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A chelate-assisted route to anatase TiO_2 nanoparticles in acidic aqueous media

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Abstract

We described a simple route to TiO_2 nanoparticles with anatase phase by the acid-catalyzed sol–gel process of titanium(IV) bis(acetylacetonate) diisopropoxide in water, and studied the effect of chelation of the precursor on the crystallite and size of anatase TiO_2. The nanocrystalline anatase TiO_2 was obtained by controlling pH of aqueous solution containing the precursor at temperatures as low as room temperature. The ligands of the precursor complex were characterized by FT-IR and UV–vis spectroscopy. The sustenance of chelation of the precursor in an acidic solution may be a key factor to determine the crystalline phase of TiO_2 at such mild conditions.

Keywords: $Ti(acac)_2(O^iPr)_2$; Anatase; Sol–gel preparation; Nanoparticle

1. Introduction

Nanocrystalline TiO_2 has widely been attracted for excellent photocatalytic efficiency and many potential applications for semiconducting materials. The catalytic activity of titania depends upon its surface area that is subject to the crystal size. A number of fabrication processes for nanoparticles have been reported including precipitation, microemulsion and sol–gel. The sol–gel process is the most popular for preparing such nanosized metal oxides. Titanium alkoxides are one of the most thoroughly studied metal alkoxides in the sol–gel process [1–4]. Depending on the hydrolysis method and the molecular structure of the alkoxide precursor, different sizes and various crystalline phases of TiO_2 can be produced. Sol–gel derived titania particles from popular titanium isopropoxide (TIPP) can sometimes have non uniformity, mixed phases and various morphologies due to unsaturated titanium coordination. Chemical approaches from TIPP to TiO_2 have been made by an increased coordinative saturation at the titanium center with β-diketonate ligands, such as acetylacetonate (acac) in order to control the chemical reactivity [5,6]. It is said that the number of bidentate ligands around the titanium center affect the final morphology of TiO_2 [7]. Titanium(IV) bis(acetylacetonate) diisopropoxide (TBADI) is particularly hydrolyzed to form 1-D TiO_2 polymers due to condensation of two *trans*-hydroxides, while $Ti(acac)(O^iPr)_3$ (TAIP) leads to 3-D TiO_2 due to three hydroxides. Thus, sol–gel process of a bisbidentate complex, $Ti(acac)_2(O^iPr)_2$ (TBADI) has been relatively unexplored [8,9].

To make the whole synthesis environmentally friendly, it is preferable not to use alcohol solvents. All acac ligands of TBADI cannot be completely dissociated under the normal hydrolytic conditions. In order to obtain rather 3-D TiO_2 from TBADI the dissociation of Ti–acac bond should be preceded under harsh reaction conditions, such as high temperatures which usually lead to uncontrolled sizes of TiO_2. Strong acidity, however, favors the protonation of acetylacetonate and may ease the cleavage of M-acac in the $M(acac)_x$ complex in sequence at ambient temperatures [10]. If we can find the partial dissociation/hydrolysis conditions of acac ligand in TBADI in the presence of strong acid, the resulting hydrolyzed species could still have a bidenate ligand whose chelation induces the precursor to form edge-sharing dimers on the other side in its octahedral structure. Previous structural studies also revealed that TBADI undergoes to redistribute its edge-sharing dimer

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$[Ti(acac)(O^iPr)_3]_2$ in solution [5]. Here, we will address a new synthetic surfactant-free approach from $Ti(acac)_2(O^iPr)_2$ complex to anatase nanoparticles by simple control of pH in aqueous media at mild conditions including room temperature.

2. Experiment

All commercial reagents were used without further purification. In the synthesis of TiO_2 nanoparticles the TBADI precursor was acidified prior to autoclaving process due to solubility of TBADI in water, similar peptization process was found in literature [11]. Typical process is as follows: first, nitric acid (0.75–9.00 mL, 0.05–1.20 M) was dropwisely added to TBADI (Aldrich, 75% in 2-propanol, 4.86 g) in a volumetric flask (100 mL) for 30 min, and then the resulting mixture was diluted by water to make 0.1 M Ti(IV). The light yellow solution was adjusted to pH 0.2–3.0 by the amount of nitric acid, and set aside for 4 h at room temperature. Finally, the solution was hydrothermally treated in a Pyrex-lined digest bomb at 100 °C for 4 h. TiO_2 nanoparticles were produced as a colloidal suspension. To obtain powdered TiO_2 samples the suspensions were centrifuged (15,000 rpm, 20 min), washed twice with water and ethanol, and vacuum-dried at room temperature. Organic ligands of the hydrolyzed complex were characterized by FT-IR spectroscopy (Spectrum 2000, Perkin-Elmer) and UV–vis spectrophotometer (Optizen 2010UV, MECASYS). The average diameters of dispersed TiO_2 nanoparticles in the aqueous solution were determined by the Scherrer equation of (1 0 1) peak of XRD (Rigaku D/Max, Cu Kα) patterns, and confirmed by TEM (JEM-2000Ex, JEOL).

