

Synthesis of Anatase TiO₂ Nanoparticles with β -Cyclodextrin as a Supramolecular Shell

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Abstract: We report a novel, green hydrothermal-synthesis route to well-dispersed anatase TiO₂ nanoparticles with particle sizes of 9–16 nm in the presence of β -CD (β -cyclodextrin). During the synthesis process, the CD-containing synthesis mixture assembled in both longitudinal and latitudinal directions. Driven by the interaction between molecules, the β -CDs assembled in the longitudinal direction to form

long-chain compounds, whereas in the latitudinal direction, they tended to form regular aggregates through coordination with the Ti species from the hydrolysis of tetrabutyl titanate. In view of the effect of the coordination

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and the steric hindrance of β -CDs as a supramolecular shell, homogeneous nuclei and slow growth of TiO₂ crystals during the synthesis process was observed, which was responsible for the formation of uniform TiO₂ nanoparticles. The low β -CD dosage and the high product yield (>90%) demonstrated well the potential of this synthesis route in the large-scale industrial production of anatase nanoparticles.

Introduction

Recently, metal oxides with nanostructures have attracted extensive attention for their fundamental size-dependent properties and important technological applications.^[1–5] TiO₂ is one of the most-studied oxides due to its widespread application in solar-energy conversion,^[6,7] photocatalysis,^[8–10] ultrathin capacitors,^[11] sensors,^[12] and so on. TiO₂ exists in nature in three distinct crystal phases: anatase, rutile, and brookite. Each phase exhibits different physicochemical properties, and anatase is the most important for its extraordinarily high photochemical activity.

Much effort has been focused on the synthesis of anatase TiO₂ nanoparticles with high purity and controlled particle size. Sol-gel processing and microemulsions prove to be successful methods and have been extensively studied.^[13–20] However, with a few exceptions,^[13,14] both methods typically either produce amorphous titanium dioxide^[15,16] or result in the presence of chemical impurities.^[17] To obtain pure anatase with high crystallinity, a subsequent calcination or an-

nealing process is usually necessary, which leads to grain growth and agglomeration.^[18–20] Hydrothermal or solvothermal processing, carried out at relatively high temperatures, can directly provide crystalline anatase TiO₂, but the agglomeration of the obtained anatase particles is also unavoidable.^[21,22]

Organic shells in the synthesis system can attach to the surface of the particles, and a bulky component within the molecule can provide spatial isolation of the nanoparticles from the environment and prevent the agglomeration caused by van der Waals interparticle attractions.^[20] Well-dispersed anatase nanoparticles can be obtained by wet-chemistry methods involving the functional groups of various organic shells, so-called surfactants or capping ligands.^[23–25] However, the synthesis processes are usually quite complicated, and the organic shells used are not easily available or even toxic, for example, trioctylphosphine oxide (TOPO).^[24]

CDs (cyclodextrins) are cyclic oligosaccharides that consist of covalently linked glucose units (6 units = α -CD, 7 units = β -CD, 8 units = γ -CD), which are characterized by a hydrophilic exterior and a hydrophobic interior.^[26] The identities of encapsulating organic molecules and self-assembly have led to the intensive studies of CDs and their inclusion complexes.^[26–28] Many nanostructured organic compounds and composites have been constructed by the self-assemblies of CDs. Although the hydroxy group was also known to mediate compatibility with an inorganic-oxide matrix through

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hydrogen bonding,^[29,30] to the best of our knowledge, the effect of CDs on the synthesis and construction of inorganic oxides instead of organic compounds is still unavailable.

Herein, an improved hydrothermal route with environmentally friendly β -CD is employed for the preparation of anatase TiO_2 . The self-assembly of CDs in this synthesis system is studied, and its use in the production of inorganic nanoparticles is discussed.

