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Nano-sized TiO_2 Synthesis in Triton X-100 Reverse Micelles

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Abstract To synthesize nano-sized TiO_2, two different methods, namely thermal hydrolysis (TH) and reverse micelles as the nano reactors in the thermal hydrolysis method (RM-TH) were used, and their effects on the shape, crystal structure, and size of the TiO_2 particles produced were investigated. In the RM-TH method, reverse micelles prepared by Triton X-100 / Cyclohexane / Aqueous $TiCl_4$ solution was used as a template since the hydrolysis reaction took place in the aqueous core of the reverse micelle that led to a controllable synthesis of TiO_2 particles. The XRD patterns of the as-prepared TiO_2 particles produced by both methods indicated that their crystal structure was rutile. In the TH method, particles were highly agglomerated resulting in a pinecone-like structure: The pinecone-like structure contained several rods with a diameter of 50 nm which were formed by conical bundles of fine rods growing radially from the center with a diameter of 6 nm and length ranged between 400 and 1000 nm. On the other hand, more uniform sphere-like nanoclusters consisting of radially growing nanorods from the center with a diameter of 6 nm and length of 200 nm were produced in the RM-TH method due to the template feature of reverse micelles. Mechanisms of nucleation and crystal growth were proposed for both production methods.

Keywords TiO_2 • Thermal hydrolysis • Reverse micelles • Rutile • Polyethylene glycol tert-octylphenyl ether (Triton X-100) • Growth mechanism

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Introduction

Syntheses of nano-sized metal oxides still need to be elucidated because of the difficulties in the control of their size, morphology, and crystal structure. The unique physical, chemical and optical properties of the nano particles depend on production methods and reaction conditions during synthesis. Since the variations in the properties of the nano particles highly affect their performance in the application fields, several production methods and reaction conditions were investigated to synthesize particles with the desired properties. TiO_2 nano particles with effective optoelectronic, electronic and catalytic properties have been widely used as pigments for paints, filler of plastics and papers [1], sensing materials [2], photocatalyst for environmental purifications [3], for the reduction of CO_2 [4-5], photovoltaic cells [6], antireflection [7], self-cleaning [8], and antibacterial-coatings [9].

TiO_2 particles can be produced by gas phase (chloride method, chemical vapor condensation and laser pyrolysis) [10], liquid phase (sol-gel, microemulsions, hydrothermal synthesis and TH) [10-14], template based [15], and solid-liquid phase (anodic oxidation of titania flakes) [16] methods. All of the methods require different reaction conditions such as high temperature, special equipment or vigorous stirring, and result in the formation of particles that are highly agglomerated, in different shapes, size and crystal structure or amorphous. In this study, on the basis of these conditions and results mentioned, a new method was developed by using reverse micelles as nano reactors in the TH method so as to be able to synthesize TiO_2 nano particles with a specific size, shape, and physicochemical properties. Effectiveness of the new method on the production of TiO_2 nano particles with desired properties was elucidated by comparing TiO_2 nano particles synthesized by both methods. Possible formation and growth mechanisms based on the experimental results were proposed for both TH and RM-TH production methods.

Experimental

Materials

Titanium tetrachloride ($TiCl_4$, > 99%, Merck), hydrochloric acid (38 wt% HCl, J. T. Baker), non-ionic surfactant-polyethylene glycol tert-octylphenyl ether (Triton X-100, n =9-10, for molecular biology, Merck), and cyclohexane (> 99.5%, Merck) were used without further purifications, and double distilled water was used in all experiments.

Phase Diagram

The partial phase diagram of the ternary system of Triton X-100 / Cyclohexane / Aqueous $TiCl_4$ solution was performed at 25°C to determine the transparent region of the reverse micelles. Reverse micelles were prepared by dissolving Triton X-100 in cyclohexane in different weight ratios. Aqueous solution of reactants was prepared by dissolving $TiCl_4$ in a 3M aqueous HCl solution under magnetic stirring. Then, the aqueous solution of the reactant was added drop by drop to the reverse micelle solution with continuous stirring. The changes in the optically clear appearances and in the viscosities of the reverse micelles with the addition of the aqueous solution of the reactant were used as an indication of the phase transition from reverse micelles to another phase. Thus, the maximum amount of aqueous $TiCl_4$ solution loaded was determined by visual observation of the transparency and apparent viscosity of the reverse micelle system. The size distribution of the reverse micelles before and after the loading of the aqueous solution of the reactant was measured by dynamic light scattering.

