# Preparation of Mesoporous Anatase $TiO_2$ Sphere for Nano-sized Pore with Narrow Size Distribution using Cyclodextrin as Templates

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## ABSTRACT

Anatase mesoporous titanium dioxide (M-$TiO_2$) sphere with pore diameter in several nanometers and narrow pore size distribution was prepared from $\beta$-cyclodextrin ($\beta$-CD), titanium precursor, and retarding agent through a sol-gel reaction and hydrothermal treatment in aqueous acidic condition. $\beta$-CD was used as template to generate the nano-sized pore, and retarding agent was utilized to control the high reactivity of titanium precursor. After sol-gel reaction, hydrothermal treatment was performed for acquirement of anatase-type crystalline with excellent photocatalytic activity. Interestingly, $\beta$-CD was removed of itself during sol-gel process and washing treatment. This may be due to the fact that the pore size of M-$TiO_2$ increased over size of $\beta$-CD (ca. 1.5~2 nm) by the growth of $TiO_2$ crystalline during the polymerization between titanium precursors. Thus, mesoporous $TiO_2$ material can be used to various applications that high photocatalytic activity was required.

***Keywords***: Cyclodextrin, mesoporous titanium dioxide, sol-gel process, hydrothermal treatment.

## 1 INTRODUCTION

Titanium dioxide ($TiO_2$) is a very useful semiconducting transition metal oxide material and exhibits unique characteristics such as low cost, easy handling, nontoxicity, and resistance to photochemical and chemical erosion. These advantages make $TiO_2$ a material in solar cell, chemical sensor, hydrogen gas evolution, and environmental purification applications [1,2]. For the preparation of $TiO_2$, the sol-gel technique is the most frequently applied. Generally, the precipitates derived from the sol-gel process are amorphous; the photocatalytic and photoelectrical conversion efficiencies of those obtained $TiO_2$ nanoparticles are not high enough for industrial purposes. Hence, several methods have been reported to improve this situation, such as crystallization by sintering, increasing the surface area, generation of defect structures to induce interfacial charge separation, and modification of the $TiO_2$ with metal or other semiconductors. Among those, mesoporous $TiO_2$ has attracted much attention because of its high surface-to-volume ratio, which is of great importance in photocatalysis and solar energy conversion. Therefore, worldwide research activity based on mesoporous $TiO_2$ has ensued. For generation of mesopore in $TiO_2$, various porogens such as surfactants and nonsurfactant organic compounds have been used. These porogens can be included in $TiO_2$ during sol-gel reaction, and then mesoporous $TiO_2$ can be prepared by removal of porogens through solvent extraction or calcination at high temperature. But preparation of mesoporous $TiO_2$ with well defined pore require the use of the stabilizing agents as well as the porogen, because of the high reactivity of Ti(IV). Uncontrolled hydrolysis and condensation lead to the formation of a dense inorganic network, generating poorly structured materials. The idea of addition of stabilizing reagents for controlling hydrolysis of $Ti(OR)_4$ is accepted extensively. For example, the used of complex $Ti(OR)_{4-n}(AcAc)_n$ precursors, combined with phosphonate anionic surfactants in slightly acid medium, resulted in the first preparation of titania-based mesoporous oxide in 1995 [3]. Moreover, a tridentate ligand (triethanolamine) has been also used as stabilizer to product phosphorus-free wormlike, mesoporous $TiO_2$ [4]. However, they require calcination process for removal of porogen. Furthermore, initially obtained mesoporous $TiO_2$ before calcination still was amorphous. Generally, it is known that calcination at high temperature may not be beneficial for improving the photocatalytic activity as it results in the collapse of mesoporous frame work and loss of surface area because of the crystallization of $TiO_2$ and subsequent crystal growth. Since the anatase phase has a far higher photocatalytic and photoelectrical conversion activity than $TiO_2$ with amorphous and rutile phase, it is still a challenge to synthesize mesoporous $TiO_2$ containing the high crystallization of anatase phase and large surface area. Peng et al has reported that hydrothermal treatment is helpful to crystallize mesoporous wall into anatase and stabilize the mesoporous structure [5]. But, to the best of our knowledge, hydrothermal treatment still have a problem the collapse of mesopore during calcination for removal of surfactant used as pore framework and stabilizing agent, although hydrothermal treatment endow the formation of anatage-type crystalline structure in $TiO_2$.

