

A study of nanocrystalline TiO₂ preparation with inorganotitanates and gelatin dispersant: thermal analysis of complex gel

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Abstract

Nanocrystalline TiO₂ was prepared by the sol–gel method. The fine and homogenous particles were obtained by calcining the complex gel consisted of precursor TiO(NO₃)₂·H₂O and gelatin dispersant in air. The complex gel was analyzed by thermogravimetric analysis and differential scanning calorimetry in air and N₂. It was found that during heating a novel and stable medium material has formed at 180°C by the chains entanglement between precursor and dispersant, the NO₃⁻ decomposition temperature in this medium is delayed and reaches the temperature range of dispersant oxidation and decomposition. The calcining procedure for the complex gel in N₂ is similar to in air but the dispersant oxidation in N₂ is only by means of NO₃⁻ decomposition and the heat evolved is greatly decreased. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Decomposition; Oxidation; TiO(NO₃)₂·H₂O; Entanglement; Calcining

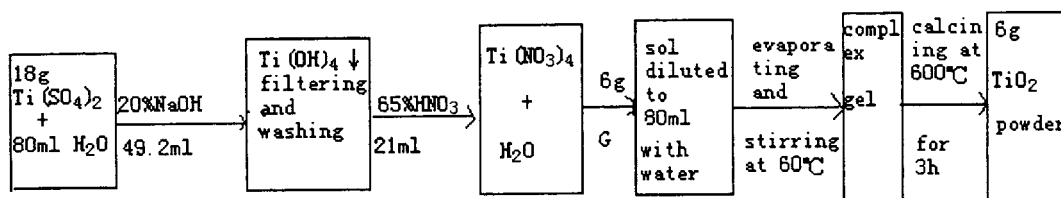
1. Introduction

Because nanocrystalline TiO₂ has played an important role in both basic and applied research [1–4], attention paid to the preparation of this fine powder has been increasing in the last few years [5]. For many different synthesis methods, pyrolysis and hydrolysis of organic and inorganic titania precursors are usually adopted [6–9]. Recently, we have prepared homogenous and nanosized TiO₂ particles with inorganotitanates and special dispersants (gelatin and polyethyleneglycol) at calcining temperatures

from 500°C to 900°C [10–12]. The relationship between dispersants and the physical properties of nanocrystalline TiO₂ as well as purification and doping during preparation were studied. In addition, the application of TiO₂ fine powders for catalyzing some polymerization reactions have also been reported [13,14].

For this pyrolysis method [10–12], studies involving thermal analysis of the complex gels are interesting, since they are related to the calcining mechanism and functional analysis of the dispersants. In particular, NO₃⁻ usually is a strong oxidation agent and can be independently used for oxidizing part of dispersant. This change of calcining mechanism may have an effect on the particle size and homogeneity of nanocrystalline TiO₂. This thermal analysis is a subject in this paper.

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Scheme 1.

2. Experimental

2.1. Preparation of nanocrystalline TiO_2

A gelatin sample (G) used in this experiment was made from pig bones in China. Other chemical agents, all analytical grade, were obtained from China.

The preparative procedure is indicated in Scheme 1.

2.2. Characterization of nanocrystalline TiO_2

The prepared nanocrystalline TiO_2 was measured using a Rigaku-2400 X-ray diffractometer (XRD, Cu, Ka) and a Hitachi-800 transmission electron microscope (TEM).

2.3. Thermal analysis

The precursor powder obtained by evaporating $\text{Ti}(\text{NO}_3)_4$ solution, raw gelatin and complex gel (1 mg for every sample) was analyzed using a Shimadzu 50 DSC (Al cell, 0–500°C) and TG(Al₂O₃ cell, 0–700°C) instruments at a heating rate of 10°C min⁻¹ in air and 99.9% N₂ respectively.