Synthesis of TiO_2 Nanoparticles

Nano sized TiO_2 particles were prepared using two different methods, TH and RH-TH. Although there was no template in the TH method, the reverse micelles formed in the cyclohexane was loaded by the aqueous solution of reactant and used as a template in the RM-TH method.

Thermal Hydrolysis Method (TH)

In the TH method, TiO_2 nano particles were synthesized by the hydrolysis of $TiCl_4$ at 95°C and normal atmospheric pressure under reflux and at a constant stirring rate. The 0.5 M $TiCl_4$ dissolved in 3 M aqueous HCl solution was used as the reactant with a molar ratio of $TiCl_4 : H_2O = 1 : 100$. After a reaction period of 3 h, white precipitate was separated from the supernatant, rinsed with distilled water several times to remove the impurities from the surface of the particles and then dried at 60°C for further analysis.

Reverse Micelles- Thermal Hydrolysis Method (RE -TH)

The synthesis of TiO_2 particles was conducted in Triton X-100 reverse micelles formed in cyclohexane with a Triton X-100 weight percent of 50%. The aqueous solution of $TiCl_4$ at the same concentration as in the case of the TH method was loaded into the Triton X-100 reverse micelles by considering the transparency of the reverse micelles determined in the phase diagram studies. The reaction was performed in the reverse micelles at 95°C and a normal atmospheric pressure under reflux and at a constant stirring rate. The reaction conditions were kept constant throughout the reaction period of 3 h. At the end of the reaction, a stable colloidal suspension was formed and water was added to the suspension to settle the synthesized particles by withdrawing the surfactant molecules from the surface of the particles. The settled particles were then separated and washed with distilled water repeatedly to remove the surfactant molecules completely. The resultant particles were dried at 60°C for characterization.

Characterization Methods

The size distribution of the reverse micelles loaded by the aqueous solution of reactant was measured by the Dynamic Light Scattering Method using the Zetasizer Nano S (DLS, Malvern, equipped with a He-Ne laser and fixed angle 173°) before and after the reaction. The crystal structure was identified by X-ray powder diffraction (XRD, Philips X'pert Pro-45W, 40mA with CuKα radiation $\lambda = 0.1541$ nm) and the size of the primary particles were estimated from the XRD data by using the Debye-Sherrer equation. The morphologies of the products were determined by Scanning electron microscope (SEM, Philips (FEI), XL30-SFEG).

Results and Discussion

The reactant $TiCl_4$ quickly hydrolyzes in water or air at normal conditions and results in the formation of orthotitanic acid ($Ti(OH)_4$). However, in the presence of acid the hydrolysis reaction slows down, $Ti(OH)_3^+$ ions are formed and

formation of the TiO_2 particles in a definite crystal structure is favored. Due to this feature of the reactant $TiCl_4$, an aqueous $TiCl_4$ solution was prepared in an aqueous HCl solution instead of H_2O to decrease the rate of reaction of the hydrolysis in this study.

Previous studies conducted for the particle production by TH indicated that this method provides production of nano particles with a definite crystal structure without any calcination process [17-19]. However, the particles synthesized by the TH method were highly agglomerated due to the absence of the surfactants that hinder the agglomeration of the particles in the reaction medium. In order to eliminate this unfavorable part of the method, reverse micelles, in which the reaction takes place in the aqueous core of the reverse micelles surrounded by surfactant molecules, is generally used to prevent agglomeration of the particles. On the other hand, particles produced in reverse micelles at 25°C are amorphous in both shape and crystal structure and need calcination at high temperatures to improve the shape and crystal structure of the particles. Calcination at high temperatures results in agglomeration of the particles which is an undesirable situation. To produce TiO_2 nano particles with a specific crystal structure and homogeneous size distribution without calcination, a new synthesis technique was developed by using the beneficial parts of TH and reverse micelles.

In the RM-TH method, since the reaction took place in the reverse micelles, a proper ternary system that would be used as a nano reactor was selected by performing phase diagram studies and dynamic light scattering measurements. Results of the partial phase diagram study of the ternary system of Triton X-100 / Cyclohexane / Aqueous $TiCl_4$ solution is given in Fig. 1 in which the area under the dots represents the single phase (reverse micelle) region. The point marked by A on the phase diagram in Fig. 1 was selected as the nano reactor system by considering the stability and aqueous reactant solution loading capacities of the reverse micelles as criterion. The weight ratio of the Triton X-100 in the selected ternary system was 48 % with a mean reverse micelle size of 13 nm from the dynamic light scattering measurements after the loading of the reactant solution. The upper regions were not mapped in the phase diagram because the reaction was conducted in the reverse micelle region.

