

Enhanced reactivity of peroxy-modified surface of titanium dioxide nanoparticles used to synthesize ultrafine bismuth titanate powders at lower temperatures

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ABSTRACT

Bismuth titanate with sillenite structure ($\text{Bi}_{12}\text{TiO}_{20}$) was prepared at lower temperatures and shorter times using a modified oxidant peroxide method (OPM). $\text{Bi}_{12}\text{TiO}_{20}$ was synthesized utilizing commercial Bi_2O_3 and reactive titanium dioxide nanoparticles having peroxy-modified surfaces. Rather than depending on particle size, the reaction mechanism is related to the highly exothermic decomposition of peroxy groups, regardless the titanium source used, which locally releases a large amount of energy that can accelerate the reaction, similar to self-propagating high temperature routes (SHS).

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1. Introduction

There is a growing need for faster and more efficient methods for synthesizing technologically important materials. In the case of nanomaterials, their physical and chemical properties are dependent on their composition and morphology [1], which makes the synthetic route a critical decision. In this context, wet-chemical routes are superior to traditional solid-state reactions [2–4]. Unfortunately, these wet methods are tedious, time consuming and have low batch yields. On the other hand, the synthesis of multi-component oxides through the simple heating of a mixture of oxides or carbonates require additional treatment at high temperatures for long periods to overcome kinetic barriers [5,6], which usually results in large particles of irregular shape, and secondary phases in some instances [7–9]. To solve this problem, new approaches have been proposed that combine the robustness of solid-state reactions with the chemical design of wet-chemical routes, with special attention being paid to self-propagating high temperature routes (SHS) [6,10–14], partial oxalate methods [15], and the oxidant peroxide method (OPM) [4,16].

Bismuth titanates with different composition and structures

have attracted considerable interest due their excellent optical, electrical and catalytic properties [17]. For instance, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has potential use in photocatalysis [18] and is a promising ferroelectric material for high-temperature applications [19], while nanostructured $\text{Bi}_{12}\text{TiO}_{20}$ shows superior photocatalytic performance [20–22].

In this study, we prepared pure $\text{Bi}_{12}\text{TiO}_{20}$ nanoparticles (referred to as BT) as a model compound to evaluate this new OPM approach, which begins with the synthesis of reactive nanoparticles of titanium dioxide modified with peroxy groups on the surface using titanium isopropoxide or titanium metal as precursor. In a second step, these reactive nanoparticles were mixed with commercial bismuth oxide, resulting in single-phase BT at lower temperatures and shorter reaction times than conventional solid-state reactions.

2. Materials and method

2.1. Synthesis of reactive titanium dioxide

Titanium dioxide nanoparticles with peroxy-modified surfaces were synthesized from a yellow gel obtained by heating solutions of peroxy complexes of titanium. In a typical procedure, 250 mg of titanium metal (98% Aldrich, USA) or 5 mL of titanium

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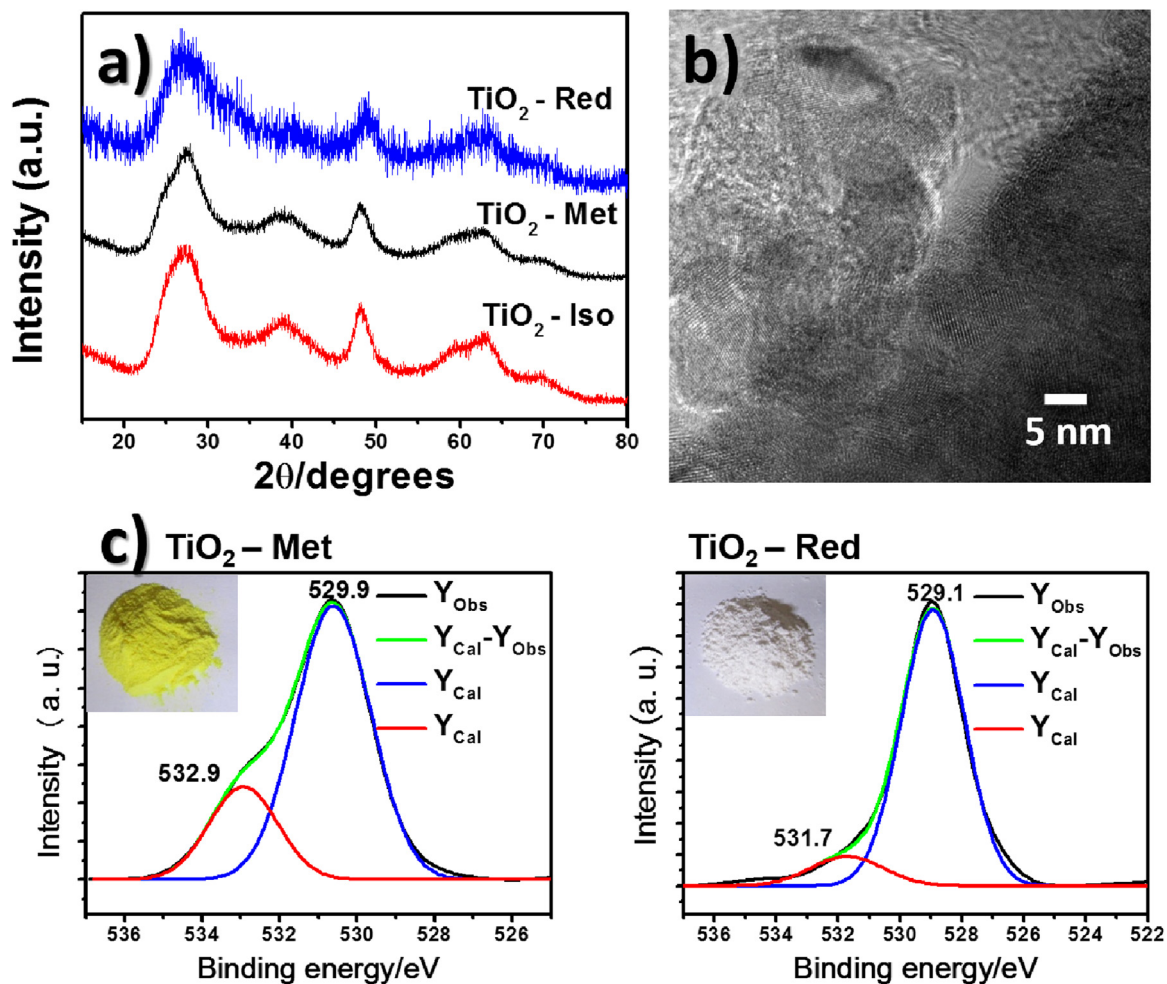


