. For the films prepared via the improved LPD process, a photocatalytic UV light response was observed even in the as-grown film. Furthermore, its activity increases drastically after a 500 °C annealing step, leading to crystallinity improvement and surface area increase.

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**Keywords:** improved LPD, titania, rugged surface, photocatalysis, micro-bubble

### 1. INTRODUCTION

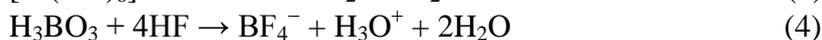
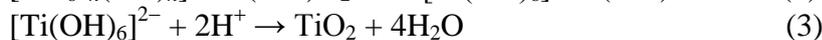
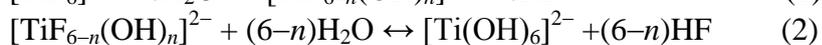
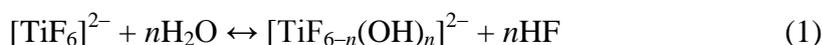
Titania is well known as a harmless and chemically stable material, and it has been widely applied in various fields [1-6]. For example, it is used in the manufacture of surface coatings, photoelectrodes, high-k dielectrics, paints, cosmetics, and many other products. In recent years, titania has attracted considerable interest as a photocatalytic functional material [6, 7]. Titania that shows specific photocatalytic properties, such as the photocatalytic decomposition of organic compounds and photo-induced hydrophilicity [1, 2], is expected to be applied in environmental fields. It has been used for a variety of purposes, such as antibacterial, antipollution and deodorization functions. Because of these unique photocatalytic properties, the applications of titania will continue to spread. Titania has been usually used in the form of thin films or particles for the purpose of practical applications.

A wide variety of deposition techniques have been developed for titania thin film preparation. They can be roughly classified as either physical or chemical processes. The physical processes include dry processes such as sputtering, vacuum evaporation, and chemical vapor deposition (CVD). The chemical processes include wet processes such as the sol-gel method, electrochemical deposition and liquid phase deposition (LPD). In general, film surfaces prepared using these techniques show comparative smoothness. For a titania photocatalyst to exhibit sufficient photocatalytic functions, an increase in surface area is practically essential; the surface area plays a potential role in enhancing the accessibility of the reactants to the active catalytic sites. Therefore, preparation techniques for titania films with rugged surfaces are important in terms of practical applications.

In this study, the LPD method is adopted. This method is a direct deposition technique using ligand-exchange hydrolysis of titanium fluoro complexes and an  $F^-$  consumption reaction with boric acid. Compared with other deposition techniques, such as the dry CVD process or the wet sol-gel method, the LPD method is a synthesis process that requires lower capital equipment, lower temperatures, and lower environmental load. This method was first used for  $SiO_2$  film deposition [8], but it is widely studied as a route for titania film deposition [9-13]. The usefulness of this technique in the formation of various metal oxide films has been recognized in the pioneering studies by Deki, et al. [14]. We propose an improved LPD method using micro-bubbles for the preparation of titania films with a rugged surface. This new preparation technique provides the titania films with cohered nanosized particles. These films exhibit a large surface area in addition to high anatase crystallinity.