XRD patterns of the particles produced by TH and RM-TH methods are illustrated in Fig. 2. XRD patterns of both production techniques signified characteristic peaks corresponding to (110), (101), (111), (211), (002) and (301) crystal planes, which are in good agreement with the JCPDS (No. 77-0441) analogous to rutile phase with lattice constants a = 4.601 and c = 2.964. It has been previously reported that rutile titania can grow from TiO_6 octahedra and that an increase in the acidity of the reaction medium increases the catalytic effect of acid on the phase transition and accelerates the arrangement of the octahedra through edge sharing resulting in the rutile phase [20]. As a consequence, titania particles were synthesized in a rutile crystal structure in a highly acidic reaction medium at 95°C without calcination using the two production methods. The crystalline size of the particles was calculated by the Debye-Scherrer equation using the XRD data and is listed in Table 1.

SEM images of the particles produced by the two different methods are given in Fig. 3. The products obtained by the TH method were highly agglomerated, had a heterogeneous size distribution (Fig. 3-a1) and the pinecone-like structure consisted of short aggregating nanorods (Fig. 3-a2). The

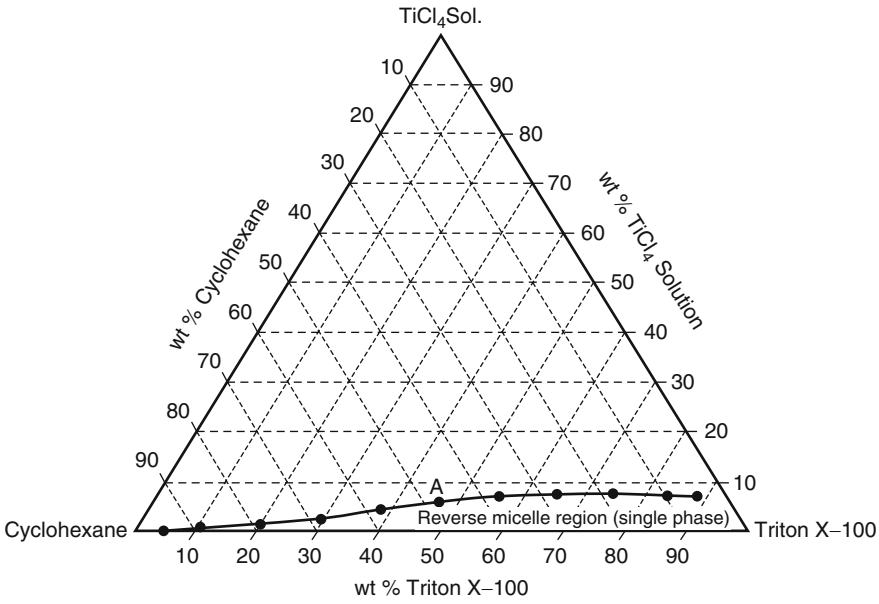

Fig. 1 The Partial phase diagram of the ternary system of Triton X-100 / Cyclohexane / Aqueous $TiCl_4$

nanorods forming the pinecone-like structure had a diameter of 6 nm and their lengths ranged between 400 nm and 1000 nm. The heterogeneously distributed nanorods formed bundles with a diameter of 50 nm. The average size of the pinecone-like structure was approximately 600 nm. SEM images of the product particles synthesized by the RM-TH method showed that the aggregates had a more homogeneous size distribution (Fig. 3-b1) and were in a flower-like structure with a mean size of 400 nm (Fig. 3-b2). The flower-like structure had nanorods that radially grow from the center. The diameter and length of the nanorods were 6 nm and 200 nm, respectively. The growth mechanism of the particles which was similar in both production methods can be clarified by the SEM images at higher magnifications given in Fig. 3-c. The particles normally looked like a sphere with a smooth surface as in Fig. 3-c1. However, higher magnifications showed that these spherical particles consists of radially growing nanorods from the center (Figs. 3-c2, c3).

