Synthesis of highly-monodisperse spherical titania particles with diameters in the submicron range

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ABSTRACT

Monodisperse titania spheres with particle diameters in the range 380–960 nm were successfully synthesized by hydrolysis and condensation of titanium tetraisopropoxide. The preparation was performed using ammonia or dodecylamine (DDA) as a catalyst in methanol/acetonitrile co-solvent at room temperature. The samples were characterized by powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy, dynamic light scattering, and nitrogen sorption measurement. The use of DDA was effective for the synthesis of monodisperse titania spheres with low coefficient of variation. When the titania spherical particles with coefficient of variation less than 4% were obtained, the colloidal crystallization easily occurred simply by centrifugation. The monodispersity was maintained even after crystallization of the particles by high temperature annealing. The titania particles prepared using DDA had mesopores near the surface of the spheres, providing high pore accessibility to the sphere from the surface–air interface. The particle size uniformity and photocatalytic reactivity of the titania prepared using DDA were higher than those of the titania prepared using ammonia.

1. Introduction

Titania nanomaterials have attracted much attention because of their unique chemical and physical characteristics. The properties of the titania nanomaterials are concerned with the performance of the electrochemical and optical properties. The use of colloidal titania as a system of photonic crystals is one of its most distinctive applications [1], and is largely determined by properties such as the crystalline phase, particle size, and particle arrangement. On the other hand, the photocatalytic activity depends on the crystal phase, crystallite size, specific surface area, and porous structure. Therefore, optimization of the appropriate titania properties is essential to improving the performance of applied systems. However, the morphology control of uniformly-sized titania particles is a difficult task due to the high reactivity of titania precursors. Titania particles have been synthesized using several methods such as thermal hydrolysis of $TiCl_4$ [2], hydrolysis of titanium alkoxide in dilute alcohol solutions with hydroxypropyl cellulose [3], and slow hydrolysis of titanium glycolate precursors [4]. Thus far synthesis of spherical titania particles with high monodispersibility has proven difficult because of the fast and uncontrollable reactions of the hydrolysis, nucleation, and growth steps during the

sol–gel processing. On the other hand, the specific surface area is a vital factor for the application of titania particles in catalysis. In addition, high photocatalytic activity is associated with crystallite size, because small crystallite size can lead to quantum size effects in the material. Research efforts to produce mesoporous titania materials with well-tailored pore systems have focused on the use of various surfactants as templates [5–7]. However, the synthesis of mesoporous titania becomes much more complicated as compared with mesoporous silica [8–10] because of the high reactivity of titanium alkoxide towards hydrolysis and condensation. In addition, it is difficult to prevent the collapse of the porous structure caused by crystallization of the framework. Recently, mesoporous titania in film morphology has been reported to be efficient for the photocatalytic decomposition [11–13], because titania with a large surface area has many active sites so that substances can be adsorbed in large quantities on to the titania surface. It is noted that besides the specific surface area, the development of porous structures with facile mass transport to the titania surface is a key prerequisite for the development of catalytic applications.

On the other hand, Mine et al. proposed a method using different combinations of solvents, i.e. acetone, ethanol, and acetonitrile [14]. The particle size and its distribution of titania can be well-controlled using this method. Monodisperse titania particles with the lowest coefficient of variation C_v, 5.7%, were produced using a ethanol/acetonitrile co-solvent with methylamine. They studied the photonic properties, such as refractive index and optical

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reflectance, of colloidal crystals, but did not examine the internal pore structure of the particles. We noted that the introduction of nanoscale pores in the titania is an efficient way to continuously control the refractive index of the titania spheres. To date mesoporous titania in uniform sphere morphology has not been fully synthesized and characterized in detail. Further development is required toward fabrication of monodisperse titania spherical particles with high pore accessibility. In this study, we report the preparation and characterization of spherical titania particles by a sol–gel method using a primary amine catalyst. The hydrolysis and condensation of titanium isopropoxide (TTIP) was performed in a methanol/acetonitrile co-solvent by reference to the ethanol/acetonitrile co-solvent reported by Mine et al. [14]. It is a novel aspect in this study is the use of dodecylamine (DDA) of which the carbon chain is longer than that of amines used by Mine et al. Our expectation was that DDA would also act as a molecular template to introduce the mesopores into the titania particles. We focus on the effects of the DDA on mean particle size, particle size distribution, pore structure, and photocatalytic activity. The morphological characteristics of titania spheres were investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and dynamic light scanning (DLS). The structural characteristics were investigated by the combination of powder X-ray diffraction (PXRD), TEM, nitrogen sorption measurements, and thermogravimetric analysis (TGA).

2. Experimental

2.1. Chemicals

Methanol, acetonitrile, ammonia solution (10 wt%), and TTIP were purchased from Wako Pure Chemical Industries and used as received. DDA was purchased from Tokyo Kasei Kogyo Co. and used as received.