Results and Discussion

Figure 1 shows the XRD patterns of the samples synthesized at different pH values. Only amorphous TiO_2 was observed under neutral conditions (pH 7), and anatase TiO_2

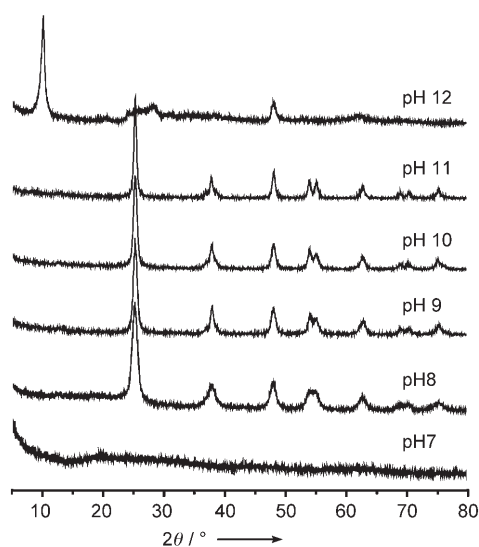


Figure 1. XRD patterns of synthesized anatase TiO_2 samples. Synthesis conditions: crystallization temperature = 150°C , crystallization time = 48 h, pH 8–12.

(JCPDS 21–1272) with high crystallinity was obtained under moderately alkaline conditions (pH 8–11) without impurities of the rutile or brookite phase. However, in stronger alkaline conditions (pH 12), the formation of titanate^[31] was observed.

The average size of the synthesized anatase TiO_2 particles was estimated according to the Debye–Scherrer equation [Eq. (1)]:^[32]

$$D = K\lambda / (\beta \cos\theta)$$

where D is the average crystal diameter, β is the corrected peak width (full width at half maximum), K is a constant related to the shape of the crystallites, λ is the wavelength of the X-rays employed ($\text{Cu}_{K\alpha}$ 0.154 nm), and θ is the diffraction angle. The width of the diffraction peak with the highest intensity (101) was selected for the calculation. The average diameter thus estimated for anatase TiO_2 samples synthesized at different pH values are displayed in Figure 2. The

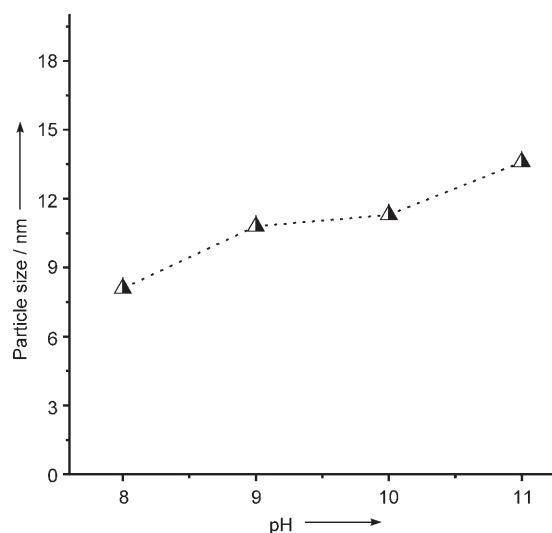


Figure 2. Effect of solution pH on particle size of anatase TiO_2 obtained.

average particle size of anatase TiO_2 is dependent on the alkalinity of the synthesis system, and an increase in the average grain size can be observed with increasing alkalinity. In the hydrothermal synthesis system, hydroxy ions act as mineralizers for the formation of the crystalline product. A higher concentration of hydroxy ions accelerates the crystallization process and thus leads to an increase in grain size.

Typical TEM images of TiO_2 particles synthesized at different pH values are shown in Figure 3. Under neutral conditions (pH 7; Figure 3a), ultrasmall wormlike TiO_2 particles could be observed, which proved to be amorphous by XRD analysis. Under strongly alkaline conditions (pH 12; Figure 3f), titanate nanowires, confirmed by XRD analysis, were obtained. Under moderately alkaline conditions (pH 8–11; Figure 3b–e), well-dispersed TiO_2 nanoparticles could be observed, and the average particle size obtained from TEM analysis were in good agreement with the results estimated from [Eq. (1)]. As far as the size distribution and the dispersion of TiO_2 particles are concerned, the optimal pH value for the synthesis was determined to be 10. A further TEM analysis of the sample synthesized at pH 10 is displayed in Figure 4. The enlarged overview TEM image (Figure 4a) shows entire well-dispersed spherical nanoparticles with a homogeneous size of 9–16 nm, which was further proved by the size-distribution curve in Figure 4d. The high-resolution TEM image (Figure 4b) shows a typical particle size of about 12 nm with well-defined lattice planes and a neat surface. The crystallinity and crystal structure of the sample were further confirmed by selected-area electron-diffraction analysis (Figure 4c): all diffraction rings correspond to pure anatase TiO_2 .

