

Rapid one-pot synthesis of ultrafine titania nanocrystals and their conversion into transparent mesoporous thin layer films



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ABSTRACT

Ultrafine titania nanocrystals were synthesized using a rapid heating, one-pot solvothermal method. These nanocrystals are extremely small with a narrow size distribution (3.0 ± 0.4 nm). The detailed structural analysis by using transmission electron microscopy reveals periodic alignment of the resultant titania nanocrystals with hexagonal symmetry due to their size uniformity. The drop-casting deposition and calcination of these nanocrystals are also enable to convert into mesoporous thin layer films with nano convex-concave surface. The resultant transparent mesoporous thin layer exhibits not only anti-reflection properties but also high photocatalytic activity.

1. Introduction

Controlling the size and morphology of inorganic nanocrystals is an important aspect of improving certain intrinsic characteristics, such as electronic, magnetic, photophysical, and catalytic properties [1,2]. Over the past decade, considerable effort has been devoted to developing new methods for the synthesis of unique nanomaterials having well-controlled sizes and specific morphologies [3,4]. The precise synthesis of titania (TiO₂) nanocrystals has been intensively researched owing to the potential applications of this oxide in energy storage, photocatalysts, solar cells, and other optoelectronic devices [5–9].

A wide variety of solution-based techniques based on sol-gel, coprecipitation, hydrothermal, and solvothermal processes have been developed for the synthesis of nanocrystalline TiO₂ [10,11]. Although these conventional approaches are able to synthesize TiO₂ crystals from 10 to 50 nm in size, there remains a need for an efficient method capable of generating crystals in sizes less than 5 nm. The synthesis of ultrafine TiO₂ nanocrystals is quite difficult as a result of sintering of the primary particles during the high-temperature reaction and/or the post annealing process. Several approaches have recently been reported as potential means of overcoming the limitations of the present-day methods [12]. Pioneering techniques meant to address this challenge include the use of self-assembled molecular cages [13] and dendrimers [14] as sacrificial templates. However, much simpler synthetic methodologies are desirable based on practical considerations.

Recently, we have successfully synthesized porous spherical nanocrystal assemblies having extremely wide surface area by our original one-pot and single-step solvothermal method [15–22]. The key factor to yield such porous spherical morphology is to control solvolysis rate of metal alkoxide in the precursor solutions under solvothermal conditions. For example, we chose carboxylic acid as additives for the preparation of TiO₂ nanocrystal assemblies. As a result, we have controlled the resultant morphologies of the solid or hollow porous nanomaterials by changing the carboxylic acid as an additive. However, the relationships between the resultant material morphology and chemical structure of carboxylic acid as an additive have yet to be well understood.

Herein, we report a simple, one-pot approach to producing ultrafine titania nanocrystals, using a rapid heating technique in conjunction with a solvothermal reaction using aliphatic carboxylic acid. This rapid heating method enhances the nucleation and crystal growth of the nanocrystals, thus avoiding undesired sintering during the high temperature solvothermal reaction and ensuring sub-5-nm sized nanocrystals.

2. Results and discussion

As noted, the present work attempted the synthesis of nanocrystals via a rapid heating solvothermal method that has been described in our previous reports [15–22]. Titanium tetrabutoxide and oleic acid were

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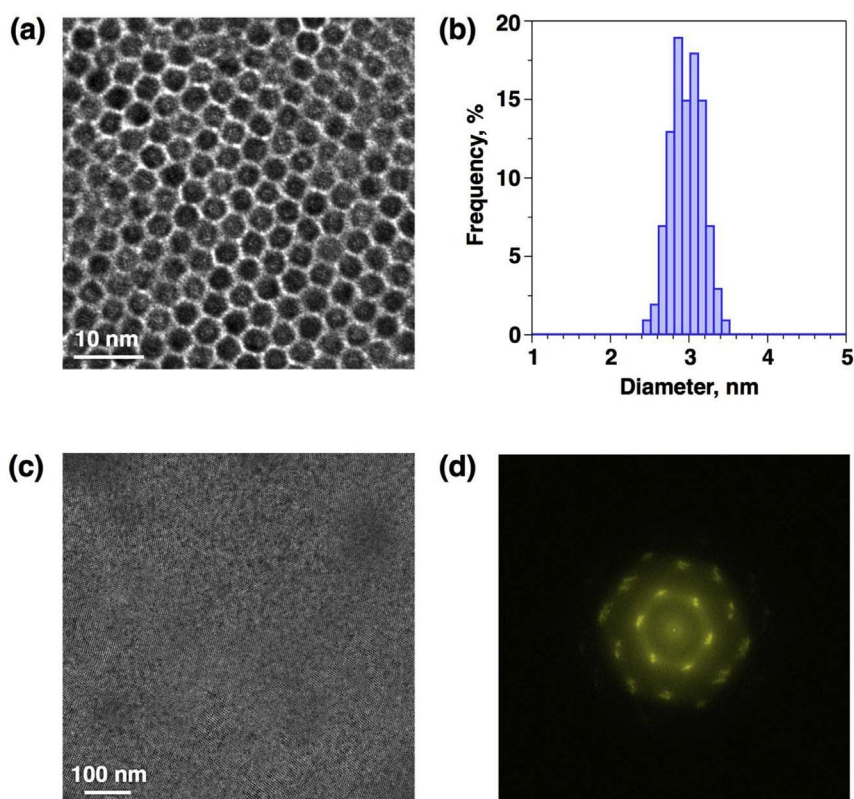


