Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 30 Aug 2012.

To cite this article: No-Kuk Park , Do Hyeong Kim , Hyun Gyu Park & Tae Jin Lee (2012): Size Control of Particles with Changing Concentration of TIP used as a Precursor for Synthesis of TiO_2 by Ultra-Sonic Spray and Pyrolysis Method, Molecular Crystals and Liquid Crystals, 565:1, 59-67

To link to this article: http://dx.doi.org/10.1080/15421406.2012.692229

Mol. Cryst. Liq. Cryst., Vol. 565: pp. 59–67, 2012

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.692229

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Size Control of Particles with Changing Concentration of TIP used as a Precursor for Synthesis of TiO_2 by Ultra-Sonic Spray and Pyrolysis Method

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The nano sized titanium dioxide was synthesized by the ultra-sonic spray method and pyrolysis of TIP (titanium iso-propoxide), which was employed as the precursor solution. The fine liquid drop of the TIP sprayed by the ultra-sonic spray nozzle was conversed into TiO_2 nano particles by pyrolysis through the hot tubular reactor. The concentration of TIP solution was controlled in the range of 0.1∼1.0 M and the morphology, the particle size, the crystal structure, and the surface area of synthesized TiO_2 were investigated by SEM, TEM, XRD and N_2-adsorption method, respectively. DSSC (dye sensitized solar cells) was also prepared by employing the synthesized TiO_2 nano powder as the electrode and the photo-electrical property of TiO_2 was compared in terms of efficiency of solar cells. It was further confirmed that the particle size of TiO_2 was controlled with changing concentration of TIP solution. When 0.1 M TIP was used as the precursor solution, the size, the surface area and the crystal structure of synthesized TiO_2 were approximately 10 nm (by TEM), 56 m^2/g and the anatase structure, respectively. The particle size of TiO_2 decreased with decreasing concentration of TIP solution. Therefore, it was concluded that the efficiency of DSSC's can be improved by employing high surface area and nano-sized TiO_2 as the electrode.

Keywords TiO_2; ultra sonic spray method; DSSCs; electrode

Introduction

The applications of TiO_2-based nanomaterials in photocatalysis [1,2] and photoelectrochemical conversion [3,4] have been extensively studied in the past decades, owing to its excellent (photo)chemical stability, low cost and non-toxic nature [1,2,5,6]. Titanium oxide, with a wide band-gap (anatase 3.2 eV, rutile 3.0 eV), is a UV absorber and utilizes only a very small fraction of the solar spectrum (<5%). There have been some successful efforts in improving the efficiency of utilization of solar energy through organic dye sensitization [7–10]; especially by employing a trimeric ruthenium complex dye, for which an efficiency of 12% was reported by Graetzel and co-worker [7].

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In dye-sensitized solar cells, photo-electrodes prepared by using anatase phase TiO_2 gives better solar cell efficiency when compared to the other crystal structures [11,12]. TiO_2 particles have a strong tendency to agglomerate into larger particles, which leads to a decrease in the surface area with resultant decrease in its applicability. Hence, it is very important to synthesize the TiO_2 nanoparticles with desired crystal structure and controlled particle size. Rao et al. [12] reported the synthesis and characterization of nanocrystalline TiO_2 with narrow size distribution and minimal agglomeration. The effect of precursor to solvent weight ratio on the crystallinity of the TiO_2 nanoparticles by the spray deposition technique had also been reported [12].

In our present study, the preparation method for the nano-sized TiO_2 with a high surface area was researched for the application of TiO_2 as the electrode in DSSCs. The efficiency of DSSCs was dependant on the content of photo sensitive dye coated over TiO_2. Therefore, it was concluded that the surface area of TiO_2 is a very important factor. Since the decrease in the particle size leads to an increase in the surface area, the small sized nano-particles were synthesized in this study. The synthesis of the small sized nano-particles is the profitable technology than the preparation of meso-porous materials.