Hydrothermal synthesis usually leads to the aggregation of bulk particles due to van der Waals interparticle attractions.^[20] However, well-dispersed anatase nanoparticles with uniform particle sizes were obtained by hydrothermal synthesis in the presence of β -CD herein. It is proposed that β -CD, with multiple hydroxy groups, can adsorb onto certain

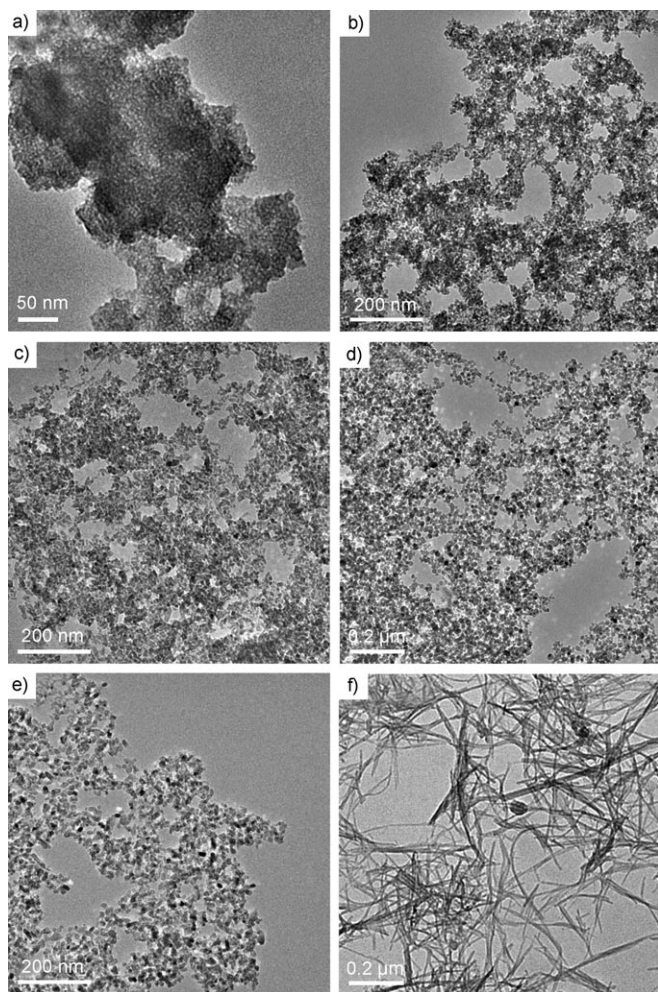


Figure 3. TEM images of TiO₂ samples synthesized at different pH values. a) pH 7; b) pH 8; c) pH 9; d) pH 10; e) pH 11; f) pH 12.

crystal planes or chelate with the Ti atoms to result in steric hindrance, similar to conventional surfactants and capping ligands.^[20] Furthermore, the self-assembly of β-CD in water may also provide the template for TiO₂ crystallization. To understand the function of β-CD herein, the changes in the structure and morphology of β-CD during the synthesis were studied.

β-CD (raw material) and the liquid-phase product obtained after synthesis were analyzed by NMR spectroscopy (Figure 5). Butanol, which should come from the hydrolysis of tetrabutyl titanate (TBOT), was found in the liquid phase after synthesis. No obvious change in the structure of β-CD could be observed after hydrothermal synthesis, as indicated by the unchanged peaks of 1-H–6-H. However, the amount of H atoms in the hydroxy groups of β-CD was reduced, because some of the weakly acid protons could be balanced out by the hydroxy ions in the synthesis system. As deduced from the NMR spectroscopic results, the β-CD did not participate in the reaction to produce anatase TiO₂; it probably acted as a pure template for homogenous TiO₂ nanoparticles.

