



Letter

Synthesis of Mesoporous TiO₂-B Nanobelts with Highly Crystallized Walls toward Efficient H₂ Evolution

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Abstract: Mesoporous TiO₂ is attracting increasing interest due to properties suiting a broad range of photocatalytic applications. Here we report the facile synthesis of mesoporous crystalline TiO₂-B nanobelts possessing a surface area as high as 80.9 m² g⁻¹ and uniformly-sized pores of 6–8 nm. Firstly, P25 powders are dissolved in NaOH solution under hydrothermal conditions, forming sodium titanate (Na₂Ti₃O₇) intermediate precursor phase. Then, H₂Ti₃O₇ is successfully obtained by ion exchange through acid washing from Na₂Ti₃O₇ via an alkaline hydrothermal treatment. After calcination at 450 °C, the H₂Ti₃O₇ is converted to a TiO₂-B phase. At 600 °C, another anatase phase coexists with TiO₂-B, which completely converts into anatase when annealed at 750 °C. Mesoporous TiO₂-B nanobelts obtained after annealing at 450 °C are uniform with up to a few micrometers in length, 50–120 nm in width, and 5–15 nm in thickness. The resulting mesoporous TiO₂-B nanobelts exhibit efficient H₂ evolution capability, which is almost three times that of anatase TiO₂ nanobelts.

Keywords: mesoporous materials; TiO₂ photocatalyst; water splitting

1. Introduction

Mesoporous metal oxides are used in a wide range applications such as energy conversion and storage [1,2], catalysis [3,4], gas sensors [5], etc., because of their high specific surface area and mesoporous networks. In particular, mesoporous TiO₂ with regular and interpenetrated porous networks have been demonstrated as an effective photocatalyst due to its low cost, environmental friendliness, good physical and chemical stability, large surface area, pore volume and tunable porous structure [6–8]. Many efforts have been devoted to developing diverse techniques towards the synthesis of mesoporous TiO₂ [9–18]. In addition, the nanostructured framework can generally not sustain strong annealing processes, since crystallite growth and atomic diffusion rapidly jeopardize the delicate pore walls. The fabrication of mesoporous crystalline TiO₂ via a simple method has therefore remained a great challenge.

TiO₂ mainly has three well-known crystallographic polymorphs, anatase (tetragonal, space group *I4₁/amd*), rutile (tetragonal, space group *P4₂/mmm*), and brookite (orthorhombic, space group *Pbca*). TiO₂-B (monoclinic, space group *C2/m*) in contrast, however, has gained less attention and fewer studies have been reported. TiO₂-B, a metastable crystal structure ($a = 1.21787$ nm, $b = 0.37412$ nm, $c = 0.65249$ nm, and $\beta = 107.054^\circ$) was first synthesized by Marchand et al. in 1980 [19]. Until now, the synthesis of various TiO₂-B nanostructures, including 0D (nanoparticles [20,21]), 1D (nanowires [22,23], nanoribbons [24], nanotubes [25], nanorods [26] and nanobelts [27]), 2D (nanosheets [28–30]), and 3D (mesoporous microspheres [31] and mesoporous microflowers [32]) nanomaterials have been realized through different techniques, such as ion-exchange from layered titanate, hydrothermal or solvothermal treatments of titanium precursors, alkaline hydrothermal treatment of TiO₂, etc. It is well known that the morphology and porosity of TiO₂-B architectures strongly affect the physical and chemical properties. For instance, TiO₂-B can be utilized as anode material for high-power lithium ion batteries (LIBs) due to its characteristic pseudocapacitive energy storage mechanism. Huang et al. demonstrated the use of graphene as a current collector to construct hybrid graphene/TiO₂-B nanostructures to optimize the performance [27]. Such a hybrid mesoporous architecture can realize fast electron transport and acceleration of diffusion of lithium ions. Due to large surface area, nanoparticles have been used for solar cell applications. However, the electron trapping/scattering at the grain boundaries usually causes high charge recombination loss, resulting in lower efficiency in solar cells. Although 1D nanorods or nanotubes have gained attention due to enhanced charge mobility and strong light absorption, they suffer from lower surface area and poor crystallinity. It is, therefore, highly desirable to fabricate highly crystalline TiO₂-B nanostructures with enhanced surface area for photocatalytic applications.

Herein, we demonstrate the successful design and facile synthesis of a new material, mesoporous crystalline TiO₂-B nanobelts. The resultant mesoporous TiO₂-B nanobelts are carefully characterized by XRD, SEM, TEM, and N₂ adsorption-desorption isotherm. Finally, we investigate the performance of H₂ evolution and compared with commercial anatase TiO₂ powder (P25).

