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Formation of the rutile TiO_2 under ultrasonic irradiation

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Ultrasound irradiation has been used in the field of materials science in recent years. The chemical effects of sonication arise from acoustic cavitation, namely the formation, growth, and implosive collapse of bubbles in a liquid. The collapse of bubbles generates localized hot spots, in which extreme conditions, such as the transient temperatures of ∼5000 K, pressures of ∼1800 atm, and cooling rates in excess of 10^{10} K/s, can be reached. These extreme conditions have been employed to prepare novel materials with unusual properties [1, 2]. TiO_2 is well-known for its potential applications in photoelectronics, catalysts, semiconductors, and pigments [3]. Studies on the preparation of nanometer TiO_2 are of fundamental importance. Up to now, many methods have been established for the synthesis of TiO_2, such as sol-gel method [4], the hydrothermal technique [5], the reversed micelle method [6], and vapor decomposition of titanium alkyloxides or $TiCl_4$ in oxygen [7]. In the present work, a novel sonochemical method for the preparation of nanometer TiO_2 by using $TiCl_4$ as a precursor is reported.

In a typical preparation, 3 ml $TiCl_4$ was added dropwise to 50 ml deionized water which was kept in an ice bath. Then the sonication was carried out for 3 h employing a direct immersion titanium horn in solution, the temperature of which was controlled at 70 °C through the use of circulating water. The resulting product was separated by centrifugation, washed twice with deionized water and once with ethanol, and dried under vacuum overnight.

The results of X-ray diffraction (XRD) and selected area electron diffraction (SAED) both show that the TiO_2 samples prepared with sonication are crystalline (rutile), as indicated by the presence of crystalline peaks in Fig. 1 and rutile electron diffraction rings in Fig. 2. The X-ray diffraction patterns were indexed on the basis of Joint Commission on Powder Diffraction Standards (JCPDS) data, which indicated that all the peaks correspond to the rutile phase of TiO_2. The titania exhibits six peaks with corresponding d spacing of 3.247, 2.487, 2.188, 1.6874, 1.4797, and 1.3599 Å, corresponding to the (110), (101), (111), (211), (002), and (301) reflection of rutile TiO_2, respectively. An average crystalline size of about 10.2 nm was estimated from the (110) peak width.

Transmission electron microscopy (Fig. 2) of TiO_2 reveals the nature of the particulates. The powder is an agglomerate of columnar particles, with an average size of about 9–13 nm, which are linked together.

Fig. 3 gives the results of thermal analysis. The differential thermal analysis (DTA) curve of the sample shows only one small endothermic peak at 99.3 °C due to the desorption of absorbed water, and there are no exothermic peaks in the temperature range 50 to 800 °C, which indicates no crystallinzation or phase transition occurred in this temperature range and that the as-prepared sample was crystalline. The thermogravimetry (TG) curve shows a weight loss from 50 to

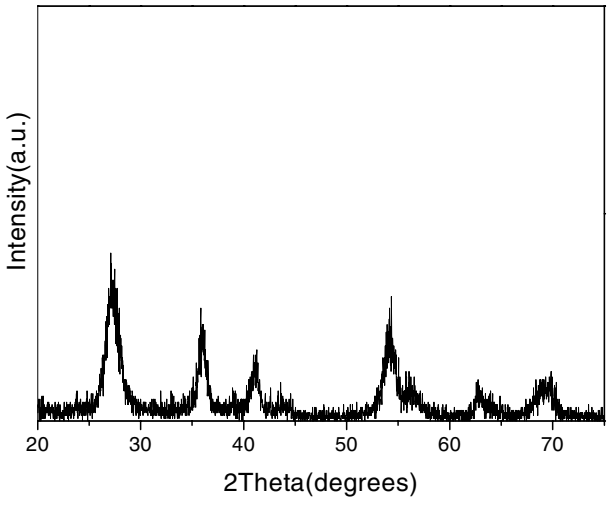

Figure 1 XRD powder patterns of TiO_2.

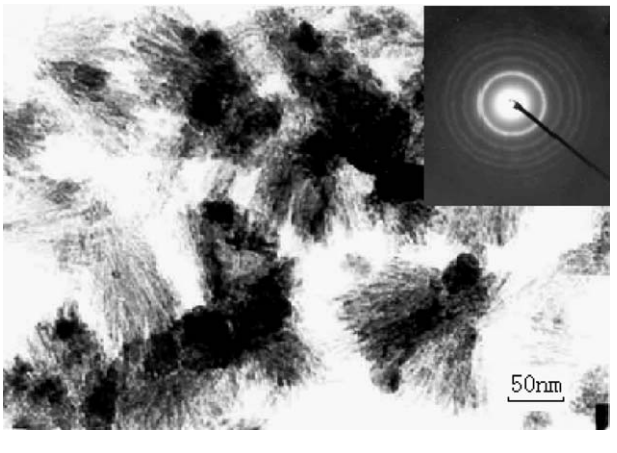

Figure 2 TEM image of TiO_2 (inset: associated SAED pattern).

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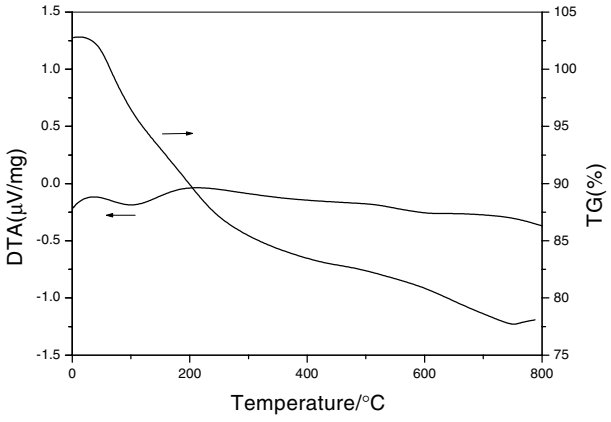

Figure 3 TG-DTA curves of TiO_2.

800 °C, which can be attributed to the loss of residual organic impurities, water and Cl^- in samples.

In the aqueous solution of $TiCl_4$, titanium ions exist in the form of various coordination monomers or polymers, which are the products of hydrolysis and condensation reaction of titanium ions in solution. The structure of the hydrolysates is related to the pH value of the hydrolysis medium. In strong acidic solution, the monomers are connected to each other by olation to form a polymer. This kind of olation reaction proceeds in the equatorial plane, forming a linear chain polymer, which is only structurally compatible with rutile [8, 9]. Ultrasonic cavitation can accelerate the interaction of the hydrolysates, the loss of hydroxyl or water, and the formation of TiO_6 octahedra. The nuclei, which can form nanometer particles with the structure of rutile, would be obtained when the concentration of octahedra achieved supersaturation.

In conclusion, a new sonochemical method to prepare crystalline rutile nanometer-scale TiO_2 has been established.

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