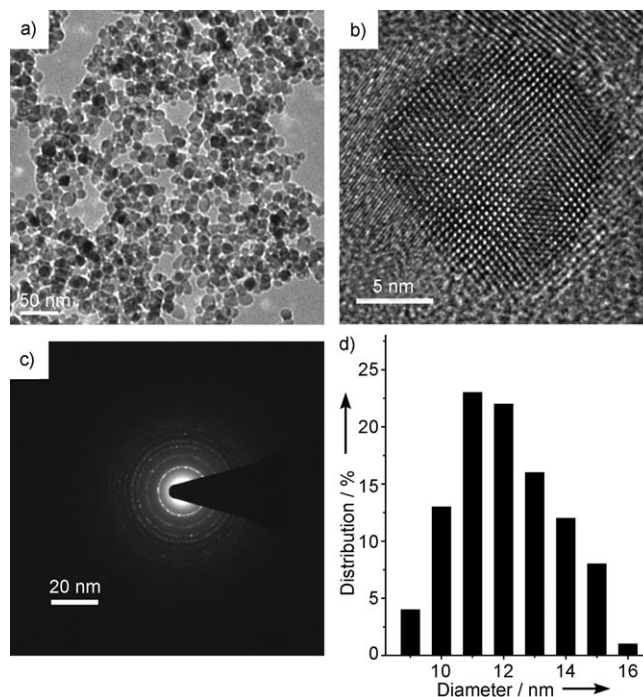


Figure 4. TEM analysis of a sample of anatase TiO₂ synthesized at pH 10. a) Overview image; b) high-resolution image; c) selected-area electron-diffraction analysis; d) particle-size distribution.

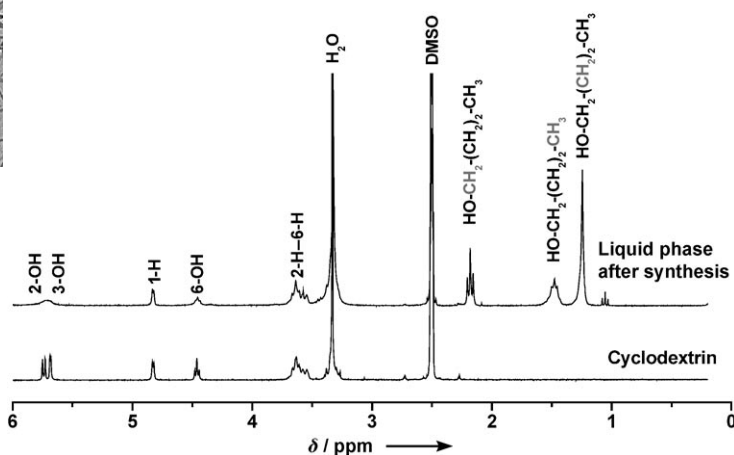


Figure 5. ¹H NMR spectra of β-CD and the liquid phase in dimethyl sulfoxide (DMSO) after hydrothermal synthesis. Synthesis conditions: crystallization temperature = 150 °C, crystallization time = 48 h, pH 10.

For a better understanding of the template function of β-CD, the synthesis mixture (β-CD + TBOT + NaOH + H₂O) before and after crystallization was analyzed by TEM (Figure 6). Though proven in theory, to the best of our knowledge, CD-containing solutions are difficult to analyze, and information about the assembly of CDs in water is rather limited.^[29] As seen in Figure 6a, self-assembly of the CD-containing synthesis mixture into long chains with widths of about 20 nm was clearly observed. The composites were homogeneously amorphous, as indicated by the selected-area electron-diffraction pattern in the inset. Ti could be