Meanwile, Antonietti et al has reported that cyclodextrins (CDs) can be used as the alternative templates for the synthesis of porous materials, for which the pore diameter corresponds exactly to the cyclodextrin size and is in the technically interesting range of 1.5-2.0 nm

[6]. They synthesized the mesoporous silica materials with nanosized pore and narrow pore size distribution by using the cyclodextrin. CDs are cyclic oligosaccharides that consist of covalently linked glucose unit (6 units = $\alpha$-CD, 7 units = $\beta$-CD, 8 units = $\gamma$-CD), which have hydrophilic exterior and a hydrophobic interior. The identities of encapsulating organic molecules and self-assembly have led to the intensive studies of CDs and their inclusion complexes. Many nanostructured organic compounds and composites have been constructed by the self-assemblies of CDs.

In this paper, we report the preparation and characterization of anatage-type mesoporous $TiO_2$ materials with pore diameter in several nanometers and narrow pore size distribution without the removal of pore forming agent by calcination. This material was synthesized in aqueous solution with hydrothermal treatment via a sol-gel process based on $\beta$-cyclodextrin ($\beta$-CD) as templates and titanium precursor mixed with 2,4-pentnedione, which is a retarding agent that limits the rate of hydrolysis and condensation. Then, it can be seen the anatage-type mesoprous $TiO_2$ material without the collapse of mesopore to $TiO_2$, because hydrothermal treatment was carried out but calcination process was not performed during the preparation of mesoprous $TiO_2$.

## 2 EXPREMENTAL

### 2.1 Materials

Titanium tetraisopropoxide ($Ti(O^iPr)_4$, 97%, Aldrich) and 2,4-pentanedione ($CH_3COCH_2COCH_3$, ≥ 99%, Aldrich) were used as a titanium precursor. 2,4-pentanedione was used as a retarding agent to control the fast hydrolysis and condensation reactions of titanium precursors. $\beta$-cyclodextrin ($\beta$-CD, Wacker-GmbH) as structure-directing agents were used as starting substances.

### 2.2 Synthesis of Mesoporous $TiO_2$

In a typical synthesis, $\beta$-CD (3 g) was dissolved in deionized water (100 ml) at a room temperature, and then sulfuric acid, 1.5 g (15.3 mmol), was added to them. Then, titanium tetraisopropoxide (2.25 g) chelated with 2,4-pentanedione (0.79 g) was slowly dropped into $\beta$-CD solution under vigorous stirring. The molar ratio of titanium tetraisopropoxide and 2,4-pentanedione is 1:1. At first, there was no precipitation, but the light yellow powders were formed in several minutes, after that the hydrothermal treatment was carried at 90 $^oC$ for about 3 h. The powders in the solutions were filtered out and washed with ethanol, and the resulting materials were dried in vacuum. We denoted this sample as M-$TiO_2$. Meanwhile, non-M-$TiO_2$ was counterpart of M-$TiO_2$, which was prepared by same process with M- $TiO_2$ excepting adding of $\beta$-CD.