3. Results and discussion

3.1. Physical properties of nanocrystalline TiO_2

As a kind of derived protein, gelatin has extensive usage [15]. One reason that the gelatin has been used in photographic materials for about 100 years is its excellent ability to disperse silver halide and other dyes in emulsions [16]. This dispersion function also can be used for nanocrystalline TiO_2 preparation. Because in calcining procedure TiO_2 particles grow slowly in gelatin gel, the nanosized powders are obtained eventually.

The XRD measurement (Fig. 1a) shows the crystal system of TiO_2 powder prepared at 600°C belongs to anatase. The average particle size (D in nm) was first determined from the XRD pattern parameters of the TiO_2 powder according to the Scherrer equation [17]: $D = k(\lambda/\beta \cos \theta)$, where k is a constant equal to 0.89, λ , the X-ray wavelength equal to 0.154 nm, β , the full width at half-maximum (FWHM in radian and measured from Fig. 1b) and θ , the half diffraction angle. The average particle size is about 30 nm by calculation. The TEM image in Fig. 2 also verifies this result and shows a homogenous particle distribution.

3.2. Thermal analysis of precursor and raw gelatin

The precursor composition has been suggested to be $\text{Ti}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in our previous studies [10–12]. This suggestion can be verified by thermal analysis, which is plotted in Fig. 3a and Fig. 4a. The differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) curves exhibit the precursor decomposes at 240°C and the decomposition procedure is hardly any different in air and N₂. The total loss mass of the precursor from 50°C to 700°C reaches 61.0% and includes the decomposition of NO_3^- and more stable coordination water. Comparatively, 61.0% loss mass is calculated from the molecular formula $\text{TiO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$.

It can be seen in Fig. 3b that the raw gelatin heated in N₂ giving some endothermic and exothermic peaks are all due to gelatin decomposition. Heating in air gives a different curve due to both decomposition and oxidation procedures, and a larger oxidation procedure in air occurs at 280–350°C and then is followed by a mixed procedure of decomposition and oxidation. Accordingly, TG curves (Fig. 4b) indicate at 0–700°C the gelatin can be totally removed in air and most gelatin (85%) is also lost in N₂ by decomposition only.