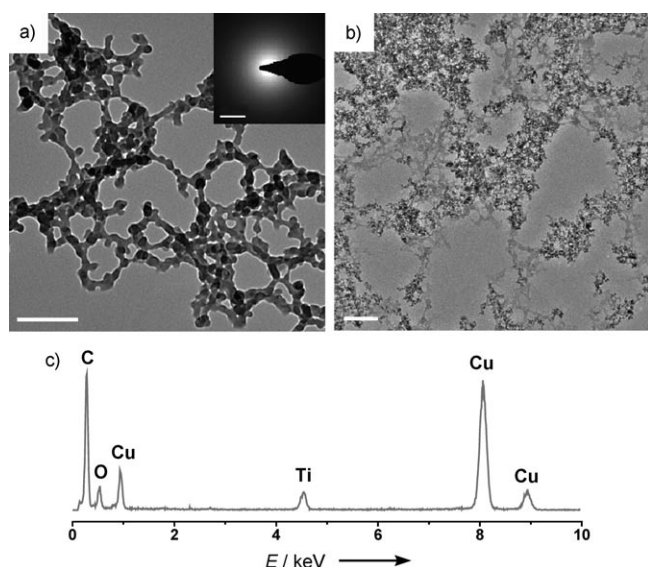


Figure 6. a) TEM images of synthesis mixture before crystallization. Inset: electron-diffraction pattern; b) TEM images of synthesis mixture after crystallization; c) EDS spectrum of synthesis mixture before crystallization.

found in the composites, according to the results of the EDS analysis (Figure 6c). Through this hydrothermal process, well-dispersed anatase TiO₂ nanoparticles with a uniform particle size can grow inside β -CD shells and finally precipitate from the assembled composites (Figure 6b). The residual Ti-free organic assembly can be removed by washing with *N,N*-dimethylformamide (DMF) or hot water to obtain the pure anatase TiO₂ nanoparticles.

β -CDs can self-assemble into regular composites and coordinate with Ti⁴⁺ ions (the initial nucleus for crystalline TiO₂). In view of the strong coordination ability of the hydroxy groups of β -CD and the rapid hydrolysis of TBOT, the rate of nucleation of the Ti species should be very high, leading to the formation of ultrathin homogeneous crystal nuclei on the composites of β -CD assembly. On the other hand, these composites acted as the supramolecular shell of the Ti species and greatly suppressed the growth and aggregation of Ti nuclei due to its steric hindrance. The rate of crystallization of TiO₂ was thus decreased. Furthermore, the mineralizers (hydroxy ions) were adsorbed onto the hydrophobic interior of β -CD (physisorption),^[34] thus further slowing the crystallization process of titania during the hydrothermal synthesis. As a result of all the above factors, the rapid nucleation and slow crystallization of titania was obtained in the presence of β -CDs, which led to the formation of uniform titania nanoparticles.

There is still the question of how β -CD and the Ti species assemble to form regular organic-inorganic composites. Based on the special properties of β -CD, a concise self-assembly process is proposed. There are many hydroxy groups on the β -CD molecules, and those at the C6 positions (so-called primary face hydroxy groups) are the most active.^[26] In aqueous solution, the Ti species produced from the hydrolysis of TBOT can adsorb onto these hydroxy groups,

preferentially on the primary face groups, by hydrogen bonding (Figure 7a). As for each β -CD molecule, the selective adsorption of the Ti species on the hydroxy groups of β -CD can be proposed as displayed in Figure 7b: the Ti species are adsorbed onto the hydroxy groups all around the β -

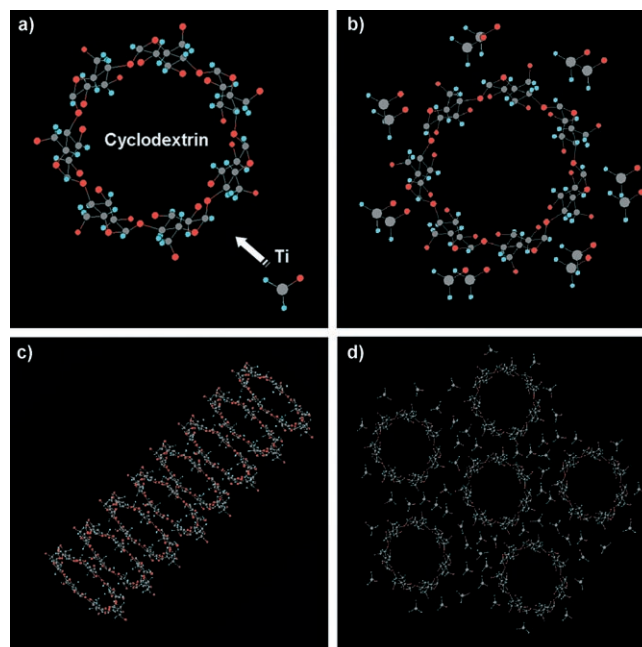


Figure 7. Proposed self-assembly process of β -CD and the Ti species. a) Preferred adsorption of Ti at a certain position on β -CD; b) single β -CD molecule with adsorbed Ti species around; c) longitudinal assembly for β -CD in synthesis mixture; d) latitudinal assembly for β -CD in synthesis mixture.

