Study of Nanocrystalline TiO₂ Prepared with Raw and Modified Gelatin Dispersants

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ABSTRACT: Nanocrystalline TiO₂ was prepared by the sol-gel method, and raw gelatin and its modified samples crosslinked with formaldehyde acted as dispersers in this method. Transmission electron microscope and X-ray diffractometer measurements showed, using modified gelatin samples, the prepared TiO₂ nanocrystals have smaller particle size and more homogeneous particle distribution at the same calcining temperature. Following Fourier transform IR spectroscope analysis, the dispersion mechanism is considered to be through the bonding of TiO(NO₃)₂ · H₂O with the peptide chains of gelatin by a hydrogen bond. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2569–2574, 1999

Key words: average particle size; disperse; hydrogen bond; network

INTRODUCTION

As a kind of derived protein gelatin, which is composed mainly of five ingredients, gelatin has extensive usage.¹ One of reasons that gelatin has been used in photographic materials for about 100 years² is its excellent ability to disperse silver halide and other dyes in emulsions. On the other hand, because of its potential usage in catalysts, electronic materials, coating materials, and so on, nanocrystalline TiO₂ has been widely studied relating to its preparations, structures, and properties.³⁻⁷ The nanocrystalline TiO₂ prepared by the sol-gel method has been reported extensively and organotitanates (e.g., titanium butoxide) are usually used.^{8,9} In our study a gelatin aqueous sol containing Ti⁴⁺ was converted into gel by evaporation, and then nanocrystalline TiO₂ was obtained by calcining the gel at temperatures ranging from 500 to 900°C. Special attention was paid to the characteristic differences of nanocrystalline TiO_2 prepared with raw gelatin and its modified samples.

EXPERIMENTAL

Preparation of Nanocrystalline TiO₂

A gelatin sample (denoted by G) used in this experiment was made in China from pig bones. The other chemical agents were analytical grade and were obtained from China.

The procedure for preparation of nanocrystalline TiO_2 is indicated in Scheme 1. Note that the modified gelatin (FG1, FG2) was formed by adding formaldehyde to the gelatin solution, according to the proportion HCHO : G = 0.066 mol : 100 gand 0.132 mol : 100 g.

Characterization of Nanocrystalline TiO₂

The prepared nanocrystals of TiO_2 were tested by Rigaku-2400 X-ray diffraction (XRD) (Cu K α) and

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Scheme 1 The procedure for the preparation of nanocrystalline TiO₂.

Hitachi-800 transmission electron microscopy (TEM) instruments.

Molecular Weight $(\overline{M_n})$ Measurement of Three Dispersers

The M_n for G was calculated, and it was estimated for FG1 and FG2 from the following equation¹⁰:

$$[\eta] = 1.66 \bar{M}_n^{0.885} \,\mathrm{mL} \cdot \mathrm{g}^{-1}$$

The intrinsic viscosities were determined in water at 35°C with an Ubbelohde viscosimeter.

Gel Characterization

For comparison, a white powder sample (TN) was obtained by evaporating the $Ti(NO_3)_4$ solution. The TN is the medium in the complex gel. The raw gelatin (G), TN, and the complex gel consisting of G and TN were heated at 130°C for 1 h and then cooled under a vacuum. In addition, the gel was also heated at 180°C for 0.5 h and treated by vacuum cooling. These four samples were tested by a Bruker Vector-22 Fourier transform IR (FTIR) spectroscope.

RESULTS AND DISCUSSION

Physical Properties of Nanocrystalline TiO₂

The XRD measurement indicated the crystal system of most of the TiO_2 powders prepared with G, FG1, and FG2 belongs to anatase; but the powders calcined at 900°C showed the appearance of rutile. An example is given in Figure 1.

The average particle size (D, in nanometers) was first determined from the XRD pattern parameters of the TiO₂ powders according to the Scherrer equation,¹¹

$$D = \frac{k\lambda}{\beta\,\cos\,\theta}$$

where k is a constant equal to 0.89, λ is the X-ray wavelength equal to 0.154 nm, β is the full width at half-maximum (FWHM), and θ is the half-diffraction angle. The XRD patterns of three TiO₂ samples are shown in Figure 2 and the whole results by calculation are shown in Figure 3. It can be seen that the particle size grows with increasing calcining temperature and at the same calcining temperature the particle size has a regular order [Fig. 3(a) < (b) < (c)]. Similar results were also obtained with the TEM test. Figure 4



Figure 1 XRD patterns of nanocrystals of TiO_2 prepared with FG2 and calcined at (a) 500°C or (b) 900°C (8°/min scanning rate).

shows the crystal shape and particle size of six TiO_2 samples. It can be seen that the results in Figure 3 were verified and TiO_2 particles prepared with modified gelatin have a more homogeneous distribution than with raw gelatin.

Dispersion Mechanism

The dispersing ability order of FG2 > FG1 > G is given in Figures 3 and 4. The preparation process from precursor to nanocrystal powders can be divided into three stages: precursors \rightarrow sol, sol \rightarrow gel, and gel \rightarrow nanocrystal powders. FTIR spectra were utilized to monitor the structure of the complex gel and its transformation with calcining. The spectra of raw gelatin, medium in gel, and complex gel are plotted in Figure 5 and its key data are listed in Table I. Figure 5(b) shows that the medium in the gel seems to have $TiO(NO_3)_2$. H_2O composition, where Ti^{4+} combines with H_2O by a coordination bond and the band at 1619.8 cm^{-1} results from the bending vibration of the O-H in this coordination water. However, this OH band shifted to 1655.9 cm^{-1} in the complex gel [Fig. 5(c)], because the $TiO(NO_3)_2 \cdot H_2O$ links with peptide chains of the gelatin by hydrogen bonding. Thus, the mechanism of gelatin dis-



Figure 2 XRD patterns of nanocystals of TiO_2 calcined at 500°C and treated with (a) FG2, (b) FG1, or (c) G (0.25°/min scanning rate).