## 2. EXPERIMENTAL

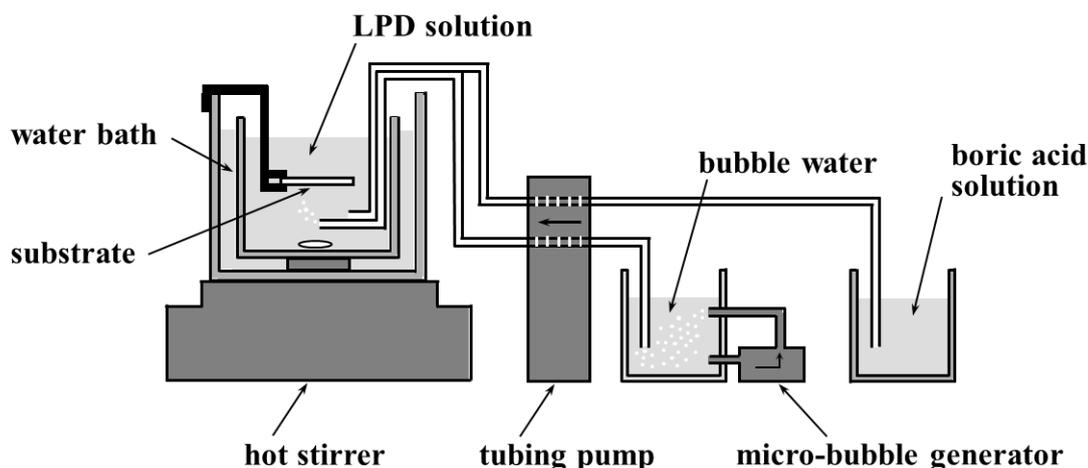
During the LPD process, the ligand-exchange equilibrium reaction (hydrolysis) is presumed to occur as follows [14];



For the hydrolysis of  $[TiF_6]^{2-}$  ions in aqueous solutions, Eq. (1) has been proposed by Schmitt et al. [15]. This equilibrium is shifted towards the right-hand side with the addition of  $H_3BO_3$ , which acts as an  $F^-$  scavenger.  $H_3BO_3$  reacts readily with  $F^-$  ions to generate the more stable  $BF_4^-$  ion by Eq. (4) [16]. The titania film formation proceeds according to Eq. (3), and the reaction is controlled by the amount of  $H_3BO_3$ . In this study, micro-bubble water is introduced into the raw solution along with  $H_3BO_3$ , for a purpose of preparing the films with rugged surface.

Figure 1 shows a schematic illustration of the LPD apparatus, which is equipped with a reaction vessel, water bath, hot stirrer, micro-bubble generator, and tubing pump. The raw ammonium hexafluorotitanate (LPD solution) in the reaction vessel was kept at constant temperature, and the boric

acid solution and micro-bubble water were introduced constantly into the reaction vessel and controlled by the tubing pump. The conditions of the LPD process are listed in Table 1.



**Figure 1.** A schematic diagram of the improved LPD system

**Table 1.** LPD process conditions

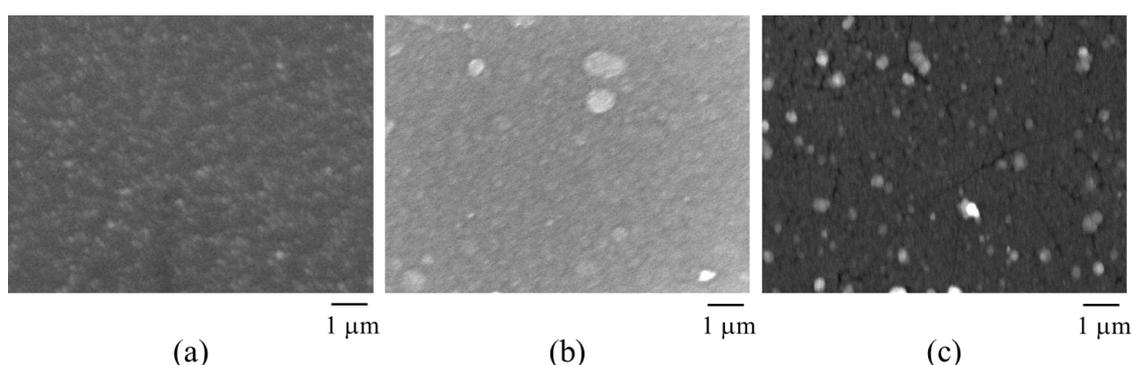
0.1 mol/l $(\text{NH}_4)_2\text{TiF}_6$	100 mL
Concentration of $\text{H}_3\text{BO}_3$	0.1 - 0.5 mol/L
Flow rate of $\text{H}_3\text{BO}_3$	53 mL/h
Micro-bubble water	42 mL/h
Temperature	55 - 65 °C
Deposition time	3 - 5 hrs