2. Materials and Methods

Preparation of anatase TiO₂ and mesoporous TiO₂-B nanobelts. Anatase TiO₂ and mesoporous TiO₂-B nanobelts were simply obtained via an alkaline hydrothermal procedure. It is well-known that the concentration and reaction time are key factors for controlling the nanostructures. To obtain our targeted mesoporous materials, we further modified the experimental process reported previously [33]. In detail, 0.5 g of P25 powder (Nippon Aerosil Co., Ltd., Tokyo, Japan) was dispersed in 20 mL of 10 M NaOH solution under magnetic stirring for 30 min at room temperature, before being transferred into a 25 mL Teflon-lined stainless-steel autoclave (Parr Instrument Company, Moline, IL, USA), and heated at 180 °C for 48 h. The product was washed with distilled water and 0.1 M HCl and collected by centrifugation three times, and finally dried at 80 °C overnight, yielding protonated titanate nanobelts (H₂Ti₃O₇). The mesoporous TiO₂-B nanobelts were obtained after further heat-treating the product at 450 °C for 2 h in air. For comparison, anatase TiO₂ nanobelts were also prepared by annealing the H₂Ti₃O₇ nanobelts at 600 °C and 750 °C for 2 h in air.

Characterizations. The crystalline phases of the as-synthesized products were measured and characterized with an X-ray diffractometer (XRD, SmartLab, Rigaku Corporation, Tokyo, Japan) using Cu K α radiation. Field-emission scanning electron microscopy (FESEM, JSM-7001F, JEOL Ltd., Tokyo, Japan) and transmission electron microscopy (TEM, JEM-2100F, JEOL Ltd., Tokyo, Japan) were used to examine the morphology of the samples. A nitrogen adsorption apparatus (BELsorp-mini II, MicrotracBEL Corp., Osaka, Japan) was used to determine the Brunauer–Emmett–Teller (BET) surface areas (S_{BET}). All the samples were degassed at 120 °C overnight before measurement.

Photocatalytic Test for H₂ Evolution. Photocatalytic H₂ evolution was evaluated *via* a well-known method using Pt as a co-catalyst and methanol as a sacrificial agent [34]. Because the H₂ evolution from water occurs through two-electron reduction, co-catalysts accumulating excited electrons and sacrificial agents scavenging holes are necessary to promote charge separation. The photocatalytic test of anatase TiO₂ and mesoporous TiO₂-B nanobelts for H₂ evolution was performed under AM 1.5 light irradiation ($\lambda > 300$ nm, 100 mW·cm⁻²). In-situ deposition of fine Pt nanoparticles on the catalysts were carried out by adding an appropriate amount H₂PtCl₆ solution [34]. 70 mg of the 0.5 wt % Pt-loaded nanobelts were dispersed into aqueous solution (220 mL of H₂O and 50 mL of CH₃OH) under magnetic stirring.

3. Results

In order to understand the formation process, X-ray diffraction (XRD) analysis and SEM observation were carried out to confirm the crystal structure and morphology of the starting P25 powder and the intermediate samples (Figure 1). As mentioned in the experimental section, firstly P25 powders (Figure 1a) were dissolved in NaOH solution under hydrothermal condition, forming an intermediate sodium titanate precursor (Na₂Ti₃O₇) phase, as shown in Figure 1b. In the present study, H₂Ti₃O₇ was obtained by ion exchange through acid washing from Na₂Ti₃O₇ via an alkaline hydrothermal treatment (Figure 1c). The obtained intermediate product is similar to that of a layered H₂Ti₃O₇ (JCPDS 41-0192), featuring a (200) reflection peak at 11°. “Dissolution-Recrystallization” process has been well-known as an important technique for crystal transformation [35]. In the present hydrothermal process, OH⁻ ions diffuse into the P25 powders, causing a gradual dissolution of the TiO₂ crystals and forming sodium titanate intermediates without pores (Figure 1b3). After ion exchange (HCl solution), H₂Ti₃O₇ nanobelts with pores are obtained (Figure 1c3).

After calcination at 450 °C, the well-defined peaks located at $2\theta = 24.9^\circ, 28.5^\circ, 43.5^\circ, 48.1^\circ$ and 62.9° can be assigned to the (110), (002), (003), (020), (313) diffraction planes of a TiO₂-B phase, respectively (JCPDS 074-1940, Figure 2a). At 600 °C, the newly formed anatase phase coexists with TiO₂-B, which completely converts into anatase when annealed at 750 °C. We notice that the porosity in the nanobelt structure is maintained after treating at 600 °C, but is lost when heated beyond 750 °C (Figure 2b–d).