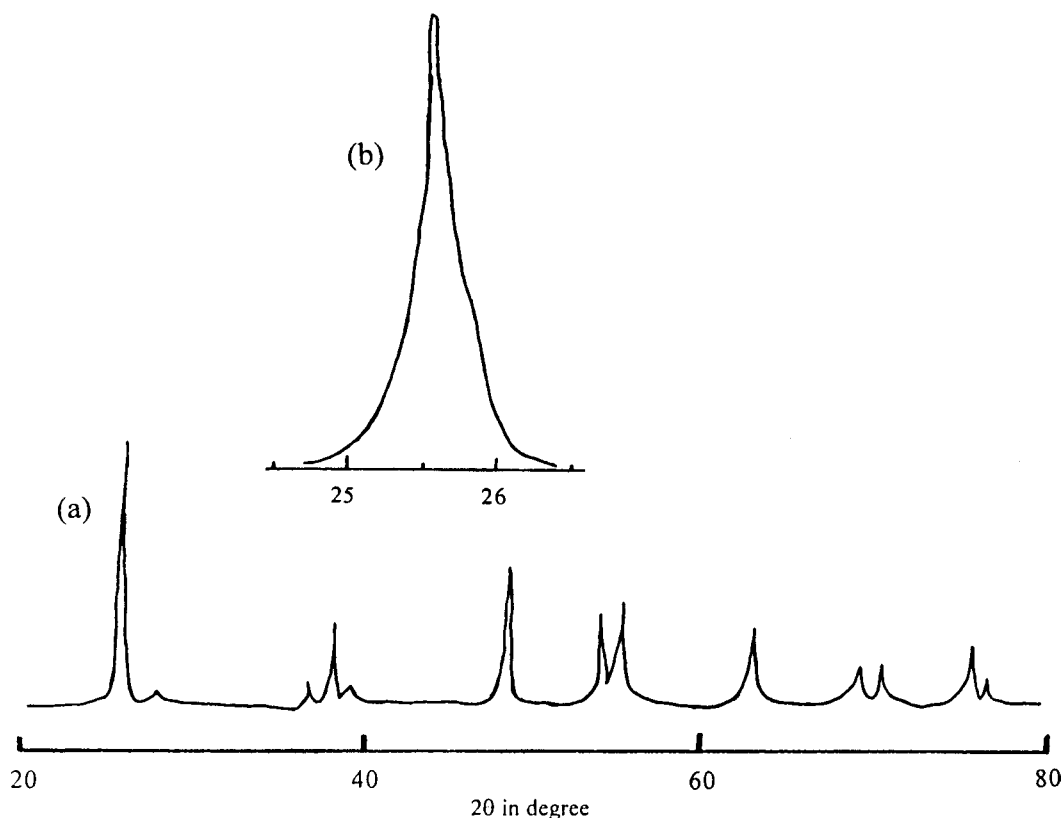


Fig. 1. XRD patterns of TiO_2 powder calcined at 600°C for 3 h, scanning rate (k min^{-1}): (a) 8; (b) 0.25.

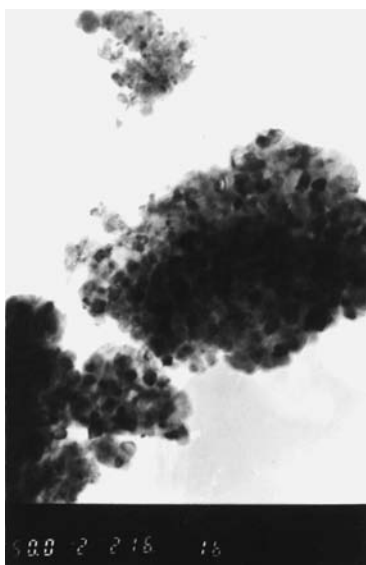


Fig. 2. TEM image of TiO_2 powder calcined at 600°C for 3 h.

3.3. Thermal analysis of complex gel

It is surprising in Fig. 3c that the complex gel heated in air and N_2 at about 180°C exhibits a large exothermic peak. Fig. 4c shows at about 150°C 15% water in complex gel has lost quickly and DSC curves in Fig. 3c partly indicate this endothermic procedure. Fourier transform infrared spectroscopy (FTIR) analysis [10,18] show that at $150\text{--}180^\circ\text{C}$ the hydrogen bond can form between $\text{TiO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and the peptide chains of gelatin. This is enhanced with increasing calcining temperature, as expressed by Scheme 2.

There are very few groups, e.g. OH, in gelatin capable of multicoordination to Ti^{4+} . Although there is a small number of OH as the residual groups of hydroxyproline section in peptide chains [15], the separation between OH groups does not allow for multicoordination with Ti^{4+} . So the hydrogen bond is the main force linking $\text{TiO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and gelatin. However, the formation of hydrogen bond cannot