Fig. 1. (a) TEM image and (b) size distribution histogram of the TiO₂ nanocrystals. The size distribution was evaluated by statistical analyses ($N = 100$) using selected TEM images. (c) Low magnification TEM image of the periodically aligned TiO₂ nanocrystals. (d) The FFT image derived from the image in (c).

first mixed in a glass vial at room temperature, after which this precursor solution was sealed in an SUS-316 stainless steel reactor. The reactor was placed in a pre-heated molten salt bath to heat the solution to 300 °C and this temperature was maintained for 10 min. Notably, in the present method, the maximum heating rate to the target temperature was 500 °C/min. Following the reaction, the powdery products were collected by centrifugation, washed with methanol, and dried *in vacuo*.

The nanostructure of the powdery product was confirmed by transmission electron microscopy (TEM). Surprisingly, the obtained materials exhibited perfectly uniform sizes and morphologies (Fig. 1a), with an average particle diameter of 3.0 ± 0.4 nm (Fig. 1b). Judging from the high-resolution TEM images, each product generated a clear lattice fringe with an interplanar distance of 0.19 nm (Fig. S1), corresponding to the (200) or (020) planes of anatase TiO₂. X-ray diffraction (XRD) patterns also demonstrated the presence of an anatase phase, although a bronze phase was present in less than 10% (Fig. S2) [23]. It is also worth noting that these nanocrystals exhibited a perfect periodic arrangement on the micrometer scale, judging from the wide-range TEM observation shown in Fig. 1c. The fast Fourier transform (FFT) of the TEM image presented in Fig. 1d also shows a hexagonal pattern, providing evidence for perfect periodicity in the observed structure. These results show that the present method synthesizes extremely fine and uniformly sized TiO₂ nanocrystals.

To confirm the role of the oleic acid in the formation of these titania nanocrystals, we performed a detailed characterization of the products using Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric (TG) analysis. As shown in Fig. 2a, the IR spectra of the powdery product show strong characteristic peaks around 3000 and 1500 cm^{-1} . These peaks can be assigned to antisymmetric and symmetric C–H stretching vibration modes, typically located at 2920 and 2851 cm^{-1} , and antisymmetric and symmetric stretching vibration modes of the COO[−] anion on the surface of the TiO₂, located at 1514 and 1427 cm^{-1} , respectively [24]. In addition, the TG data demonstrate a mass loss of approximately 30% in the temperature range from

200 to 400 °C (Fig. 2b), indicating the inclusion of organic material. These results show that the surfaces of the nanocrystals were covered with oleate anions. The surface covering of oleate anion on the nanocrystals may also contribute the hexagonal periodic alignment of the nanocrystals through the lipophilic interaction between unsaturated aliphatic chains.

As a result of the strong interaction between the oleate anions on the TiO₂ surfaces, the nanocrystals could be redispersed in non-polar solvents, such as hexane and toluene, in a stable manner. This enabled the spectroscopic analysis of the nanocrystal structure using small-angle X-ray scattering (SAXS). Fig. 2c presents the SAXS profile for a hexane dispersion of the TiO₂ nanocrystals. Theoretical curve fitting determined that the SAXS profile (the blue trace) could be matched to the curve generated using a rod model (gray line), indicating that the dispersed TiO₂ nanocrystals had an anisotropic rod structure with a small aspect ratio (length/diameter = 2.5). The average diameter based on calculations using the rod model was estimated to be 3.6 nm (Fig. 2d). This value is consistent with that derived from the TEM observations in Fig. 1a. To confirm the formation of an anisotropic rod structure, we performed an acid treatment of the as-prepared TiO₂ nanocrystals to remove the oleate anions and then isolated the nanocrystals. Rod-like nanocrystals were subsequently observed by TEM, as shown in Fig. S3. This fact is again consistent with the surface covering of oleate anion on the TiO₂ nanocrystals through the chemical adsorption.

The factors influencing the formation of the ultrafine nanocrystals were assessed by examining the effect of the heating rate. In comparison with the products obtained from the rapid heating reaction, clear structural differences were observed when using slow heating. The products of the slow heating reaction showed an agglomerated structure (Fig. S4b) in contrast to the nanocrystals prepared by rapid heating (Fig. 1a and Fig. S4a). The maximum reaction temperature also affected the ultrafine structure of the products, even when applying rapid heating. The reaction at a relatively low temperature (250 °C) with rapid heating gave amorphous agglomerates (Fig. 3a). In contrast, the product prepared at a higher temperature (400 °C) with rapid heating

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