In this study, the fine droplets of the precursor solution were formed by the ultra-sonic spray method and TiO_2 nano-particles were prepared by the pyrolysis of droplets at high temperature. During these procedures, the concentration of precursor solution was controlled for the synthesis of nano-sized TiO_2. Since TiO_2 crystals were produced during the pyrolysis, grown at high temperature and sintered, the spray pyrolysis method was also used for the prevention of crystal growth and sintering. The precursor solution was sprayed into the reactor through the ultra-sonic spray nozzle. The sprayed fine droplets were decomposed at zero contacting state with other droplets of surroundings. Therefore, it was expected that the nano-sized TiO_2 can be uniformly synthesized by the ultra-sonic spray and pyrolysis method due to the independent crystal growth and sintering of the droplets and its size can be controlled with changing concentration of precursor solution.

Experiments

Ultra-Sonic Spray Method

The ultra-sonic spray and pyrolysis apparatus were manufactured for the synthesis of the nano-sized TiO_2 and the representative schematic diagram is shown in Fig. 1. The equipment consisted of the ultra-sonic spray nozzle, the micro liquid pump, the vertical type tubular reactor (O.D = 2 inch, length = 100 mm) and the particle collecting filter. The temperature profile in the reactor for the pyrolysis is shown in Fig. 2 and the temperature range in the bottom of reactor was between 50∼100°C , 100∼750°C in the center and 200∼750°C at the top, respectively. Therefore, the solvent in the precursor solution was removed at the bottom of the reactor and the pyrolysis of TIP occurred at the center of the reactor. The solid materials produced by pyrolysis were crystallized into TiO_2 at the top and center of the reactor. TIP (titanium iso-propoxide) was used as the precursor and its concentration was controlled at 0.1, 0.5 and 1.0 M by using methyl alcohol as the solvent. The precursor solution was filled in the round flask connected to the bottom of the reactor and was supplied to the ultra-sonic spray nozzle by the liquid micro-pump, as shown in Fig. 1. The fine droplets sprayed into the round flask by the ultra-sonic spray nozzle were passed into the tubular reactor by using nitrogen as the carrier gas.

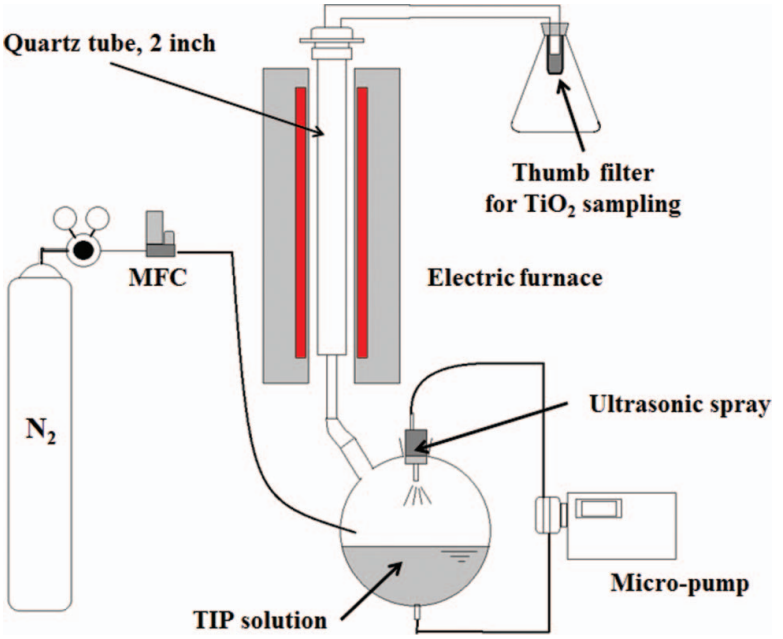

Figure 1. Schematic diagram representing experimental apparatus for ultra-sonic spray and pyrolysis method.