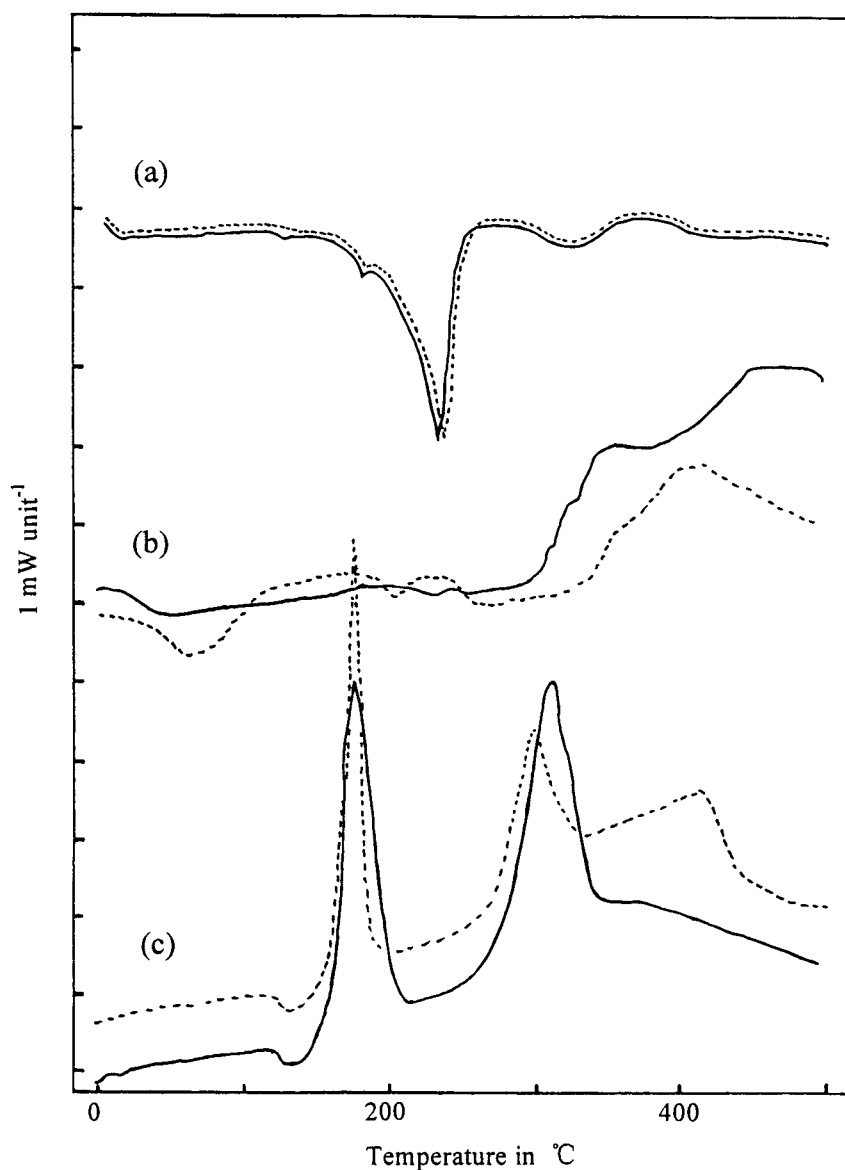


Fig. 3. DSC curves: (a) precursor; (b) raw gelatin; (c) complex (—), in air, (---), in N₂.

evolve so much heat. It is implied that after the loss of 15% water some very tight entanglement occurs between $\text{TiO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ chains and gelatin peptide chains with each other. (Just as this entanglement, a lot of heat is released, in air and N₂ the $\text{TiO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in complex gel no longer decomposes at 240°C and the gelatin in complex gel cannot be totally removed at 0–700°C.)

Although the calcining procedure of the complex gel in N₂ is similar to that in air (Figs. 3 and 4), it is interesting in Fig. 3c that the complex gel heated in N₂ also shows a smaller exothermic peak at about 300°C resulting from the gelatin oxidized by the NO_3^- decomposition. So the decomposition temperature of $\text{TiO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in a complex gel can be estimated in this way. The reason that the endothermic peak for