Figure 3 Average particle size, determined by FWHM from XRD patterns using the Scherrer equation, of the TiO_2 samples prepared with (a) FG2, (b) FG1, or (c) G.

persed $TiO(NO_3)_2 \cdot H_2O$ can be expressed by Scheme 2.

The dispersion mechanism of the sol-gel method for nanocrystalline TiO₂ preparation in protic solvents is considered to be Ti⁴⁺ multicoordinated to hydroxy groups (OH) of the solvent (e.g., CH₃COOH and CH₃CH₂OH).¹² However, there are hardly any groups in the gelatin that are capable of multicoordination to Ti⁴⁺. Although there are a small number of OH as the residual groups of the hydroxyproline section in peptide chains,¹ the separation between OH groups does not allow for multicoordination with Ti^{4+} . So the hydrogen bond is the main force linking $TiO(NO_3)_2 \cdot H_2O$ and gelatin. It can be seen in Figure 5(d) that with increasing the calcining temperature to 180°C, the decomposition of $TiO(NO_3)_2 \cdot H_2O$ and gelatin in the complex gel has occurred. The $TiO(NO_3)_2 \cdot H_2O$ disappears more quickly and the other complicated chemical reactions have begun. The molecular weight measurements indicate that the $\overline{M_n}$ of modified gelatin samples has been changed from 1.0×10^5 for raw gelatin to $6.0 imes 10^5$ for FG1 and $8.0 imes 10^5$ for FG2. This is attributed to the gelatin peptide chains crosslinking with formaldehyde to form a network structure. A previous study¹³ found that only some residual groups of gelatin peptide chains (e.g., -NH2 in lysine and arginine sec-



Figure 4 TEM images of nanocrystals of TiO_2 calcined at 600°C and treated with (a) FG2 (0.5 cm, 100 nm), (b) FG1 (0.8 cm, 100 nm), or (c) G (0.8 cm, 100 nm) and calcined at 800°C and treated with (d) FG2 (0.6 cm, 100 nm), (e) FG1 (0.7 cm, 100 nm), or (f) G (0.4 cm, 100 nm).

tions) can crosslink with formaldehyde and the —C(O)—NH— structure in gelatin cannot be related to this kind of chemical reaction. Thus, the mechanism of FG1 and FG2 to disperse $TiO(NO_3)_2 \cdot H_2O$ is the same as that expressed in Scheme 2. The modified gelatin, which has more excellent dispersing ability than raw gelatin, may depend on the network density in the gelatin. This network structure is of benefit to forming the hydrogen bond between gelatin and $TiO(NO_3)_2 \cdot H_2O$, thereby enhancing this supramolecular force.

CONCLUSION

It is implied that the gel method of gelatin and gelatin modified with formaldehyde is a convenient way for obtaining nanocrystals of TiO_2 . In particular, the nanocrystalline TiO_2 prepared with modified gelatin samples had a smaller particle size and a more homogenous particle distribution than TiO_2 nanocrystals prepared with raw gelatin. The raw materials used in this preparation method can be obtained more easily than titanium butoxide or other organic solutions containing Ti^{4+} .



Wavenumber in cm⁻¹

Figure 5 FTIR spectra of three samples treated at 130° C for 1 h: (a) G, (b) TiO(NO₃)₂. $\rm H_2O,$ and (c) complex gel; and (d) the complex gel treated at 180°C for 0.5 h.

Table I Key Wave Number (cm⁻¹) of FTIR **Spectra from Figure 5**

Sample		${ m H_2O}$ Coordination	NO_3^-	Ti—O
а	1657.4, 1546.9	/	/	/
b	/	1619.8	1383.5	800-400
c d	$1657.4,^{\rm a}1551.5\\1657.4,^{\rm a}1541.7$	$1655.9 \\ 1670.5$	$\begin{array}{c} 1384.1\\ 1384.6\end{array}$	800-400 697.8^{b}

^a The band of C=O is weak and covered by a strong band of O—H. ^b Being suggested.



Scheme 2 The mechanism of gelatin dispersed $TiO(NO_3)_2 \cdot H_2O.$

2574 LIU ET AL.

REFERENCES

- 1. Veis, A. The Macromolecular Chemistry of Gelatin; Academic Press: New York, 1964.
- 2. Thiry, H. J Photogr Sci 1987, 35, 150.
- Lin, W.; Wei, C.; Krishnan, R. J Electrochem Soc 1993, 140, 2477.
- Fukushima, K.; Yamada, I. J Appl Phys 1989, 65, 619.
- 5. Haro–Paniatowski, E.; Rodriguez–Talavera, R. J Mater Res 1994, 9, 2102.

- Birkefeld, L. D.; Azad, A. M.; Akbor, S. A. J Am Ceram Soc 1992, 75, 2964.
- 7. Lawandy, N. M. Nature 1994, 368, 436.
- 8. Sakka, S. Am Ceram Soc Bull 1985, 64, 1463.
- 9. Yutakal, O.; Hisao, S. J Am Ceram Soc 1996, 79, 825.
- 10. Brandrup, J.; Immergut, E. H. Polymer Handbook; John Wiley & Sons: London, 1975; Chapter IV.
- Xiong, G.; Zhi, Z. L.; Wang, X. J Mater Sci Lett 1997, 16, 1064.
- Doeff, S.; Henry, M.; Sanchez, C. J Noncryst Solid 1987, 89, 207.
- 13. Albert, K. Z Naturforsch 1986, 41B, 351.