

Sonochemical preparation of TiO₂ nanoparticles

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Abstract

TiO₂ nanoparticles with mean diameter of about 20 nm, average crystallite size of 15 nm and BET specific surface area of 78.88 m²/g, were prepared through a simple sonochemical method and initial treatment in 10 M NaOH aqueous solution. XRD results exhibited that the obtained nanoparticles composed of pure rutile phase. During the initial treatment with NaOH aqueous solution, the Ti–O–Ti bonds in the TiO₆ octahedra structure of the raw material were broken, and new octahedras formed after ultrasonic irradiation. It is supposed that edge sharing was favored during ultrasonic treatment, leading to formation of the rutile nanoparticles.

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1. Introduction

Titania (TiO₂) has three main polymorphs e.g. anatase, rutile and brookite, which rutile is the most thermodynamically stable phase [1]. Due to its chemical stability [2], biocompatibility [3], photocatalytic reactivity [4], strong oxidizing power [5] and low cost [6], titania has extensive applications as photocatalysts [7], gas sensors [8], self cleaning surfaces [4], water and air purification components [9] and pigments [10]. In addition, rutile structure has a band gap energy of about 3.0 eV [11], high dielectric constant, electrical resistivity [12] and refractive index [6] which makes it a relevant choice for dye-sensitized solar cells (DSCs) [6] and capacitors [13].

Among various methods developed for synthesizing titania nanostructures, chemical processing routes based on hydrothermal treatment of TiO₂ raw powder with 5–10 M NaOH, introduced by Kasuga et al. [14], has attracted great attention for preparing titania nanostructures such as nanotubes [15] and nanowires [16].

Controversial mechanisms have been proposed for the formation of these 1D nanostructures [14–20]. Kasuga et al. [17], believed that the formation of titania nanotubes is related to the final treatment with HCl aqueous solution and distilled water. While Du et al. [18], showed that titania nanotubes were

formed during treatment with NaOH aqueous solution. Yao et al. [19] proposed a mechanism based on TEM observations for the formation of titania nanotubes during treatment with NaOH aqueous solution at temperatures above 90 °C.

Zhu et al. [20] utilized ultrasonic irradiation instead of conventional hydrothermal processes for preparing titania nanotubes and whiskers. They have shown that direct sonication of the TiO₂ raw powder and NaOH aqueous solution mixture at high sonicating power led to the formation of titania whiskers while lower powers together with subsequent thermal treatment resulted in the nanotubes formation. Here we show that the dissolution of the TiO₂ raw powder in NaOH solution before ultrasonic treatment resulted in the formation of titania nanopowders instead of nanotubes.

2. Experimental

In a typical experiment, 0.5 g TiO₂ pellets were dissolved into 30 ml NaOH solution (10 M) under vigorous stirring at room temperature for 2 h. Then the yellowish solution was irradiated in an ultrasonic bath (Power Sonic 405, 40 kHz and 350 W) for 2 h in ambient temperature. The resultant precipitates were then centrifuged, washed and decanted with deionized water several times and dried at 60 °C for 24 h. The obtained white powders were characterized with scanning electron microscopy (SEM, Philips XL30), transmission electron microscopy (FEG-STEM, Philips CM200) and X-ray

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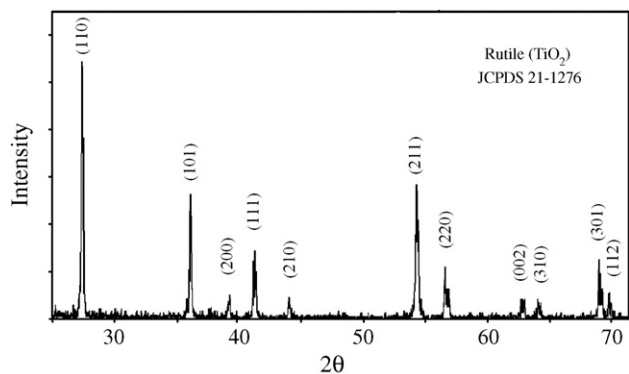


Fig. 1. XRD pattern of TiO_2 nanoparticles. All the peaks are indexed as JCPDS 21–1276 for rutile structure.

diffraction analysis (XRD, Philips X'Pert diffractometer). The specific surface area of the synthesized material was determined by analyzing the N_2 adsorption isotherm obtained at 77 K using Micromeritics Gemini 2375 equipment. The powders were degassed at 200 °C and 10^{-6} Torr for 2 h prior to the measurement. The surface area of the powder was calculated with the Brunauer–Emmett–Teller (BET) equation.