Analysis of Physical Properties

The crystal structure and the crystallite size of the sample collected in a filter were investigated by XRD (X-ray diffractometer, PANalytical, MPD for bulk) and its morphology and the size of particles were observed by SEM (scanning electron microscopy, HITACHI,

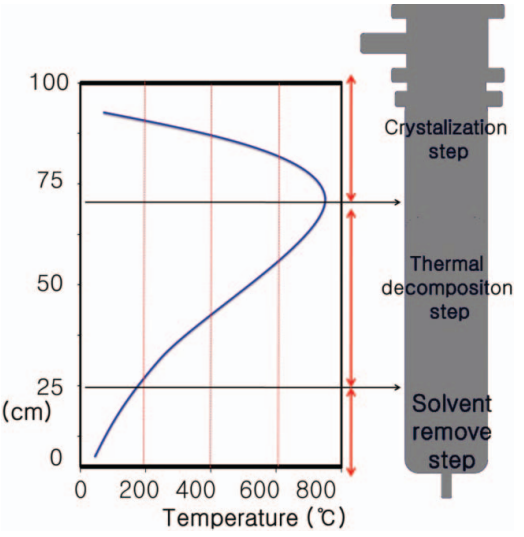

Figure 2. Temperature profile in vertical type tubular reactor for pyrolysis.

S-4100) and TEM (transmission electron microscopy, HITACHI, H-7600). Its surface area was measured by BET surface area measurement (Gemini, GEMINI2375) by employing N_2 adsorption method.

Preparation of DSSCs

The module of DSSCs (dye sensitized solar cells), which employed TiO_2 as an electrode, was also manufactured for assessing the photo-electric property of synthesized TiO_2. The efficiency of DSSCs was compared with relation to different particle size of TiO_2 synthesized by the ultra-sonic spray and pyrolysis method. The transparent nanocrystalline-TiO_2 layer was coated on the Fluorine-doped Tin Oxide (FTO, sheet resistance: 10 Ω per square) glass plates by screen printing and then gradually heated under the atmosphere at 325°C for 5 min. In order to get the dyes adsorbed onto the surface, the resultant electrode was immersed into the N719 dye solution (50mM of N719 in ethanol solution) at room temperature for 24 h. The dye-adsorbed TiO_2 electrode and FTO glass were assembled into a sealed sandwich-type cell. Subsequently, a drop of the electrolyte solution (AN50) was placed on a drilled hole in the counter electrode of the assembled cell and was driven into the cell by means of vacuum backfilling. Finally, the hole was sealed with an additional cover glass.

Results and Discussion

Determination of Flow Rate for Spray

In this study, the nano-sized TiO_2 was synthesized through a dry for the removing solvent, a pyrolysis, and oxidation of Ti components contained in TIP droplets sprayed with the ultra-sonic spray nozzle, in the tubular reactor. Therefore, the fine droplets sprayed by the ultra-sonic spray nozzle should be formed of uniform size for the production of final products with homogeneous size. The spray nozzle used in this study was made with the TIP mist, which consisted of the fine droplets in association with strong ultra sonic wave. The precursor (TIP) was supplied to the spray nozzle with the help of a micro-pump. The fine droplets of heterogeneous size can be formed based on the high or low flow rate of TIP supplied in the spray nozzle. Therefore, the morphology of mist sprayed in the nozzle was observed in association with the recycling rate of TIP injected in the ultra-sonic spray nozzle to determine the suitable flow rate of TIP. The recycling rate of TIP was changed by controlling the rpm of the micro-pump and the droplet size of TIP increased with an increase in rpm of the micro-pump due to the contact between a droplet and other droplets of the surrounding (Fig. 3). It was also confirmed that the heterogeneous large droplets were sprayed from the nozzle when the rpm of micro-pump was above 20 rpm. Therefore, the recycling rate of TIP was chosen to be 2 rpm in agreement with the flow rate of 4 ml/min. All the experiments in this study were carried out at the recycling rate of 2 rpm of micro-pump for the synthesis of nano-sized TiO_2. Based on the measurement by laser scattering method, the mean size of single droplet sprayed with 2 rpm of micro-pump was found to be approximately 11.8 μm.