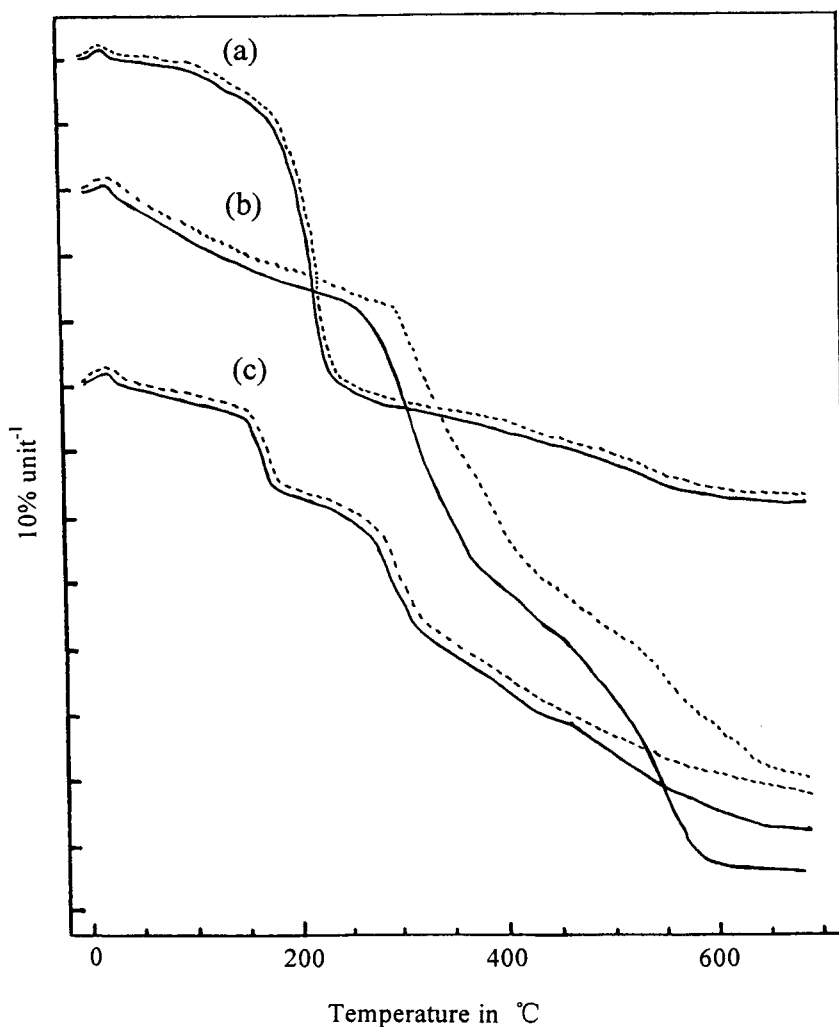


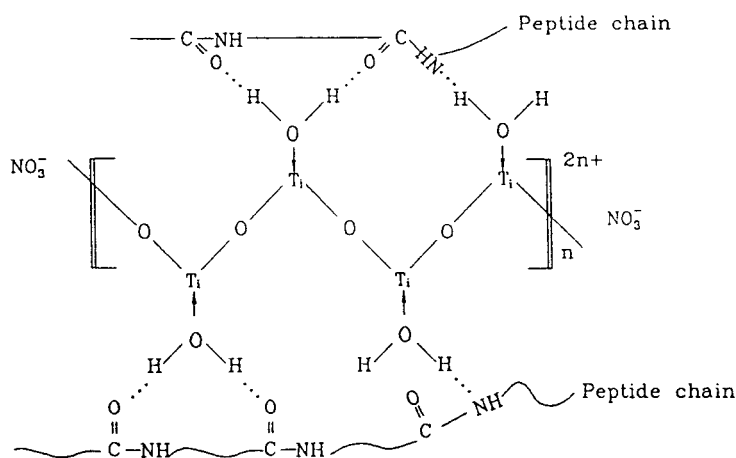
Fig. 4. TG curves: (a) precursor; (b) raw gelatin; (c) complex (—), in air, (---), in N₂.

the original $\text{TiO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ has disappeared in Fig. 3c may be that this procedure has been overwhelmed by the exothermic oxidation. In addition, the complex gel heated in N₂ at about 420°C gives a exothermic peak of gelatin decomposition.

4. Conclusions

The gelatin gel method is a potential way for obtaining nanocrystalline TiO_2 . The key preparation procedure is considered to be through a very tight

entanglement of various chains in the complex gel. In this entangled medium the growth of TiO_2 particles from $\text{TiO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ decomposition is stopped effectively. When the complex gel is calcined in air and N₂, there are different oxidation and decomposition mechanisms. Especially, the smaller oxidation heat accompanying $\text{TiO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ decomposition in N₂ may benefit obtaining characteristic TiO_2 powder, because the intrinsic temperature for the TiO_2 particles nucleated in calcining procedure has some effect on the character of the TiO_2 powder prepared.



Scheme 2.

Acknowledgements

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