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Preparation of nanosized titania powder via the controlled hydrolysis of titanium alkoxide

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By controlling the hydrolysis of titanium butoxide, followed with or without an ethanol washing process, the preparation of nanoscale titania powder was studied in detail. The characteristics of different powders produced by the direct precipitation (without an ethanol wash) and ethanol wash processes were studied by X-ray diffraction, transmission electron microscopy, BET, thermogravimetry and differential thermal analysis techniques. By comparison, it was found that both the direct precipitation and ethanol wash methods can obtain slightly agglomerated nanoscale titania powders of less than 15 nm, but the ethanol wash can further reduce the agglomeration. The particle sizes of titania powders can be modified while still retaining the anatase structure.

1. Introduction

Nanosized titania powder can be used to serve as pigments, adsorbents, catalytic supports and sensor materials [1–3]. Recently, nanosized titania powders have also been widely used for sintering process and for studying the profound mechanical and superplastic properties of nanoceramics [4]. In all these applications, the morphology, structure, size and size distribution of the powder are the main factors that can control the performance in these usages.

The preparation of titania powder mainly includes physical and wet-chemical methods. The method of inert-gas condensation of metal vapours followed by post-oxidation of the nanosized clusters can be employed to fabricate nanoscale powder with a clean surface [5, 6]. But due to the simplicity, low cost and easy extension of production, precipitation from a liquid precursor is still the most popular technique to produce oxide powder at the micro- or nanometer scale [7–9]. One disadvantage of this chemical method is that it is difficult to avoid the hard agglomeration of the powder which will affect directly the compact density and microstructure of the required materials. To minimize the hard agglomeration, ethanol wash and *n*-butanol azeotropic distillation processes have been used to replace the adsorbed and hydrated water within the precipitate and the hydroxyl bond formed on the surface of the precipitated colloid particle [10, 11].

In the present work, the preparation of nanosized titania powder was studied in detail by controlling the hydrolysis of titanium butoxide, followed by an ethanol wash process. The characteristic of the powders prepared via the ethanol wash and direct precipitation (without ethanol wash) methods were studied and compared by using BET, thermogravimetry-differential thermal analysis (TG–DTA), transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques.

2. Experimental procedure

In our study, titanium butoxide (of chemical purity) was used as precursor. All the experiments, including the hydrolysis process, were performed under atmospheric conditions. Owing to its ease of hydrolysis, $Ti(OC_4H_9)_4$ was first dissolved in anhydrous ethanol to form a 10% solution by volume before hydrolysis, so that the hydrolysis rate could be controlled to form well-dispersed colloid particles and diminish hard agglomeration. The experimental flow chart is illustrated in Fig. 1.

As shown in this figure, the $Ti(OC_4H_9)_4$ solution was dripped into the vigorously-stirred distilled water

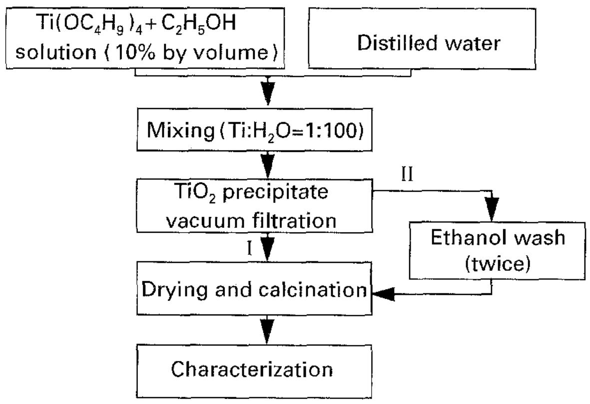

Figure 1 The flow chart for the preparation of nanosized TiO_2 powder. I, direct precipitation; II, ethanol wash.

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and the overall Ti/H_2O molar ratio was 1:100. After vacuum filtering, the resulting precipitate was either directly dried at 80 °C (direct precipitation, i.e. via process I), or washed twice with ethanol and then dried at 80 °C (via process II). The titania powders prepared via direct precipitation and ethanol wash are denoted powders I and II, respectively. Their characteristics were determined as follows. Thermogravimetric and differential thermal analysis (TG–DTA) was employed to determine the suitable calcining temperature. X-ray line broading (XLB) and BET techniques were used to measure the particle size. The powder phase was obtained by the X-ray diffraction method (XRD). Their morphologies were directly observed by transmission electron microscopy (TEM).