3. Results and discussion

TiO_2 powders can be prepared by the acid-assisted reaction of TBADI in aqueous media at room temperature for 1 day without further heat-treatment (see Fig. 1). Their crystalline phases were observed mainly in anatase with impurity phase of rutile as well as the traces of amorphous phases at pH 0.2, while only amorphous powders were produced at pH 0.5. The crystallinity of TiO_2 particles can be improved with increasing reaction temperature of the hydrolyzed precursor at pH 0.2, but higher heat-treatment results in a similar composition with that of untreated species. It is noticeable that room-temperature preparation of nanocrystalline TiO_2 is relatively rare, even though hydrolysis of TIPP at pH 0.7 has been reported to produce mixture of three crystalline phases of TiO_2 at room temperature [2].

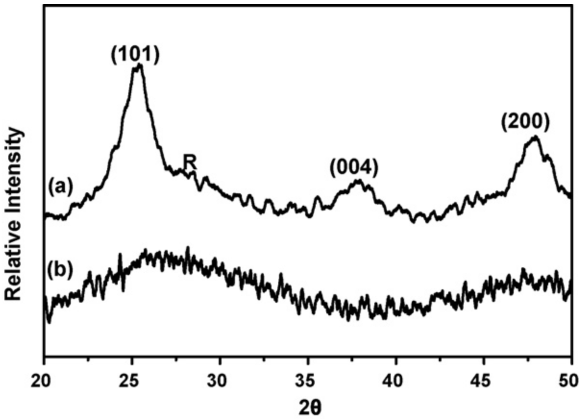

Fig. 1. XRD patterns of titania powders obtained from sols which were produced at room temperature for 1 day by acidification of TBADI at pH 0.2 (a) and 0.5 (b). Capital R designates rutile phase.

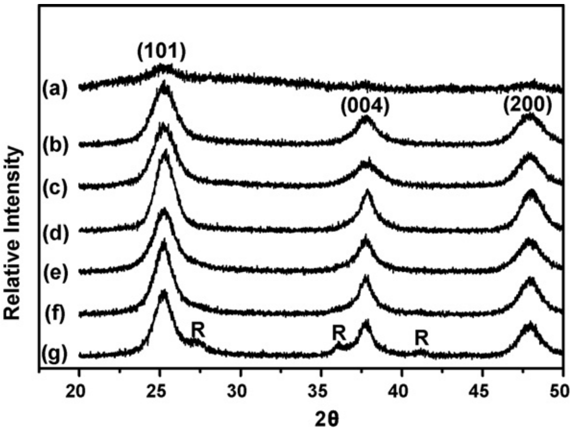

Fig. 2. XRD patterns of titania nanoparticles obtained from sols which were produced at 100 °C for 4 h by acidification of TBADI at pH 3.0 (a), 1.9 (b), 1.3 (c), 0.9 (d), 0.5 (e), 0.3 (f) and 0.2 (g). Capital R designates rutile phase.

The pH of the reaction solution had a magnificent effect on the formation of crystalline phase of TiO_2 at elevated temperatures. Fig. 2 shows XRD patterns of TiO_2 nanoparticles obtained under different pH conditions at 100 °C for 4 h. Only anatase phase was observed at pH between 0.3 and 3.0, whereas the mixture of anatase and rutile was at pH below 0.2 and no solid was obtained at pH above 3.0, respectively. Fig. 3 is TEM images of the obtained titania, which supports the effect of pH on the formation of the different morphology of TiO_2. At pH 1.3 single anatase phase was observed but its size increases as the hydrothermal temperature rises from 100 to 300 °C. At lower pH below 0.2, however, the mixed phases were observed due to hydrolysis of all ligands at such strong acidic conditions. These results are quite different from those obtained from TIPP at the same range of pH or TAIP at pH 4.6, respectively [2,6]. It means that hydrolytic polymerization of the precursor does not occur due to strong chelation of the acac ligand at such weak acidic conditions but acac ligands of the precursor partially dissociate at strong acidic conditions below pH 3.0. If the solution, however, is too strongly acidic below pH 0.3, both of acacs are simultaneously decomposed to be hydrolyzed and randomly condensed to anatase and rutile.

The decomposition of ligands of the complex was confirmed by spectroscopy. Fig. 4 shows the FT-IR spectrum of the precursor solution and the room-temperature drying powders after acidification. In Fig. 4(a), the characteristic bands corresponding to $Ti(acac)_2(O^iPr)_2$ and 2-propanol are located at 1600 and 1100 cm^{-1}, respectively. Fig. 4(b) shows the spectrum of hydrolyzed $Ti(acac)_2(O^iPr)_2$ where the characteristic bands of the isopropoxy group at 1280, 1120 and 1030 cm^{-1} disappear upon hydrolysis but C–O vibrations of the acac group