Fig. 1. (a) XRD patterns of TiO₂-Met, TiO₂-Iso and TiO₂-Red reactive precursors, in which crystalline structure and particle size were maintained even after removing the peroxy groups from the surface using H₂. (b) TEM image 5 nm TiO₂-Iso crystalline particles, and (c) XPS profiles of O1s region of TiO₂-Met and TiO₂-Red showing the elimination of peroxy groups by H₂ treatment.

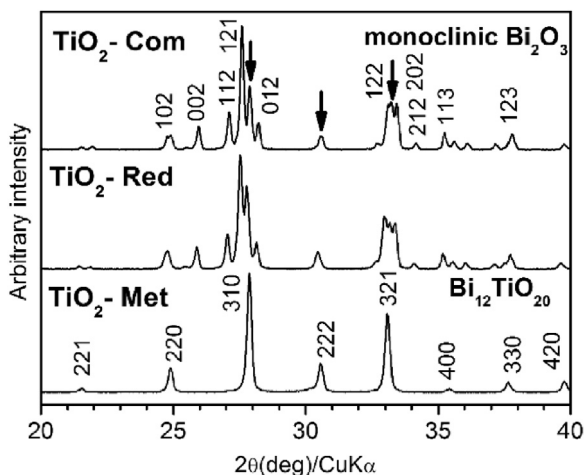


Fig. 2. XRD patterns of three different mixtures of Bi₂O₃ and titanium precursors (TiO₂-Met, TiO₂-Red and TiO₂-Com) calcined at 600 °C for 1 h. Note the absence of any secondary phases in the TiO₂-Met pattern and the presence of unreacted Bi₂O₃ in the TiO₂-Com and TiO₂-Red patterns. Arrows in the pattern of TiO₂-Com indicate the presence of Bi₁₂TiO₂₀.

isopropoxide (97% Aldrich, USA) were added to 100 mL of an aqueous solution of hydrogen peroxide (60 mL, 30% Synth, Brazil) and ammonia (40 mL, 28% Synth Brazil). This mixture was left in an ice-water cooling bath until complete dissolution of the

titanium precursors (i.e. several hours for the metal and a few minutes for the isopropoxide), which resulted in a transparent yellow aqueous solution of the soluble peroxytitanate ion [Ti(OH)₃O₂]⁻ [4,16,20]. In order to obtain titanium dioxide nanoparticles covered by peroxy groups, the solutions were heated to 80 °C until a yellow gel formed, and was held at this temperature for several hours to form yellow powders of TiO₂-Met (from titanium metal) or TiO₂-Iso (from titanium isopropoxide). The control material was obtained by heating TiO₂-Met at 250 °C for 30 min under H₂, which resulted in a white powder of titanium dioxide (TiO₂-Red) with reduced surfaces free of peroxy groups, but with the same morphological and structural properties of the original yellow nanoparticles covered with peroxy groups.

2.2. Synthesis of bismuth titanate

Analytical grade Bi₂O₃ (99.99% Aldrich, USA), commercial TiO₂ anatase (99% Alfa Aesar; TiO₂-Com) and the as-prepared TiO₂-Met, TiO₂-Iso, and TiO₂-Red were used to prepare bismuth titanate with a selenite phase structure (Bi₁₂TiO₂₀) through a solid-state reaction. Appropriate amounts of the constituent oxides were weighed and mixed in a conventional ball-mill for 24 h using small zirconia spheres and ethanol as milling media. The slurries were dried at 60 °C and sieved through 120-mesh sieves. The mixtures were calcinated at different temperatures for 1 h at a heating rate of 10 °C min⁻¹ in closed alumina boats.

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