3. Results and discussion

3.1. Characteristics of the dried powders

Fig. 2 shows the morphologies of the as-prepared dry powders and their electron diffraction patterns. As shown in Fig. 2a, it can be clearly seen that powder I is composed of tiny particles, which are found to be about 6 nm diameter using the XLB method (as shown in Table I). The electron diffraction pattern (in Fig. 2b) indicates that the powder has already become crystalline. In contrast, after the ethanol wash process, the fringe of powder II cannot be clearly seen as shown in Fig. 2c, and the image resolution is greatly reduced. The electron diffraction pattern shows that the particles have almost completely changed to amorphous structure (in Fig. 2d). The X-ray diffraction patterns of powders I and II also illustrate that powder I is of anatase structure while powder II is amorphous (shown in Fig. 3). So during the preparation processing, the ethanol wash process has greatly changed the structure of the colloid precipitate, and after drying, the lattice of powder II is largely distorted to become amorphous.

3.2. TG–DTA analysis of the dried powders

The results of TG and DTA analysis of the dried powders I and II are shown in Fig. 4. For powder I, the maximum weight loss is about 13.7%, and an endothermal peak exists at about 120 °C, which is mainly caused by the desorption of physically adsorbed water. In contrast, the maximum weight loss of powder II is much larger – finally up to 28% of the weight is lost. Apart from an endothermic peak at about 145 °C, which is similar to powder I, two high exothermic peaks exist between 270 and 400 °C, which could probably be attributed to the decomposition or pyrolysis of the organic residues. It can be concluded that there is much more organic residue in the ethanol washed powder than in the directly precipitated powder.

From Fig. 4, it can also be seen that after heating at 450 °C, these two powders approximately begin to show no additional weight loss. The minimum calcining temperature can be selected at 450 °C. In our experiment, after calcining at 450 °C for 1 h, powders I and II have already turned to white.

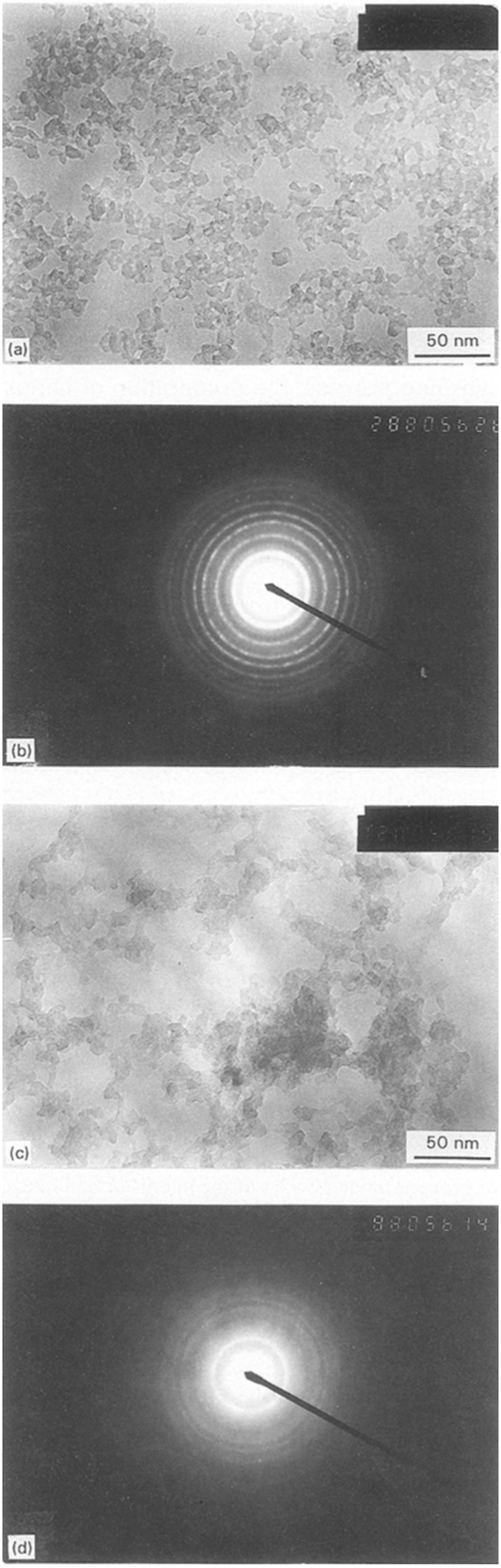

Figure 2 Transmission electron micrographs and electronic diffraction patterns of the as-prepared dry powders: (a, b) powder I; (c, d) powder II.