Figure 3a shows a typical low-magnification SEM image of the mesoporous TiO₂-B nanobelts annealed at 450 °C. The nanobelts are uniform with up to a few micrometers in length, 50–120 nm in width, and 5–15 nm in thickness, as supported by the low-magnification TEM image (Figure 3b). Interestingly, it can also be seen from the TEM image that the surface of the nanobelts is nanoporous. The high resolution TEM (HRTEM) image (Figure 3c) shows a single mesoporous TiO₂-B nanobelt with a fringe spacing of ~ 5.8 Å, which corresponds to the (200) interplanar distance of the TiO₂-B phase. The clear lattice fringes indicate that this material is highly crystalline in nature. The electron diffraction (ED) pattern in Figure 3d exhibits diffraction spots corresponding to the [001] zone axis of the TiO₂-B phase. The corresponding fast Fourier transform (FFT) confirms the presence of the (200), (1-10), (-1-10) crystallographic planes of the TiO₂-B monoclinic C2/m crystal structure.

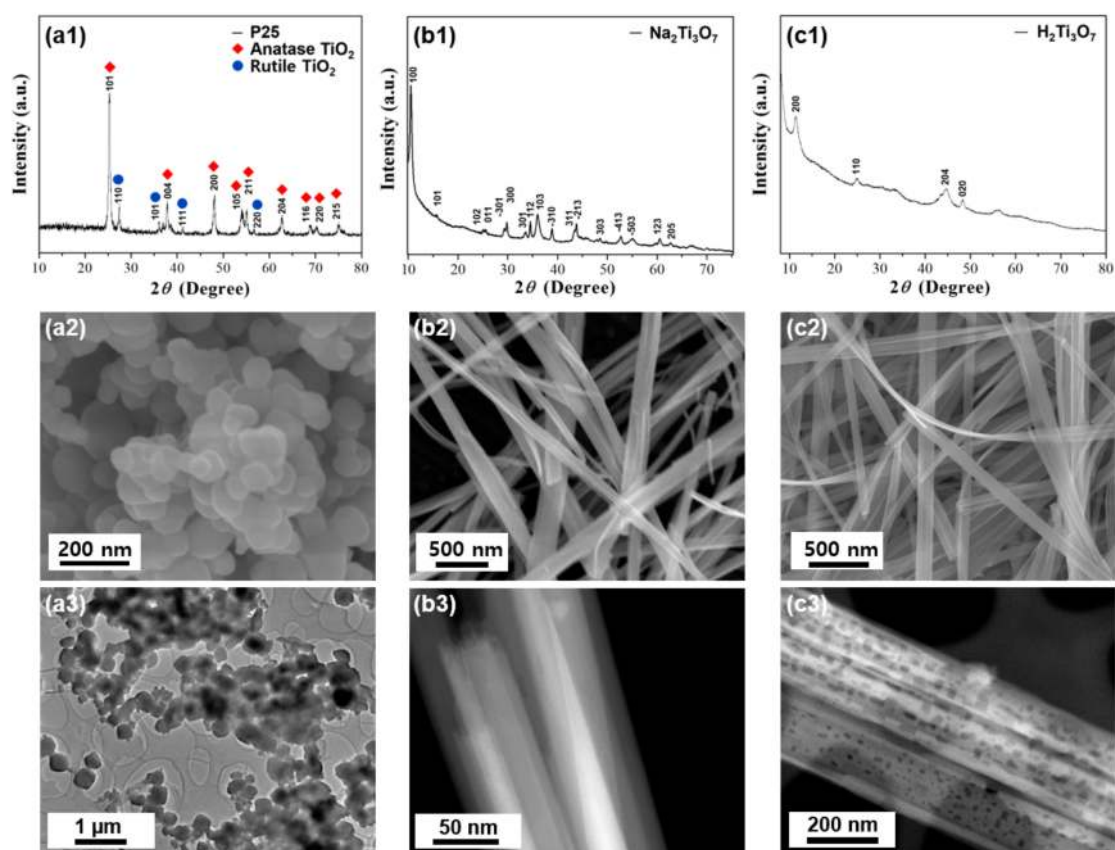


Figure 1. X-ray diffractometer (XRD) patterns, SEM images, and transmission electron microscopy (TEM) images of (a1-3) the starting P25 powders, (b1-3) Na₂Ti₃O₇ nanobelts, and (c1-3) H₂Ti₃O₇ nanobelts, respectively.

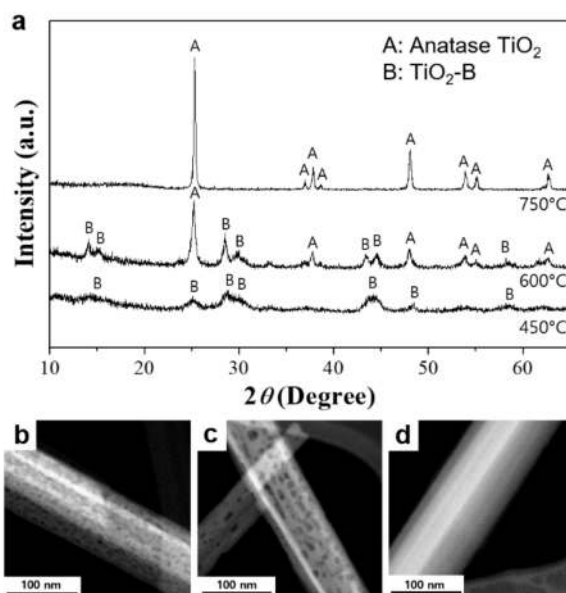


Figure 2. (a) XRD patterns of the TiO₂ nanobelts obtained at different calcination temperatures, TEM images of TiO₂ nanobelts obtained at (b) 450 °C, (c) 600 °C, and (d) 750 °C.