### 2.3 Characterization

Nitrogen adsorption-desorption isotherms were at 77 K collected on a Micrometrics ASAP 2000 apparatus after all the samples were degassed at 100 $^oC$. The specific surface areas were estimated by the Brunauer-Emmett-Teller (BET) method and the pore size distributions were determined by the Barrett-Joyner-Halenda (BJH) method using the nitrogen desorption branches of isotherms. The morphologies and pore structures of mesoporous $TiO_2$ particles were observed by the field emission scanning electron microscopy (FE-SEM, JEOL JSM-6330F) and transmission electron microscopy (TEM, JEOL JEM-2000EXII) images. The crystal compositions and crystallite sizes of each sample were determined using wide angle X-ray diffraction (XRD, MAC/Sci. MXP 18XHF-22SRA with Cu $K_\alpha$ radiation) at room temperature. The accelerating voltage of 50 kV and emission current of 100 mA were used. The crystallite sizes were calculated by the Scherrer equation ($\Phi = K\lambda/\beta\cos\theta$), where $\Phi$ is the crystallite size, $\lambda$ is 0.154 nm that is the wavelength of the X-ray radiation, $K$ is usually taken as 0.89, $\beta$ is the full width at half maximum intensity (FWHM), and $\theta$ is the diffraction angle of the (101) peak for anatase ($2\theta = 25.3^o$). Thermogravimetric analysis (TGA) was carried out using a TA instruments TGA 2050 thermal analyzer from room temperature to 600 $^oC$ at a heating rate of 10 $^oC$/min under $N_2$ flow.

## 3 RESULTS AND DISCUSSION

### 3.1 $N_2$ Adsorption-Desorption Analysis

Figure 1 shows $N_2$ adsorption-desorption isotherms of M-$TiO_2$ and non-M-$TiO_2$. M-$TiO_2$ reveals the classical type IV with H2 hysteresis between the adsorption and the desorption curves, indicating the characteristic of mesoporous materials according to the IUPAC classification.

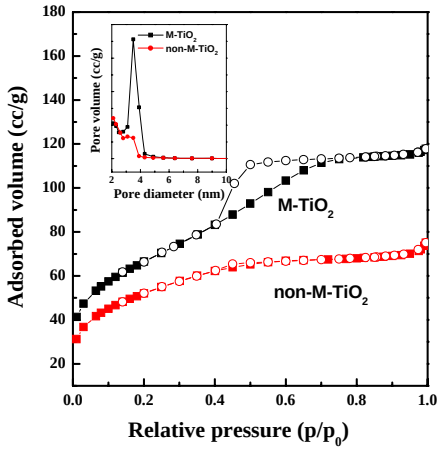


Figure 1: $N_2$ adsorption-desorption isotherms of M-$TiO_2$ and non-M-$TiO_2$.

But, no the classical type IV with H2 hysteresis between the adsorption and the desorption curves was shown for

non-M-$TiO_2$. This implies that non-M-$TiO_2$ does not have the pore structure. In addition, specific surface area of M-$TiO_2$ determined with the BET method was larger than that of non-M-$TiO_2$ (M-$TiO_2$ = 238.05 $m^2/g$, non-M-$TiO_2$ = 186.00 $m^2/g$), because of porous structure of M-$TiO_2$. In particular, it was verified that pore size of M-$TiO_2$ is 3.5 nm and this pore size distribution is very narrow.

## 3.2 FE-SEM and HR-TEM Analysis

In order to investigate the existence of the pores and shape of M-$TiO_2$, HR-TEM and FE-SEM images were taken, as shown in Figure 2.

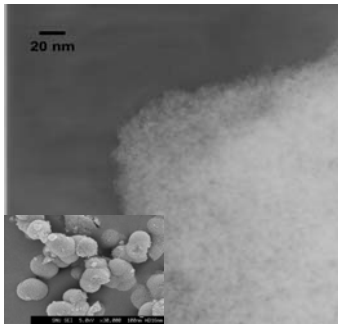


Figure 2: HR TEM and FE-SEM images of M-$TiO_2$.

From HR-TEM image, M-$TiO_2$ obviously shows the pore with non-ordered worm-hole like structure, coincident with $N_2$ adsorption-desorption isotherms of M-$TiO_2$. In addition, FE-SEM image exhibits that M-$TiO_2$ has spherical morphology. But no pore structure and spherical morphology were found for non-M-$TiO_2$.

## 3.3 WAXD Analysis

Figure 3 shows the WAXD patterns of M-$TiO_2$ and non-M-$TiO_2$.

