Bismuth titanate nanobelts through a low-temperature nanoscale solid-state reaction

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Abstract

In this study, an effective low-temperature method was developed, for the first time, for the synthesis of bismuth titanate nanobelts by using $Na_2Ti_3O_7$ nanobelts as the reactants and templates. The experimental procedure was based on ion substitution followed by a nanoscale solid-state reaction. In the first step, $Na_2Ti_3O_7$ nanobelts were soaked in a bismuth nitrate solution where ion substitution at the nanobelt surfaces led to the formation of a bismuth compound overlayer. The resulting bismuth-modified nanobelts were then subject to a calcination process at controlled temperatures. At the calcination temperature of 400 °C, the top layer was converted to Bi_2O_3 whereas the interior was converted to $TiO_2(B)$, forming $TiO_2(B)@Bi_2O_3$ core–shell nanobelts. When the calcination temperature was increased to 450 °C, a metastable interphase $Bi_{20}TiO_{32}$ was produced on the nanobelt surface whereas the interior structure remained virtually unchanged, and the nanobelts now exhibited a $TiO_2(B)@Bi_{20}TiO_{32}$ core–shell structure. At calcination temperatures higher than 550 °C, the shell of the nanobelts became $Bi_4Ti_3O_{12}$. At even higher temperatures (600–700 °C), no $TiO_2(B)$ was found and the nanobelts exhibited single-crystalline characteristics that were consistent with those of $Bi_4Ti_3O_{12}$. Such a structural evolution was manifested in X-ray diffraction, Raman and Fourier transform infrared spectroscopic measurements, and scanning electron microscopic and transmission electron microscopic studies showed that the belt-like surface morphology was maintained without any apparent distortion or destruction. A mechanism based on nanoscale solid-state reactions was proposed to account for the structural evolution. Photoluminescence measurements showed that the core–shell nanobelts exhibited a markedly suppressed emission intensity, suggesting impeded recombination of photogenerated carriers as compared to the single-phase counterparts. Such a unique feature was found to be beneficiary to photocatalysis, as exemplified by the photodegradation of methyl orange under UV irradiation, where $TiO_2(B)@Bi_{20}TiO_{32}$ core–shell nanobelts were found to exhibit the best performance among the series.

1. Introduction

In recent decades, Bi-based titanates have been extensively studied because of their potential applications as photorefractive materials, ferroelectric materials, capacitors, dielectric materials, actuators and photocatalysts [1–4]. Bismuth titanates include a very large family of different chemical compositions, such as $Bi_2Ti_2O_7$, $Bi_2Ti_4O_{11}$, $Bi_4Ti_3O_{12}$, $Bi_{12}TiO_{20}$, and $Bi_{20}TiO_{32}$ [5]. Among these, $Bi_{20}TiO_{32}$, with a band gap of ca. 2.38 eV, displays the highest photocatalytic activity due to the hybridized valence band (VB) by Bi6s and O2p orbitals [6]. Recently,

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a number of methods have been reported for the preparation of crystalline bismuth-based titanates, including solid-state [7], sol–gel [8,9] and hydrothermal methods [10]. For instance, Cheng et al. [6] reported the synthesis of granular $Bi_{20}TiO_{32}$ nanoparticles through the melting of oxide precursors at 1000 °C, followed by quenching process at room temperature. In this procedure, $Bi_{20}TiO_{32}$ was formed as a metastable phase. In another study, by Yao et al. [11], granular $Bi_4Ti_3O_{12}$ nanoparticles were fabricated using metal–organic polymeric precursors, which showed good photocatalytic properties. It should be noted that the bismuth titanates reported in most early studies are in granular forms in which the abundant barriers of charge transport limit the photocatalytic performance. Furthermore, the nanoparticles are difficult to recycle, which limits their practical applications in continuous filtering photo-catalytic devices.

In contrast, photocatalysts with a nanobelt morphology may provide efficient pathways for charge transport and hence reduce the rates of charge carrier recombination as compared to other nanostructures [12]. In addition, the high specific surface area of nanobelts may offer abundant active sites for the assembly of secondary phase particles to form nanoscale heterostructures with Schottky, p-n and band matching effects [13–20], so as to improve the photo-catalytic performance as a result of the diminishment of photo-induced carrier recombination, the enlargement of light active facets and widening of the light absorption range [21]. Most importantly, nanobelts may be assembled into paper-like membranes [22] and exploited for continuous photocatalysis [23]. Therefore, it is of both fundamental and technological significance to develop effective protocols for the preparation of one-dimensional bismuth titanates. Nevertheless, whereas bismuth titanates have been prepared in the forms of nanospheres, nanosheets and nanocones [24,25], reports for the synthesis of bismuth titanate nanobelts have been scarce [26]. In fact, pure belt-like $Bi_{20}TiO_{32}$ and $Bi_4Ti_3O_{12}$, with lengths of several tens of micrometers, have not been reported until now.