Titania films were deposited on Si wafers, and the surface morphology and film thickness were examined with a scanning electron microscope (SEM; HITACHI S-2000). After annealing at 500 °C and 700 °C for 1 hour in nitrogen ambient, the crystalline structures were examined with an X-ray diffractometer (XRD; RIGAKU RINT-2100, Cu  $K_\alpha$  X-ray source operating at 30 kV and 20 mA). The photocatalytic activities of the films deposited on quartz substrates were evaluated with a pigment degradation measurement. A black light with an intensity of 0.5 mW/cm<sup>2</sup> was used as the UV light source. The degradation rate of the pigment methyleneblue was evaluated by measuring the absorbance changes at 654 nm with a UV-VIS spectrometer (Ocean Optics USB2000). The films were soaked in a 1 mmol/L methyleneblue solution for 1 hour, after which excess methyleneblue on the back surface was wiped off and the samples were dried in the dark. The absorbance at 654 nm was measured after each 15-min UV light irradiation was performed.

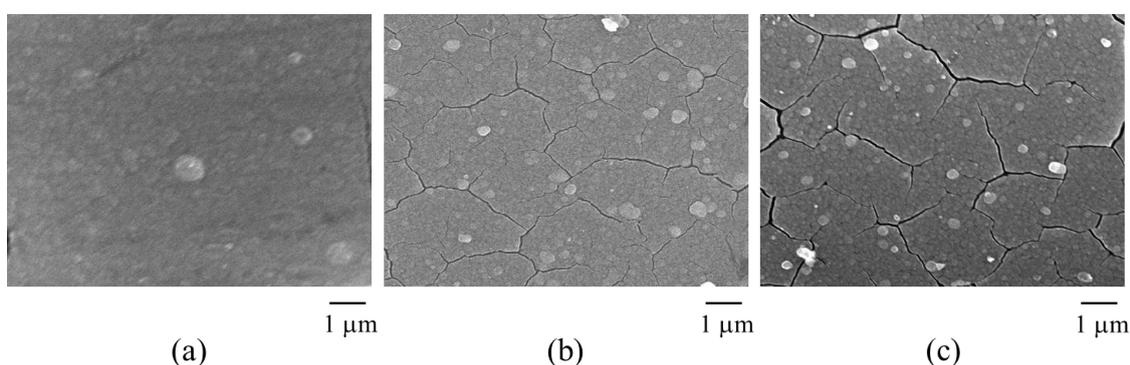
### 3. RESULTS AND DISCUSSION

#### 3.1 Surface morphology

The thicknesses and surface morphologies of the films were evaluated using SEM. The thicknesses of the films prepared by normal LPD process (without micro-bubbles) at the deposition time of 5 hours varied from 0.8 to 1.0  $\mu\text{m}$ , when the  $\text{H}_3\text{BO}_3$  concentration and the raw solution temperature were changed in the range of Table 1. In the case of improved LPD process (with micro-bubbles), thicknesses cannot estimate exactly because the film surface is intensely rough, as described below. However, average thickness of the improved LPD films was about 1.0  $\mu\text{m}$  which was almost same as those of the normal LPD films.



**Figure 2.** Surface morphology of the titania films prepared by a normal LPD process. The  $\text{H}_3\text{BO}_3$  solution concentrations are (a) 0.1 mol/L, (b) 0.3 mol/L, and (c) 0.5 mol/L. The raw solution temperature and deposition time are 55  $^\circ\text{C}$  and 5 hours, respectively.