Figure 4 illustrates the proposed growth mechanism of the particles produced by the two different methods. The growth process consisted of the formation of the nuclei and growth of the crystals. In both methods, after the formation of the nucleus TiO_2, Ti^{4+} ions in the reaction medium connected to the active sides of the nucleus in all directions. Due to the anisotropic growth habit of the TiO_2, the growth occurred preferentially in a radial direction. In case of the TH, since both formation of the nucleus and connection of Ti^{4+} ions took place in the aqueous bulk reactant solution, the large amount of Ti^{4+} ions in the reaction medium resulted in an asymmetrical distribution on the surface of the nucleus. In addition, the particle interactions were highly favored since there were no surfactant molecules in the reaction medium. Consequently, pinecone-like structures with a non-uniform morphology and size distribution were formed (Fig. 4-a). On the other hand, in the RM-TH method, the size of the nucleus was restricted to the size of the reverse micelles (Fig. 4-b) since hydrolysis of the $TiCl_4$ took place in the aqueous core of the reverse micelles. The exchange of the core material during agitation caused attachment of Ti^{4+} ions on the nucleus surface. The surfactant molecules that surrounded the growing crystals in all directions restricted the attachments of Ti^{4+} ions on the nucleus surface and prevented the interaction between the particles. Nevertheless, the size of the synthesized nano particles ($\sim$ 400 nm) by the RM-TH method was larger than the size of the reverse micelles (13 nm) measured by dynamic light scattering since the size of the reverse micelles was especially effective on the size of the nucleus at the nucleation stage. Thus, the particles synthesized by the RM-TH method were more uniform in morphology and size distribution.

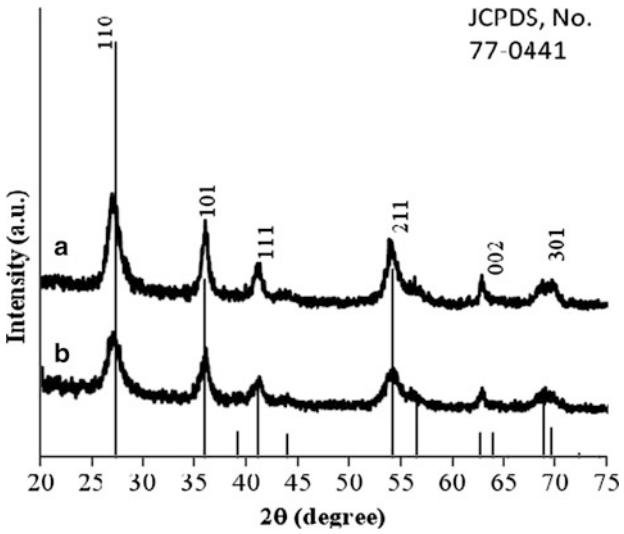

Fig. 2 The XRD patterns for particles synthesized by (a) TH, (b) RM-TH methods

Conclusion

TiO_2 nano particles in pinecone-like and flower-like structures were produced by TH and RM-TH methods, respectively. Both methods provided formation of the particles in a pure rutile crystal structure at 95°C without the calcination process. In the RM-TH method, the size of the Triton X-100 reverse micelles restricted the size of the secondary particles (aggregates) and prevented the interactions among the aggregates. Thus, the aggregates synthesized by the RM-TH method were more uniform in both shape and size distribution. On the other hand, a large number of the nucleus formed in the aqueous bulk reactant solution in the TH method resulted in the production of a lot of highly agglomerated secondary particles due to the interaction among the aggregates with heterogeneous size distribution. All of the above results indicated that the RM-TH method in which Triton X-100 reverse micelles were used as a template is the most effective in the production of particles of controlled size and

Table 1 The morphologies and crystal structures of the particles synthesized by TH and RM-TH methods

Production Method	Crystal Structure	Crystalline size (nm)*	Secondary particles				Clusters	
			Morphology	d (nm)	L (nm)	Aspect ratio (L/d)	Morphology	d (nm)
TH	Rutile	6.9	nanorod	6	400-1000	67-166	Pinecone-like	$\sim$ 600
RM-TH	Rutile	7.3	nanorod	6	200	33	Flower-like	$\sim$ 400