SEM/TEM Analysis

TIP solutions of 0.1, 0.5 and 1.0 M diluted with methyl alcohol were prepared for the synthesis of nano-sized TiO_2 and these solutions were sprayed by the ultra-sonic spray

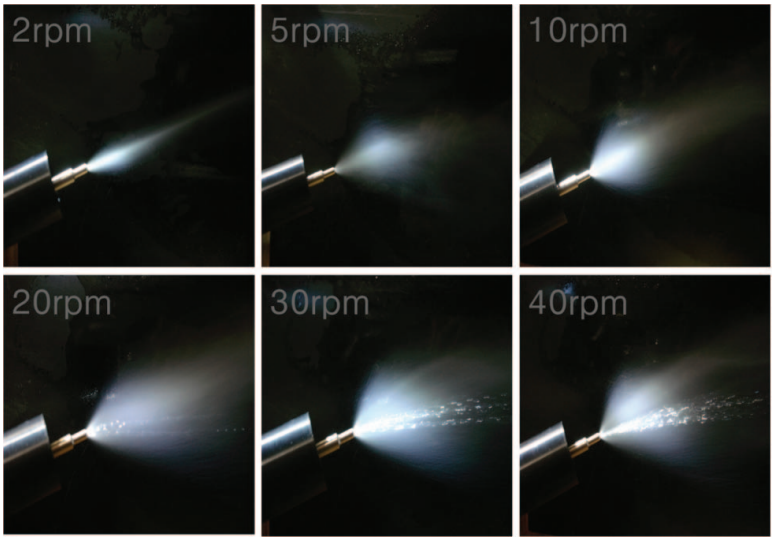

Figure 3. Morphologies of mist sprayed with different recycling rate of TIP injected in the ultra-sonic spray nozzle.

nozzle. The mist of TIP formed by the spray nozzle was crystallized into TiO_2 after the dry process and pyrolysis in the tubular reactor of vertical type. The SEM images of samples synthesized by the ultra-sonic spray and pyrolysis method are shown in Fig. 4. The size of nano-particle synthesized by this method varied with change in concentration of TIP used as the precursor, and decreased with decreasing concentration of TIP. It was observed by SEM analysis that the sizes of particles synthesized with 0.1, 0.5 and 1.0 M TIP were below 60, 60∼100 and 120∼180 nm, respectively. If the concentration of precursor was lowered, the mole amount of precursor in the fine single droplet formed by the spray nozzle was also lowered. Thus, the contact between the materials could not supplementally occur because the remaining solid material after the thermal decomposition of solvent and alcoholic liquid components was crystallized at the floating state in a gas phase. From the SEM images as seen in Fig. 4, it was confirmed that the size of solid particle synthesized by the ultra-sonic spray and pyrolysis method can be controlled with the concentration of precursor.

The size of TiO_2 synthesized by the ultra-sonic spray and pyrolysis methods was investigated by TEM images, as shown in Fig. 5. Their sizes were approximately 10,

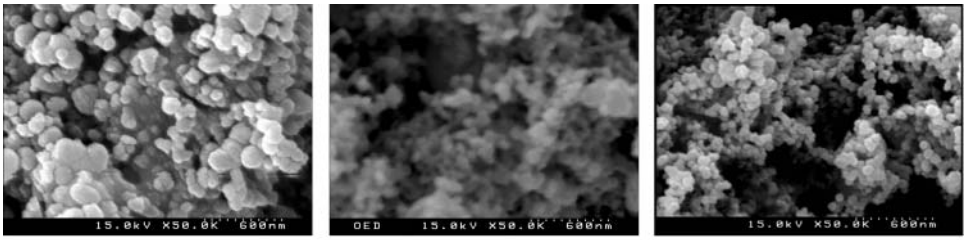

Figure 4. SEM images of TiO_2 synthesized with changing concentration of TIP solution by ultra-sonic spray and pyrolysis method; (a) 1.0 M, (b) 0.5 M, (c) 0.1 M.