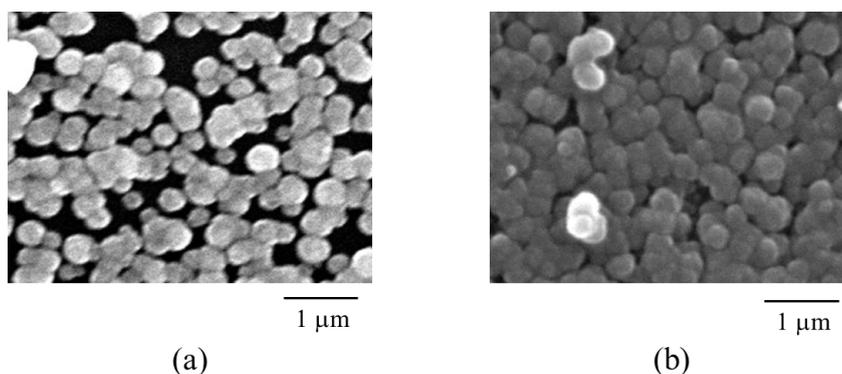


**Figure 3.** Surface morphology of the titania films prepared by the normal LPD process. The raw solution temperatures are (a) 55  $^\circ\text{C}$ , (b) 60  $^\circ\text{C}$ , and (c) 65  $^\circ\text{C}$ . The  $\text{H}_3\text{BO}_3$  solution concentration and deposition time are 0.3 mol/L and 5 hours, respectively.

The SEM photographs of the films prepared by the normal LPD process are shown in Figs. 2 and 3. Figures. 2 (a) - (c) show how the films were prepared by changing the  $\text{H}_3\text{BO}_3$  concentration, and Figs. 3 (a) - (c) show how the films were prepared by changing the raw solution temperature. In every case, smooth surfaces were observed. It should be noted that several cracks were sometimes observed

in the films; these cracks could have been generated by internal stress due to film contraction upon drying. Similar surface morphologies have been reported by several researchers [5, 14, 17, 18]. In the LPD process, titanium hydroxide complex ions are supersaturated with the  $F^-$  abstracted by  $BO_3^{3-}$ . Titania films are formed through nucleation of these titanium hydroxide complex ions. This nucleation process proceeds according to the following steps: (i) corpuscle nucleation due to the hydrolysis reaction following the ligand-exchange reaction and (ii) lateral and vertical growth of nuclei. Because the rate of step (ii) increases as the  $H_3BO_3$  concentration and raw solution temperature increase, continuous film surfaces with some cracks were observed.

Figures 4 (a) and (b) show the SEM photograph of the films prepared using the improved LPD process for 3 and 5 hours, respectively. The  $H_3BO_3$  solution concentration and the raw solution temperatures are 0.3 mol/ L and 60 °C, respectively. These surface morphology where many titania particles with a few hundred nm in diameter cohered differs greatly from those of the normal LPD films. In addition, the particles exist comparably sparsely for 3-hours deposition, while those are piled up for 5-hours deposition. Because the micro-bubble remains throughout the deposition process due to its long lifetime, the nucleation process in the lateral direction was considered to be obstructed by the coexisting micro-bubble on the substrate surface. As a result, many nanosized titania particles formed in initial stage of the LPD process. While the reaction progresses, these particles were piled up and rugged surface film was formed.