CD molecule. In the synthesis mixture (β -CD + TBOT + NaOH + H₂O), the assembly of β -CD occurs in two directions: both longitudinal and latitudinal. In the longitudinal direction, the β -CDs assemble into long chains (Figure 7c), and this kind of assembly is driven by the intermolecular forces between the β -CD molecules. Each β -CD molecule contains a hydrophilic exterior and a hydrophobic interior.^[26] In solution, attractive forces exist between the hydrophilic exteriors of different β -CD molecules. The lowest-energy arrangement is for β -CD to line up in solution, but with slightly bent or staggered geometries.^[29,33] In the latitudinal direction, β -CDs tend to form regular aggregates through intermediate Ti species (Figure 7d). As for each β -CD molecule, the Ti species can adsorb onto the hydroxy groups all around the β -CD molecule (Figure 7b). For a solution with a high concentration of β -CD, the Ti species should adsorb onto the hydroxy groups of different β -CD molecules with equal opportunity and thus couple to different β -CD molecules. As opposed to longitudinal assembly, the presence of the Ti species is indispensable for assembly in the latitudinal direction. Thus, β -CD and the Ti species assemble to form regular organic-inorganic composites in both longitudinal and latitudinal directions.

Conclusions

We have reported an improved hydrothermal route to pure anatase TiO₂ nanoparticles with β-CD as a supramolecular shell. During the synthesis process, β-CD assembles in both longitudinal and latitudinal directions to form ordered organic-inorganic composites with the Ti species. The latter is then greatly stabilized inside the supramolecular shell of β-CD, and the aggregation of anatase TiO₂ particles during crystallization is suppressed to a great extent. Thus, well-dispersed pure anatase TiO₂ with uniform particle size can be obtained.

Compared to other synthesis methods, the method reported herein exhibits many advantages that can be summarized as follows:

1. It is a green synthesis method; all starting materials, including the supramolecular shell β-CD, are nontoxic and easily available.
2. Well-dispersed pure anatase nanoparticles with high crystallinity and uniform particle size can be obtained directly through this simple hydrothermal synthesis route, and no posttreatment is needed.
3. The simple aqueous synthesis system, high yield (>90%), and relatively low β-CD dosage make this synthesis route suitable for large-scale and industrial synthesis of anatase TiO₂ nanoparticles. Furthermore, the β-CD is renewable after the synthesis through a simple extraction process.
4. Based on the mechanism, hydrothermal synthesis with β-CD as a supramolecular shell is a promising route that can be further developed for the production of other metal oxides. Other supramolecular compounds with similar properties of self-assembly can also be used as supramolecular shells for the synthesis of nanostructure metal oxides.

Experimental Section

All chemicals were analytical grade and used without further purification. In a typical synthesis, β-CD (10 mmol) was dissolved in deionized water (180 mL) at a constant temperature of 60°C, and TBOT (100 mmol) was added dropwise with vigorous stirring. The pH of the solution was adjusted by adding sodium hydroxide. After homogenization for about 2 h, the mixture obtained was transferred into a teflon-lined autoclave (250 mL capacity) for crystallization at 150°C for 48 h. The resulting precipitate was separated from the liquid phase by centrifugation and then washed with DMF to remove the β-CD of other organic compounds remaining. The final product was dried at 80°C overnight and appeared as a fine white powder.

The synthesized TiO₂ samples were characterized by XRD performed on a Rigaku D/max 2500 diffractometer with a graphite monochromator and Cu_{Kα} radiation. TEM images of samples were acquired on a Tecnai G² 20 S-TWIN transmission electron microscope at an acceleration voltage of 200 kV. Energy dispersive X-ray spectroscopy (EDS) was performed on an EDAX Genesis instrument. The β-CDs before and after hydrothermal synthesis were analyzed by ¹H NMR spectroscopy on a Varian Mercury Vx 300 spectrometer with sample solutions in DMSO.

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