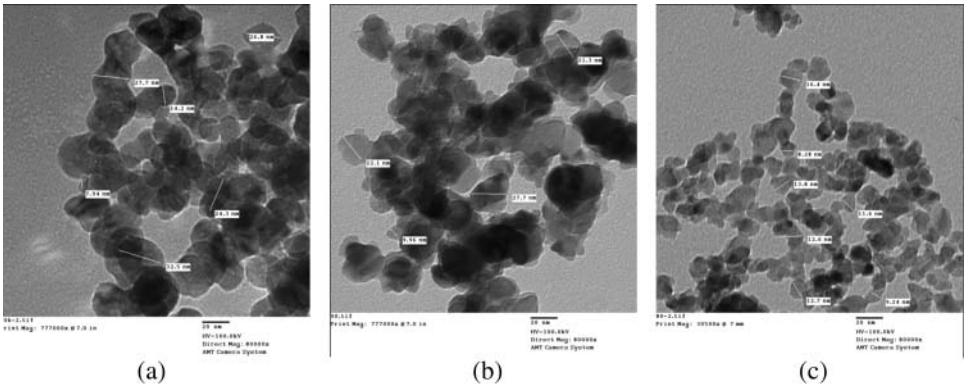

Figure 5. TEM images of TiO_2 synthesized with changing concentration of TIP solution by ultrasonic spray and pyrolysis method; (a) 1.0 M, (b) 0.5 M, (c) 0.1 M.

20 and 25 nm, when TIP solutions of 0.1, 0.5 and 1.0 M were used as the precursor, respectively. However, the particle size as observed by TEM was lower than that estimated by SEM. Since the nano-particles were well dispersed in the solvent and did not precipitate during sampling, they were only collected on the grid for sampling solid particles. Only few nano-sized particles were observed by TEM. However, it was confirmed that the size of particle changed by controlling the concentration of TIP as the precursor and TiO_2 crystals were formed of uniform size.

XRD and Surface Area Analysis

The crystal structure of the nano-materials synthesized by the pyrolysis of TIP droplets at 750°C was analyzed by XRD and their XRD patterns are shown in Fig. 6. The crystal phase of solid material synthesized with various concentration of TIP was found to be anatase structure of TiO_2. Commonly, the crystal phase of TiO_2 changes to rutile structure after the

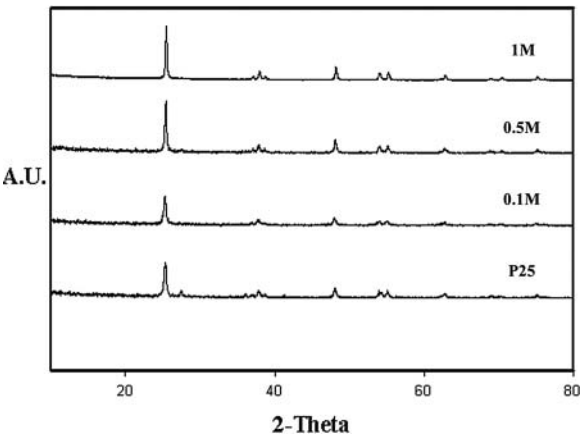

Figure 6. XRD patterns of P25 and TiO_2 synthesized with changing concentration of TIP solution by ultra-sonic spray and pyrolysis method.

Table 1. Particle size and surface area of TiO_2 synthesized with changing concentration of TIP solution by ultra-sonic spray and pyrolysis method

Concentration of TIP, M	Particle size, nm	Surface area, m^2/g
0.1	52.9	53.4
0.5	85.3	29.2
1.0	169.7	20.3
[a]P25[13,14]	∼20	51.2

[a]Commercial TiO_2 produced by Dagussa.