Herein, for the first time ever, we report a facile approach to the synthesis of bismuth titanate nanobelts through a solid-state reaction by using $Na_2Ti_3O_7$ nanobelts as the reactants and templates. In this procedure, $H_2Ti_3O_7@BiONO_3$ nanobelts were first synthesized by the immersion of $Na_2Ti_3O_7$ nanobelts into a bismuth nitrate solution, which were then subject to a calcination process at controlled temperatures. At low temperatures (e.g. 400 °C), a $TiO_2(B)@Bi_2O_3$ core–shell structure was formed; when the calcination temperature was increased to 450 °C, the shell was transformed into $Bi_{20}TiO_{32}$ on the surface of the $TiO_2(B)$ nanobelts. With a further increase in the calcination temperature (600–700 °C), single-crystalline $Bi_4Ti_3O_{12}$ nanobelts were produced as the final products most probably through a nanoscale solid-state reaction between the Bi_2O_3 shell and the $TiO_2(B)$ core. The photocatalytic activity of the three kinds of TiO_2-based nanobelts, $TiO_2(B)@Bi_2O_3$, $TiO_2(B)@Bi_{20}TiO_{32}$ and $Bi_4Ti_3O_{12}$, demonstrated that the core–shell nanobelts possess much enhanced UV photocatalytic activity, as exemplified by the photodegradation of methyl orange, in comparison with that of the single-crystalline $Bi_4Ti_3O_{12}$ nanobelts. This was accounted for by the reduced recombination of photogenerated carriers in the core–shell nanobelts.

2. Experimental section

2.1. Materials

Analytic grade sodium hydroxide (NaOH) and bismuth nitrate $(Bi(NO_3)_3·5H_2O)$ were used directly, without further purification. Titania P25 (TiO_2; ca. 80% anatase and 20% rutile) was used as the titanium source to prepare $Na_2Ti_3O_7$ nanobelts. Deionized water was used throughout the experiments.

2.2. Preparation of $Na_2Ti_3O_7$ and $TiO_2(B)$ nanobelts

$Na_2Ti_3O_7$ nanobelts were prepared by an alkaline hydrothermal process, as detailed in our previous study [27]. In a typical procedure, 0.30 g of commercial TiO_2 powder (P25) was dispersed in 60 ml of a 10 M NaOH aqueous solution, which was then placed in an 80 ml Teflon-lined autoclave. The autoclave was heated to and maintained at 200 °C for 72 h. The precipitate was collected and washed thoroughly with deionized water, affording $Na_2Ti_3O_7$ nanobelts.

To prepare $TiO_2(B)$ nanobelts, $Na_2Ti_3O_7$ nanobelts were immersed in a 0.1 M HCl aqueous solution for 24 h and washed thoroughly with distilled water to obtain $H_2Ti_3O_7$ nanobelts, which were then annealed at 400 °C for 4 h to afford $TiO_2(B)$ nanobelts [27].

2.3. Preparation of bismuth titanate nanobelts

Bismuth-modified titanate nanobelts were prepared by using the $Na_2Ti_3O_7$ nanobelts obtained above as the templates. In brief, 2.425 g of $Bi(NO_3)_3·5H_2O$ was added to 200 ml of deionized water, followed by ultrasonification and magnetic stirring for 30 min to obtain a suspension. Next, 0.3775 g of $Na_2Ti_3O_7$ nanobelts was added to the above solution. The mixture was ultrasonicated for 10 min and gently stirred for another 30 min. The white precipitates were collected by filtration, washed with deionized water and then dried at 70 °C. Finally, the precipitates were annealed in air at 400, 450, 550 and 600 °C for 2 h to obtain $TiO_2(B)@Bi_2O_3$, $TiO_2(B)@Bi_{20}TiO_{32}$, $TiO_2(B)@Bi_4Ti_3O_{12}$ and $Bi_4Ti_3O_{12}$ nanobelts, respectively.

2.4. Preparation of $BiONO_3$ nanoparticles

In brief, 2.425 g of $Bi(NO_3)_3·5H_2O$ was added to 200 ml of deionized water, followed by ultrasonification and magnetic stirring for 30 min. The white precipitates were