TABLE I Characteristics of powders I and II before and after calcination

	After-drying		Calcined at 450 °C for 2 hours				
	Phase	Size (XLB) (nm)	Phase	Size (XLB) (nm)	BET ($m^2 g^{-1}$)	Size (BET), D(nm)	Mean agglomeration factor, D^3/d^3
Powder I	Anatase	6.3	Anatase	10.7	108.91	14.1	2.3
Powder II	Amorphous	–	Anatase	14.4	95.7	16.1	1.4

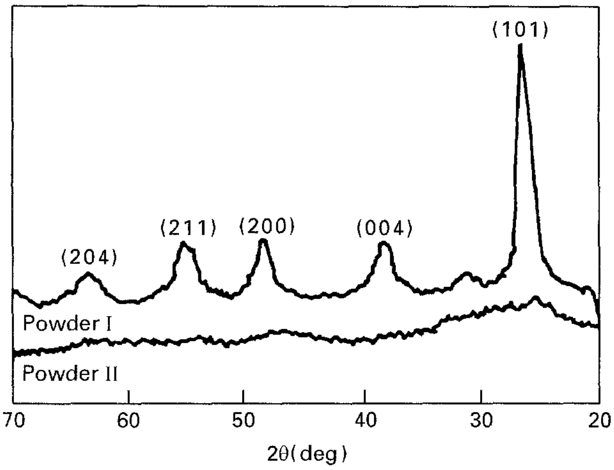

Figure 3 X-ray diffraction patterns of the as-prepared dry powders I and II.

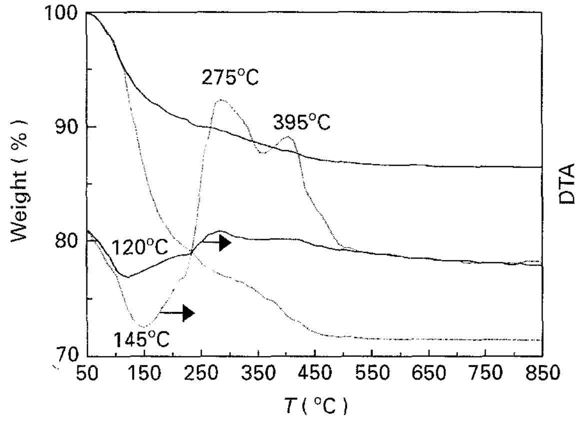

Figure 4 TG and DTA curves of the as-prepared dry titania powders: powders (——) I and (– – –) II.

3.3. Characteristics of the calcined powders

The particle sizes of the two powders calcined at 450 °C for 2 hours were determined by XLB and BET methods, and the results are shown in Table I. The phases of the calcined powders as well as the as-prepared powders are also listed in Table I. Powders I and II are both loose, white powders, and have large nitrogen adsorption specific surface areas up to 108.91 and 95.7 $m^2 g^{-1}$, respectively. Using XLB method, the crystallite size of the calcined powder I was found to be less than 11 nm, while the size of powder II was about 14–15 nm. Commonly, the size determined by XLB can be regarded as the size of the primary crystallites, d, and size deduced from BET can be used as the mean agglomerated particles, D, so D^3/d^3 can be regarded as the mean agglomeration factor of the powder. As shown in the table, the agglomeration of the two powders is quite small, and the agglomeration of powder II is smaller than that of powder I. Therefore, the ethanol wash process does have a useful effect in reducing the agglomeration of titania powders. This is different from the results given by Hague and Mayo [7], which indicated that the ethanol rinse process cannot improve the agglomeration status during the preparation of nanocrystalline titania.

Usually, the hydrolysed titania has been described to precipitate as the hydrous oxide $TiO_2 \cdot nH_2O$ [12]. It is most likely that when the precipitate is washed with ethanol, the ethanol molecule does not only replace the adsorbed water on the surfaces of colloids, but also enters the lattice of the colloid particles to replace the hydrated water, which can be deduced from the large weight loss during TG analysis, so this

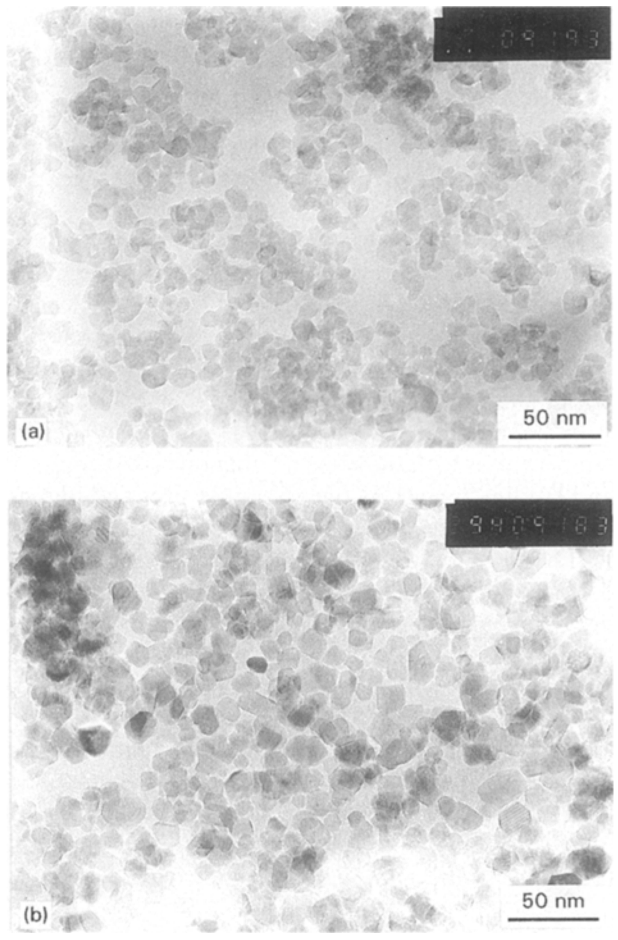

Figure 5 Transmission electron micrographs of titania powders after calcining at 450 °C: (a) powder I, (b) powder II.

