

Experimental variables in the synthesis of anatase phase TiO₂ nanoparticles

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Abstract – Fine crystalline nanoparticles of pure anatase titanium dioxide (TiO₂) (average crystallite size ~ 5 – 156 nm) with a high surface area (~ 192 m²/g) were synthesized in the pure anatase phase, either with or without H₂O₂, using isopropanol (IP) or acetic acid (HAc) as a reaction medium. The synthesized powder was characterized by using XRD, BET surface area and STEM. The product that was obtained differed according to the reaction medium used.

Titanium dioxide (TiO₂) is a very useful semiconducting transition metal oxide material and exhibits unique characteristics such as low cost, easy handling and nontoxicity, and resistance to photochemical and chemical erosion [1]. The properties of TiO₂ are significantly dependent on the crystalline phase, i.e., anatase, rutile, or brookite. In this work, we report the preparation and characterization of nanocrystalline TiO₂ materials with different phases synthesized by using different solvents as reaction medium at 100 °C/48h.

Analytical-grade reagents were used as supplied without further purification. Titania nanoparticles (TiO₂) were synthesized using three methods: *Method A*: by mixing 2.5 mL of titanium isopropoxide (TIP, Ti[OCH(CH₃)₂]₄, > 99%, Acros Organics) in 50 mL of isopropanol (IP, 99.5%, Vetec) or Acetic Acid (HAc, 99.5%, Vetec). *Method B*: by mixing 2.5 mL of titanium isopropoxide and 8 mL of hydrogen peroxide (H₂O₂ 10% V/V, > 99%, Acros Organics), was dissolved in 50 mL of isopropanol. *Method C*: TiO₂ was obtained by mixing 2.5 mL of TIP and 8 mL of H₂O₂, which was dissolved in 50 mL of Acetic Acid. The solution was poured into an autoclavable bottle. The bottle was then placed in a regular laboratory oven at a constant 100 °C for 48 h. A gel was formed and it was hydrolyzed by adding 50 ml of milliQ water. The solutions were poured into an autoclavable bottles. The bottles were then placed in a regular laboratory oven at a constant 100 °C/72h (method A), 48h (method B) and 24h (method C).

Fig. 1(a and b) shows the patterns of X-ray diffraction of the synthesized TiO₂ samples beginning with titanium isopropoxide, then hydrogen peroxide, isopropanol and acetic acid. No peaks corresponding to the rutile or brookite phases were observed, which indicates that the TiO₂ powders obtained had a monophasic anatase structure (PDF #21-1272 anatase TiO₂). The crystal structure of the TiO₂ powders was not affected by changing the reaction medium. The narrow diffraction peaks suggest that the TiO₂ that was obtained was nano sized. TiO₂ obtained without H₂O₂ (Fig. 2) had the same profile as DRX (not shown). The TiO₂ that was obtained was identified as pure anatase TiO₂ and, no peaks corresponding to any other phase were observed, which indicates that the obtained TiO₂ powders also exhibited a monophasic anatase structure.

The morphology and average size of the synthesized pure nanocrystalline anatase TiO₂ as a function of the reaction medium were investigated in detail using electronic microscopy (FEG-STEM). Fig. 1 e 2 shows the STEM micrographs of the anatase TiO₂ samples synthesized with hydrogen peroxide in isopropanol (~ 7 nm and 192 m².g⁻¹) as reaction medium for a constant reaction time (48h) (Fig. 1) and without H₂O₂ (Fig. 2). The STEM images of all the samples show an irregular spherical shape (Fig 1) and rods shape (Fig. 2). The diameters of the rods in the sample obtained without H₂O₂ (148 m².g⁻¹) are much smaller, reaching a maximum of about 27 nm and 156 nm long, as shown in Fig. 2.

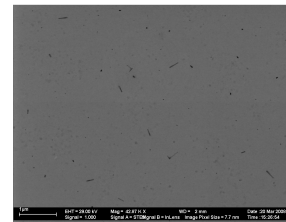
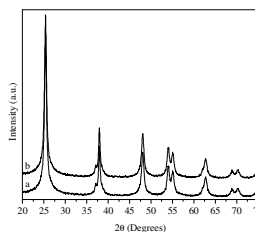
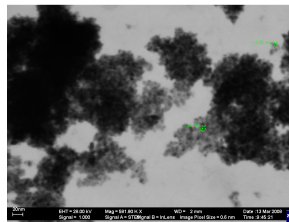
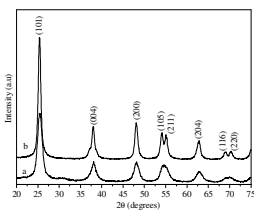


Figure 1: XRD patterns of TiO₂ obtained in the presence of H₂O₂ using isopropanol (a) or acetic acid (b) as reaction medium and SEM images of TiO₂ samples obtained in the presence of H₂O₂ using isopropanol as reaction medium.

Figure 2: XRD patterns of TiO₂ obtained in absence of H₂O₂ using isopropanol (a) or acetic acid (b) as reaction medium and SEM images of TiO₂ samples obtained in absence of H₂O₂ using isopropanol as reaction medium.

References

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