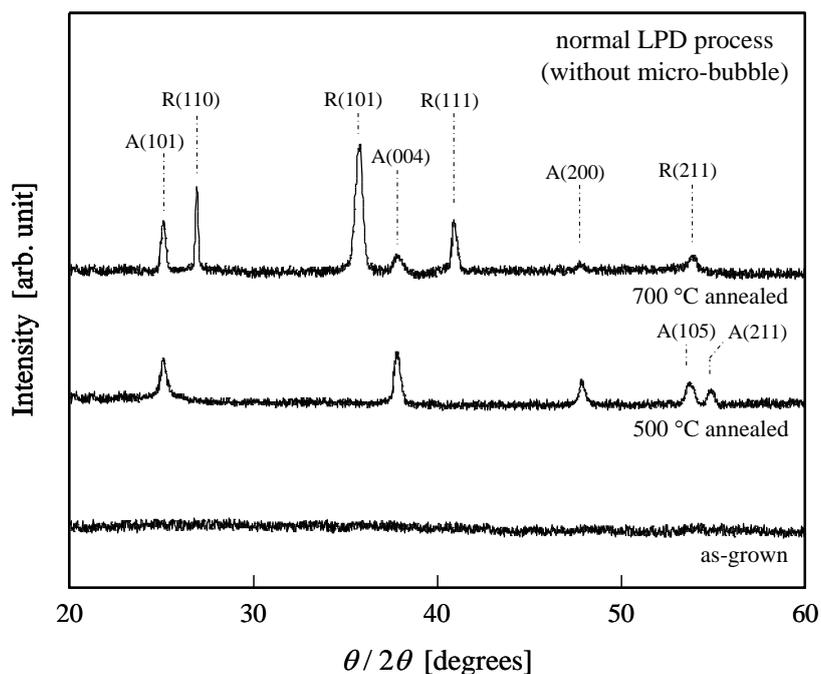


**Figure 4.** Surface morphology of the titania films prepared by the improved LPD process. Deposition times are (a) 3hours and (b) 5 hours. The  $H_3BO_3$  solution concentration and the raw solution temperatures are 0.3 mol/ L and 60 °C, respectively.

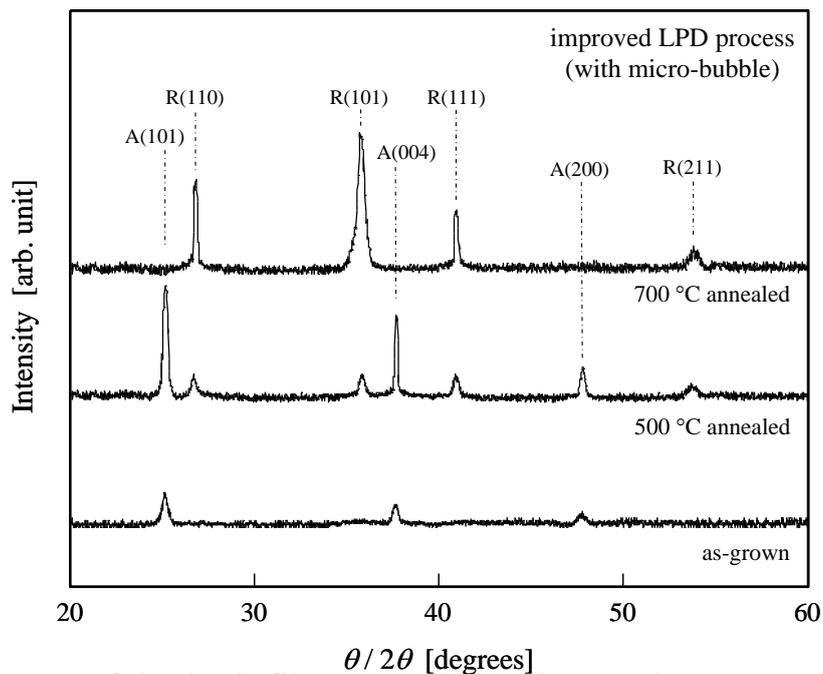
### 3.2 Crystallinity

The crystalline structures of the films shown in Fig. 3(b) (normal LPD film) and Fig. 4 (improved LPD film) before and after annealing were examined using an XRD measurement. Figure 5 shows the diffraction patterns of the normal LPD films. No diffraction peak was observed for the as-grown film. The diffraction lines assigned to anatase planes were observed for the 500 °C-annealed film, and lines assigned to both the anatase and rutile planes were observed for the 700 °C-annealed

film. These results indicate that the anatase and rutile are low- and high-temperature phases, respectively.