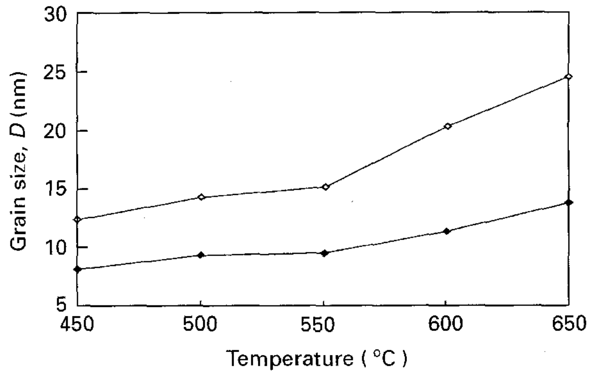

Figure 6 Grain-size dependence of powders (◆) I and (◇) II on calcining temperatures (heating rate 10 °C min^{-1}, holding time 1 h).

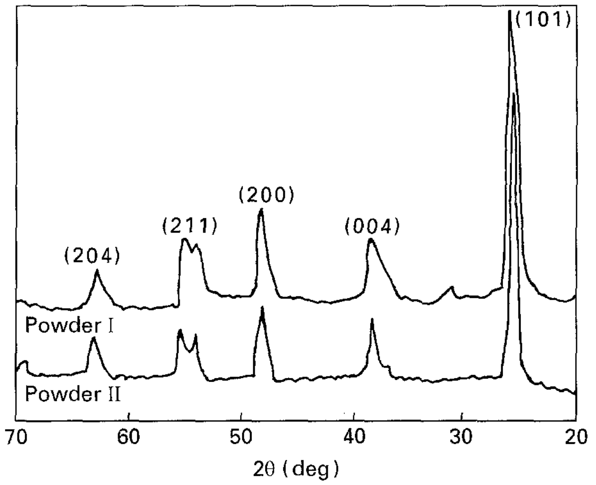

Figure 7 The XRD patterns of the titania powders I and II after calcining at 650 °C.

process can reduce the hard agglomeration. In addition, as ethanol molecules are larger than H_2O molecules, the lattice of the dry powders is then greatly distorted by the adsorbed ethanol molecules.

Fig. 5 shows transmission electron micrographs of the particle morphologies of the calcined powders. It can be clearly seen that powder II is more easily dispersed than powder I, which also means that the ethanol wash has a positive effect of reducing hard agglomerates.

By calcining powders I and II at different higher temperatures with the same heating rate (10 °C min^{-1}) and holding time (1 h), the crystallite sizes and phases of powders I and II are also obtained with XLB and XRD, respectively. As shown in Fig. 6, when the powders are calcined between 450 and 550 °C, the crystallite growth rate of powder II is approximately equal to that of powder I, while when calcined between 550 and 650 °C, the growth rate of powder II is greater than that of powder I. The different growth rates of those two powders at the same temperature might correlate with the degree of perfection of their structure. The lattice of powder I might be more perfect than that of powder II, due to the lattice distortion of powder II, as the lattice of the as-prepared dry powder II is largely distorted by the ethanol wash process and the structure is amorphous. From this figure, it can also be shown that by calcining at different temperature, the particle size can be modified to a certain degree (8–15 nm for powder I and 12–50 nm for powder II). The structures of powders I and II when calcined up to 650 °C are still anatase, which is shown by the XRD patterns in Fig. 7.

4. Conclusions

By controlling the hydrolysis of titanium butoxide, nanoscale titania powder can be successfully prepared. The characteristics of different powders via direct precipitation (powder I) and ethanol wash (powder II) methods are summarized as follows.

1. The as-prepared dry powder I is of anatase structure and with a size of 5–6 nm, while powder II is amorphous. On calcining at 450 °C, those two powders show approximately no further weight loss.
2. On calcining at 450 °C, nanoscale titania powders of anatase structure with a size < 15 nm can be prepared by those methods. The ethanol wash process can further reduce the agglomeration factor of the titania powders if compared with the direct precipitation method.
3. The particle size of titania powders can be modified to a certain extent by calcining at different temperatures. In our experiment, the particle sizes of powders I and II can change from 8–15 nm to 14–25 nm, respectively, while retaining anatase structure.

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