*Crystalline size was calculated with Debye-Scherrer equation using XRD data

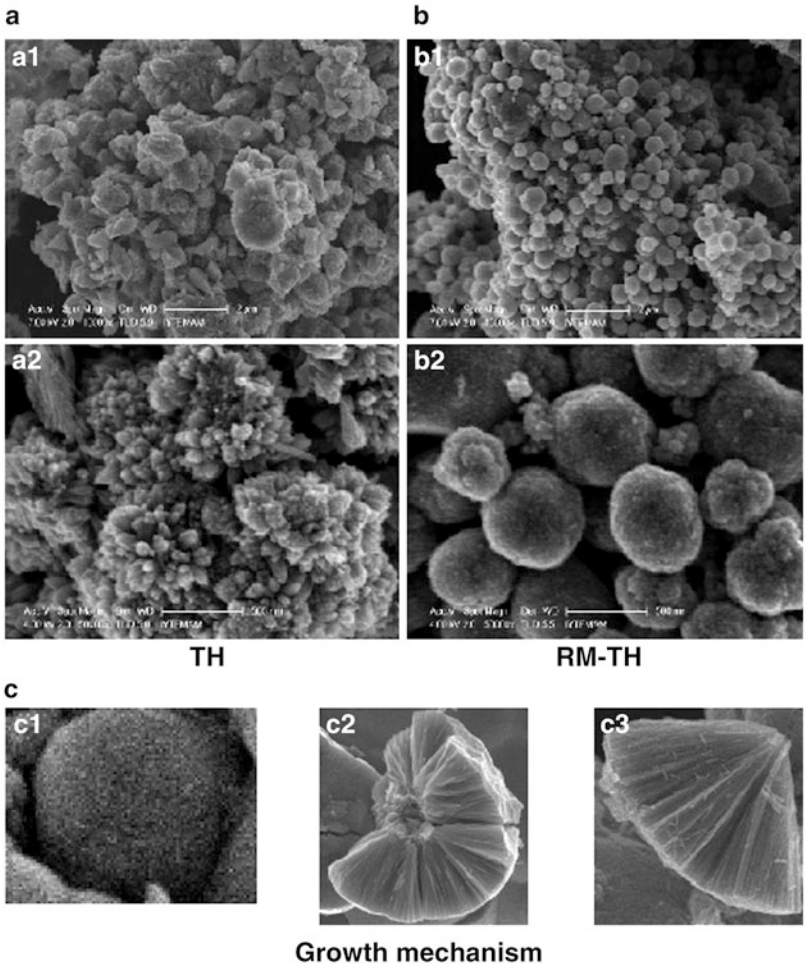

Fig. 3 SEM images of the produced particles

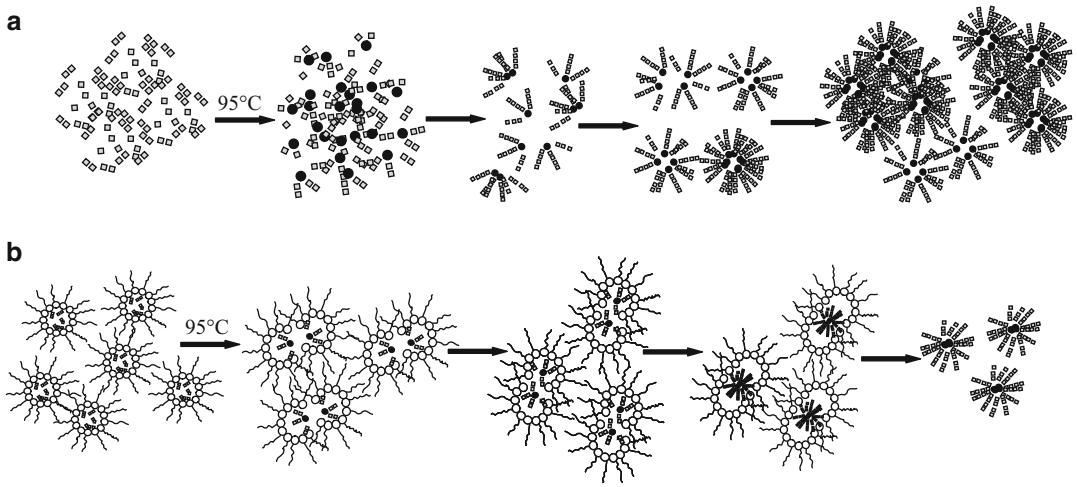

Fig. 4 The schematic diagram of the proposed growth mechanism of the particles produced by (a) TH, (b) RM-TH methods

morphology. A growth mechanism was proposed based on the experimental results and will be supported by considering the effects of the reaction conditions in future studies.

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