**Figure 5.** XRD patterns of the titania film prepared by a normal LPD process (Fig. 3 (b)) before and after annealing. A and R refer to the anatase and rutile planes, respectively.



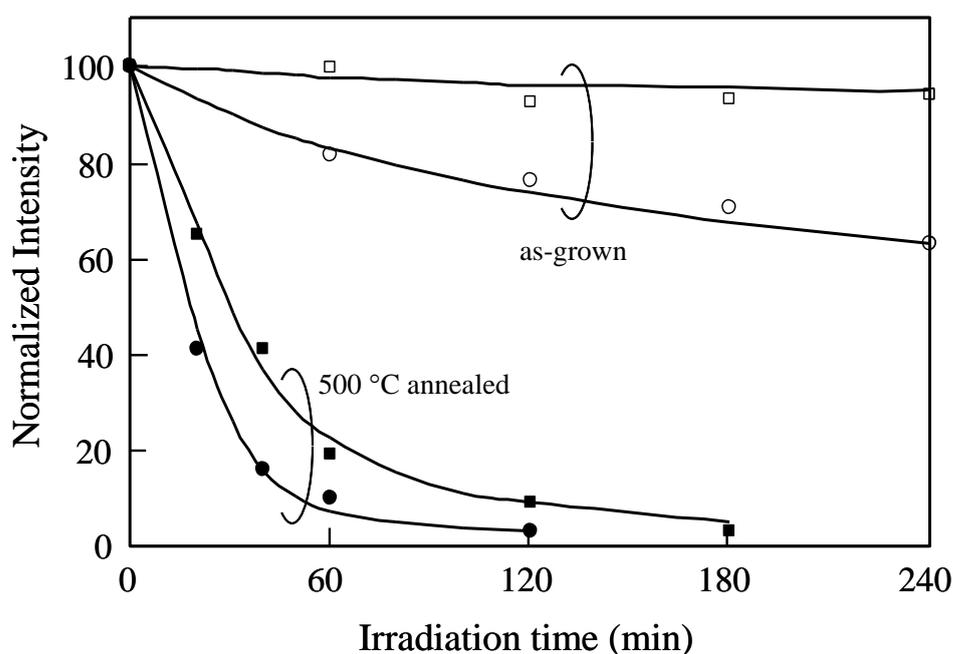
**Figure 6.** XRD patterns of the titania film prepared by an improved LPD process (Fig. 4) before and after annealing. A and R refer to the anatase and rutile planes, respectively.

As shown in Fig. 6, in the films deposited by the improved LPD process, anatase plane diffraction lines were observed even for the as-grown film, though the diffraction intensities were weak. The intensities of these anatase diffraction lines increase and rutile diffraction peaks appear in the 500 °C-annealed film, but only rutile lines remain in the 700 °C-annealed film.

In the grain growth process, the inside of the corpuscle reaches a high pressure and temperature; pressure remains constant due to nucleus growth in the surrounding area, and crystallization is promoted. Moreover, when a micro-bubble collapses on the film surface, temperature locally becomes several thousand °C for several picoseconds, and the crystallization of the surrounding titania grains is considered to be promoted under the temporarily high temperature. After annealing at 500 - 700 °C, the crystallinity of the films is improved further. This crystalline process caused lowering of transition temperature from the anatase phase to the rutile phase in the films deposited by the improved LPD process.

### 3.3 Photocatalytic activity

When the titania is irradiated by UV light, it exhibits the peculiar photocatalytic function of causing photo-induced decomposition of organic compounds. Here, this effect was evaluated by measuring the degradation of methyleneblue.



**Figure 7.** Absorbance of methyleneblue at 654 nm as a function of UV light irradiation time. Squares represent the normal LPD films and circles represent the improved LPD films.