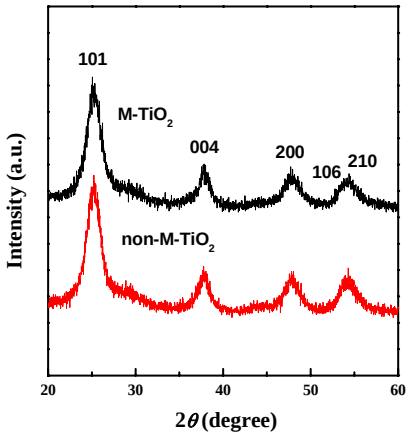


Figure 3: WAXD profiles of M-$TiO_2$ and non-M-$TiO_2$.

Although calcination were not carried out to these materials, distinct (101) peak was observed in both samples. This implies formation of the anatage structure attributed to the hydrothermal treatment. In addition, crystal sizes of both M-$TiO_2$ and non-M-$TiO_2$ calculated by Scherrer equation are about 8.1 and 8.6, respectively. This similar crystal size between M-$TiO_2$ and non-M-$TiO_2$ reveal that CD did not hinder the crystallization of M-$TiO_2$.

## 3.4 Thermal Analysis

Thermal properties of both samples were investigated by TGA, as shown in Figure 4.

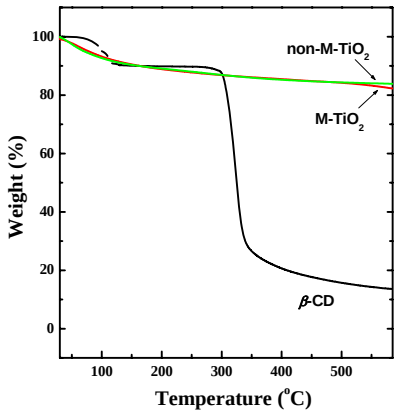


Figure 4: TGA thermoprofiles of M-$TiO_2$ and non-M-$TiO_2$.

Interestingly, no thermal degradation of $\beta$-CD was observed in M-$TiO_2$, and TGA scan curves of both samples are the same. This indicates that M-$TiO_2$ does not further have $\beta$-CD component used as porogen, and $\beta$-CD was already eliminated in spite of absence of calcination treatment. These results were also verified by FT-IR experiment. (not shown in this study) Thus, it is considered that $\beta$-CD was removed of itself during sol-gel process and washing treatment, because the pore size of M-$TiO_2$ increased over size of $\beta$-CD (ca. 1.5~2 nm) by the growth of $TiO_2$ crystalline attributed to the polymerization between titanium precursors. (Figure 5)

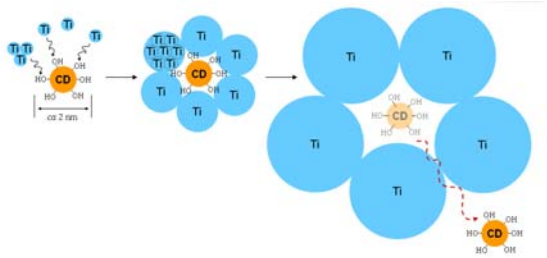


Figure 5: Schematic illustration of pore generation mechanism of CD-$TiO_2$

Then, intermolecular interaction such as hydrogen bonding between $\beta$-CD and $TiO_2$ weaken, and then $\beta$-CD can be extracted in M-$TiO_2$.

## 4 CONCLUSIONS

In the present study, the anatase-type mesoporous $TiO_2$ material with pore diameter in several nanometers and narrow pore size distribution was synthesis through the sol-gel process and hydrothermal treatment in acidic condition using $\beta$-CD and retarding agent, although calcination was not performed. This material showed high surface area attributed to the worn-hole like pore structure and spherical shapes. In addition, anatase structure existed in spite of absence of calcination process, because of the hydrothermal treatment. In particular, $\beta$-CD was removed of itself during sol-gel process and washing treatment. Thus, this materials is able to avoid the collapse of pore structure by calcination, and be used to various applications that high photocatalytic activity were required.

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