3. Results and discussion

Rutile (TiO_2) has tetragonal symmetry (simple tetragonal) and belongs to D_{4h}^{19} - I_4 /amd space group with lattice constants of $a = 0.3733$ nm, $c = 0.937$ nm and $c/a = 2.51$ [21]. The crystal structure of the obtained powder was characterized by powder X-ray diffraction (XRD) analysis. As it is indicated in Fig. 1, all the diffraction peaks can be indexed as the pure rutile phase for TiO_2 according to the JCPDS card No. 21–1276. No characteristic peak of anatase or brookite phases or other impurities such as Na_2TiO_3 were detected, indicating the high purity of the obtained powder.

The average crystallite size of the particles were determined to be about 15 nm utilizing Sherrer formula ($d = k\lambda / B\cos\theta$, where d is the mean crystallite size of the powder, λ is the wavelength of $\text{CuK}\alpha$, 1.54056 Å, B is the full width at half maximum (FWHM) intensity of the peak in radian, θ is Bragg's diffraction angle and k is a constant usually equal to ~ 0.9 [22]).

There are controversial reports on obtaining crystalline powders by ultrasonic treatment. While there are some reports on preparing

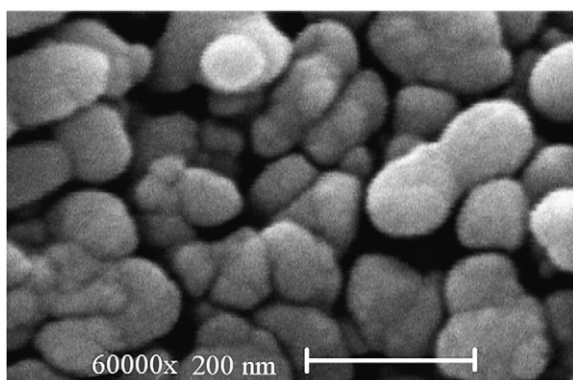


Fig. 2. SEM image of nanostructure TiO_2 nanoparticles.

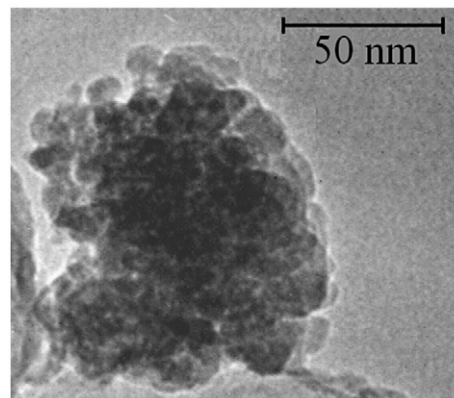


Fig. 3. TEM image of TiO_2 nanoparticles which are agglomerated due to ultrasonic shock waves.

amorphous materials via sonochemical methods [23,24], nanocrystalline powders have been obtained by various researchers [9,12]. Here, ultrasonic irradiation culminated in formation of nanostructured rutile phase with high crystallinity which is usually difficult to be obtained at low temperatures [1,10].

The morphology of the powder is exhibited in the scanning electron micrograph. SEM image (Fig. 2) revealed the presence of spherical, peanut-like and irregular shapes with average diameter of about 120 nm. The observed peanut-like particles approved the collision between the particles due to the shock waves produced via ultrasonic irradiation [23].

TEM investigations (Fig. 3) exhibit the rutile nanoparticles with an average particle size of ~ 20 nm. It is obvious that these primary nanoparticles formed larger particles due to collisions caused by ultrasonic shock waves. These secondary particles formed morphologies observed in SEM images (Fig. 2). Measuring the surface area of TiO_2 nanoparticles via nitrogen adsorption by Brunauer–Emmett–Teller (BET) method revealed a specific surface area of $78.88 \text{ m}^2/\text{g}$ which seems relevant for surface area dependent applications such as photocatalysis.

A possible formation mechanism of these nanoparticles can be as follows: during the initial treatment with NaOH aqueous solution, the Ti–O–Ti bonds in the TiO_6 octahedra structure of the raw material are broken, and Ti–O–Na and Ti–OH bonds are formed [17]. As ultrasonic irradiation resulted in formation of hydroxyl (OH^\bullet) radicals [24], it is suggested that Ti–O–Na and Ti–OH bonds are react with hydroxyl groups to form new Ti–O–Ti bonds and TiO_6 octahedras. Depending on face- or edge-sharing rearrangement of octahedras, the anatase or the rutile phases form, respectively [9,11]. Totally, it can be concluded that edge sharing is favored during ultrasonic treatment leading to formation of the rutile nanoparticles.

4. Conclusion

Rutile nanoparticles with average crystallite size of about 15 nm, mean particle size of ~ 20 nm and specific surface area of $78.88 \text{ m}^2/\text{g}$, were prepared through a sonochemical method. It has been shown that solution treatment before ultrasonic irradiation culminated in the formation of rutile nanoparticles.

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