thermal treatment at 750°C. However, it was concluded that anatase structure of TiO_2 was crystallized due to the short residence time of TIP droplet for being heated at 750°C in the tubular reactor. Meanwhile, the change in XRD peak intensity with changing concentration of TIP was observed and the high peak intensity was exhibited when TIP of the higher concentration was used as the precursor. The size of TiO_2 crystallite was calculated from FWHM (full width at half maximum) of XRD peak (2 theta = 25.3°) by employing Scherrer equation, because the XRD peak intensity can be increased with increasing size of TiO_2 crystallite. As shown in Table 1, the size of TiO_2 crystallite calculated with XRD peak was 52, 85 and 169 nm when TIP of 0.1, 0.5 and 1.0 M were used as the precursor, respectively. It was concluded that these results were in accordance with the SEM images as shown in Fig. 4. The surface area of each sample was also measured by N_2 adsorption method and the date is shown in Table 1. The surface area of TiO_2 increased with decreasing concentration of TIP and their surface areas were 20.3, 29.2 and 53.4 m^2/g when TIP of 1.0, 0.5 and 0.1 M were used as the precursor, respectively. It was concluded that the surface area increased with decreasing size of crystallite.

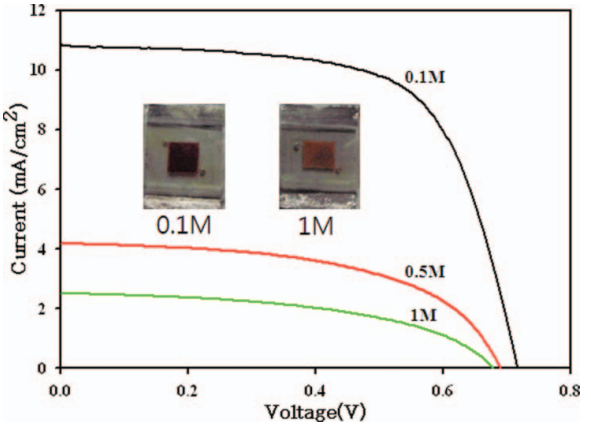

Figure 7. I-V curves of DSSCs manufactured by TiO_2 synthesized with changing concentration of TIP solution.

Table 2. Efficiency of DSSCs manufactured by TiO_2 synthesized with changing concentration of TIP solution

Con. of TIP, M	V_{oc}, V	J_{sc}, mA/cm^2	Fill factor	Efficiency, %
0.1	0.7191	10.75	0.6411	5.0
0.5	0.6637	4.64	0.6637	2.3
1.0	0.6899	4.06	0.5770	1.6
[a]P25[15]	0.7940	9.50	0.7450	5.6

[a]Efficiency of DSSCs made with P25, N719 as the dye.

Photo-Electrical Property of TiO_2

The photo-electrical property of TiO_2 anatase synthesized by the ultra-sonic spray and pyrolysis methods was investigated and compared in terms of the efficiency of DSSCs, which was made by using TiO_2 as the electrode. The efficiency of DSSCs varied with the change in particle size of TiO_2. There was an increase in the efficiency with decrease in the size of TiO_2 because the high efficiency of cells was obtained when the high amount of dye was adsorbed over the unit cell area. The DSSCs modules exhibited different colors due to the presence of different amount of dye over the unit cell area, as shown in Fig. 7 and Table 2. Especially, DSSCs module made with TiO_2 of high surface area exhibited deep red color and possessed high efficiency. Therefore, it was concluded that TiO_2 with high surface area can be used as the profitable electrode for the highly efficient functioning of DSSCs. It was also expected that the ultra-sonic spray and pyrolysis method along with changing concentration of precursor solution, could be efficiently employed for the synthesis of nano-sized TiO_2.

Conclusion

The nano-sized TiO_2 particles were synthesized from the pyrolysis of the fine droplet of TIP solution formed by the ultra-sonic spray nozzle. The particle size and the surface area of TiO_2 were also controlled with changing concentration of TIP solution used as the precursor and the nano-sized particle synthesized by this method was TiO_2 of anatase structure. It was also expected that the ultra-sonic spray and pyrolysis method in association with changing concentration of precursor solution, could be efficiently employed for the synthesis of nano-sized TiO_2 and other nano materials.

Acknowledgement

This work was supported by the 2011 Yeungnam University Research Grant and the Human Resources Development Program of Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant (No 20104010100580) funded by the Korean Ministry of Knowledge Economy.

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