Figure 7 shows the absorbance of methyleneblue at 654 nm as a function of UV light irradiation time for both the as-grown and 500 °C-annealed films described in Sec. 3.2. Methyleneblue

was not degraded on the as-grown film prepared by the normal LPD method. For the film prepared using the improved LPD method, however, it can be observed that the degradation of methyleneblue took place in the as-grown film, though weakly. After the 500°C annealing step, methyleneblue degradation drastically increases for films prepared using either the normal or improved LPD method. As shown in Figs. 5 and 6, these films exhibit predominately anatase crystallinity; strong photocatalytic activity was observed for both films. Photocatalytic activity of the improved LPD film is considered to be stronger than that of the normal LPD film due to differences in the surface area and the crystallinity intensity of the anatase phase.

#### 4. CONCLUSION

The preparation and characterization of titania films with cohered nanosized particles has been studied. We proposed an improved liquid phase deposition method in which micro-bubbles were introduced to the film formation process. The micro-bubbles play a role in the film formation process by not only preventing the nucleation in the lateral direction but also creating a hot spot of several thousand °C for several picoseconds. These effects lead to formation of titania films with cohered nanosized particles; these films possess large surface areas and anatase crystallinity, even in the as-grown film. These films additionally exhibit photocatalytic properties when they are irradiated by UV light. Photo-induced decomposition of organic compounds depends on both surface area and the crystallinity of anatase. The films prepared by the improved LPD method are considered to have great potential for application in environmental fields as photocatalytic materials.

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#### References

1. C. Kim, J. T. Kim, K. S. Kim, S. Jeong, H. Y. Kim and Y. S. Han, *Electrochim. Acta*, 54 (2009) 5715
2. A. Fujishima, X. T. Zhang and D. A. Tryk, *Surf. Sci. Rep.*, 63 (2008) 515
3. C. X. Lei, H. Zhou, Z. D. Feng, Y. F. Zhu and R. G. Du, *J. Alloy. Comp.*, 513 (2012) 552
4. D. Li, H. Tong and L. Zhang, *Trans. Nonferrous Met. Soc. China*, 23 (2013) 3306
5. H. Maki, Y. Okumura, H. Ikuta and M. Mizuhata, *J. Phys. Chem.*, 118 (2014) 11964
6. H. Park, K. Y. Kim, and W. Choi, *J. Phys. Chem.*, B106 (2002) 4775
7. G. X. Shen, Y. C. Chen and C. J. Lin, *Thin Solid Films*, 489 (2005) 130
8. H. Nagayama, H. Honda and H. Kawahara, *J. Electrochem. Soc.*, 135 (1988) 2013.
9. K. Koumoto, S. Seo, T. Sugiyama, W.S. Seo and W.J. Dressick, *Chem. Mater.*, 11 (1999) 2305
10. T. P. Niesen and M. R. De Guire, *J. Electrochem. Soc.*, 6 (2001) 169
11. D. Gutierrez-Tauste, X. Domenech, M. A. Hernandez-Fenollosa and J. A. Ayllon, *J. Mater. Chem.*, 16 (2006) 2249
12. J. G. Yu, H. G. Yu, C. H. Ao, S. C. Lee, J. C. Yu and W. K. Ho, *Thin Solid Films*, 496 (2006) 273
13. Y. B Ding, C. Z. Yang, L. H. Zhu and J. D. Zhang, *J. Haz. Mater.*, 175 (2010) 96

14. S. Deki, Y. Aoi, O. Hiroi and A. Kajinami, *Chem. Lett.*, 25 (1996) 433
15. R. H. Schmitt, E. L. Glove and R. D. Brown, *J. Am. Chem. Soc.*, 82 (1960) 5292
16. C. A. Wamser, *J. Am. Chem. Soc.*, 73 (1951) 409
17. A. Dutschke, C. Diegelmann and P. Löbmann, *Chem. Mater.*, 15 (2003) 3501
18. M. Mallak, M. Bockmeyer and P. Löbmann, *Thin Solid Films*, 515 (2007) 8072

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