2.2. Synthesis of monodisperse titania spheres using NH_3 or DDA as catalyst

Titania particles were prepared by hydrolysis and condensation reaction of TTIP with ammonia or DDA as a catalyst in a co-solvent of methanol/acetonitrile. The molar compositions of the reaction mixtures were in the range of 714 methanol/271 acetonitrile/2.8 water/1 TTIP/0–0.17 ammonia or 714 methanol/271 acetonitrile/0.8–16 water/1 TTIP/0–6.4 DDA. In a typical preparation, 0.18 ml of water was added to 150 ml of methanol/acetonitrile solution. Then 0.28 g of DDA was dissolved in the mixture. After stirring for 10 min, 1 ml of TTIP was added and stirred for 12 h. Hydrolysis and condensation reaction occurred, and a suspension of titania particles was obtained. The suspension was centrifuged at 1500 rpm for 10 min. The particles obtained were washed with methanol and centrifuged again; the process was repeated three times. No other sedimentation treatments were carried out for colloidal crystallization. The products were then dried at 60 °C followed by calcination at 400 °C for 5 h.

2.3. Characterization

SEM images were recorded on a VE-8800 Keyence microscope at an acceleration voltage of 5 kV. Samples for SEM analysis were prepared by carefully scratching the powder onto a mortar, where they were crushed before depositing them onto carbon adhesive tape. The diameters of more than 200 particles in the SEM images were measured to determine average particle size, d_n, and C_v, defined by the following equations:

$$d_n = \sum n_i d_i / \sum n_i \tag{1}$$

$$C_v = \sqrt{\sum (d_i - d_n)^2 / \sum n_i} / d_n \tag{2}$$

Average particle size was also determined using a ELS-8000 (Otsuka Electronics) DLS system. TEM images were recorded on a JEM-2010S JEOL microscope at an acceleration voltage of 200 kV. PXRD patterns were recorded on a RINT-TTR III Rigaku diffractometer using Cu Kα radiation with $\lambda = 1.5418$ Å. The copper anode was operated at 40 kV and 20 mA. The nitrogen adsorption/desorption isotherms of the titania powder were measured at 77 K using a BELSORP 28 instrument (Bel Japan) and the surface area found using the Brunauer–Emmet–Teller (BET) formalism. The pore size distribution was derived from the adsorption branches of the isotherms by the Barrett–Joyner–Halenda (BJH) model. TGA was carried out on a DTG-60H (Shimadzu) with a heating rate of 10 °C/min.

The photocatalytic activity was measured through the formation rate of I_3^- due to the oxidation photo-reaction of I^- to I_2 in excess I^- conditions [15]. A 50 mg sample of titania was added to 10 ml of 0.2 M KI aqueous solution and stirred. The mixture was irradiated with 365-nm light (UV-lamp 20 W) for 60, 120, and 180 min. The reactant solution was collected by centrifuge and diluted with deionized water, and then the absorbance of the solution was measured with a UV-2450 UV–vis spectrophotometer (Shimadzu). No I_3^- formation was observed when the experiments were performed in the dark or in the absence of the titania samples. For comparison, commercially available titania nanoparticles P25 (Nippon Aerosil) were tested in the same manner.

3. Results and discussion

SEM images of titania particles prepared with different ammonia concentrations were shown in Supporting Information (Figures SI1a–f). The titania particles prepared at an ammonia/TTIP molar ratio less than 0.1 were highly dispersed in size and aggregated. On the other hand, at an ammonia/TTIP molar ratio of 0.15, the titania particles were isolated and of more uniform size, with d_n of 450 nm and C_v of 10.6%. Fig. 1 shows the variation in the d_n and C_v as a function of ammonia/TTIP molar ratio. The d_n was found to decrease with increasing ammonia/TTIP molar ratio. Moreover, the d_n was constant for ammonia/TTIP molar ratios above 0.1.

Fig. 2 shows d_n and C_v of titania particles as a function of DDA concentration. The d_n and C_v values varied from 380 to 960 nm and from 2.6% to 7.2%, respectively. Compared to the particles prepared using ammonia, a lower C_v was achieved using DDA. Fig. 3a–k show SEM images of titania spheres prepared with different DDA
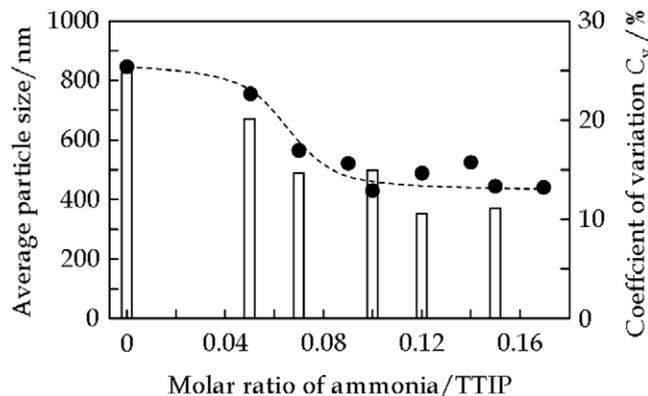
Fig. 1. The variation in the d_n and C_v as a function of the ammonia/TTIP molar ratio. Black circles and bar indicate the average particle size and coefficient variation, respectively.