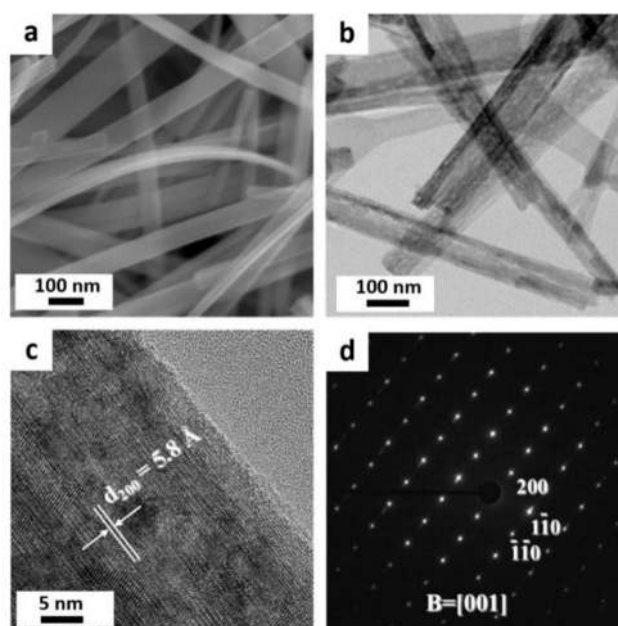


Figure 3. (a) Low magnification field-emission scanning electron microscopy (FESEM) and (b) TEM image of mesoporous TiO₂-B nanobelts, (c) high resolution TEM (HRTEM) image of one single nanobelt, showing the fringe spacing of crystalline TiO₂-B and (d) the corresponding electron diffraction (ED) patterns.

The morphology and porosity of the mesoporous TiO₂-B nanobelts were further confirmed by electron microscopy characterization. The high magnification SEM image in Figure 4a highlights a single nanobelt, revealing a relatively rough surface with numerous pores, further supported by high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) (Figure 4b).

The HRTEM image (Figure 4c) shows a clear mesoporous structure, where the high contrast regions correspond to 6–8 nm pores (Figure 4d) uniformly dispersed on the surface. This is also confirmed through the Barrett-Joyner-Halenda (BJH) pore size analysis calculated from the nitrogen (N₂) adsorption/desorption isotherms (Figure 4e). The isotherms show typical type IV curves with a sharp capillary condensation step at $P/P_0 = 0.8$ – 0.9 . At relatively high pressure, the curves exhibit a small hysteresis. The Brunauer-Emmett-Teller (BET) specific surface area is measured to be 80.9 m² g⁻¹.

TiO₂ materials are promising candidates for photocatalysis [36], such as efficient water splitting into H₂. This half-reaction of water splitting converts solar energy into chemical or electrical energy in an economical way. To evaluate the photocatalytic activities of the anatase TiO₂ and mesoporous TiO₂-B nanobelts, H₂ evolution tests were carried out in the presence of methanol. Figure 5 compares photocatalytic water splitting tests of the mesoporous TiO₂-B and anatase TiO₂ nanobelts, both Pt-loaded (0.5 wt%), under the same conditions, i.e., with the same surface area (ca. 0.23 m²) and the same mass (70 mg).

As shown in Figure 5, mesoporous the TiO₂-B nanobelts exhibit a superior photocatalytic activity with a H₂ evolution rate of 656.10 μmol h⁻¹, about three times that of anatase TiO₂ nanobelts (282.06 μmol h⁻¹). Commercially available P25 powders consisting of anatase and rutile crystalline phases cannot realize efficient H₂ evolution, but after loading with Pt, the H₂ evolution rate can be greatly enhanced up to 100 μmol h⁻¹ (in case of 15 mg catalyst) [37]. Compared to anatase and rutile crystalline phases, TiO₂-B phase is known to be more active towards H₂ evolution. Cai et al. reported that pure TiO₂-B nanobelts without Pt nanoparticles showed a H₂ evolution rate of ~107 μmol h⁻¹ [38]. In our study, the photocatalytic rate of our Pt-loaded mesoporous TiO₂-B nanobelts greatly increases around 6 times higher than that of pure mesoporous TiO₂-B nanobelts without Pt [38].

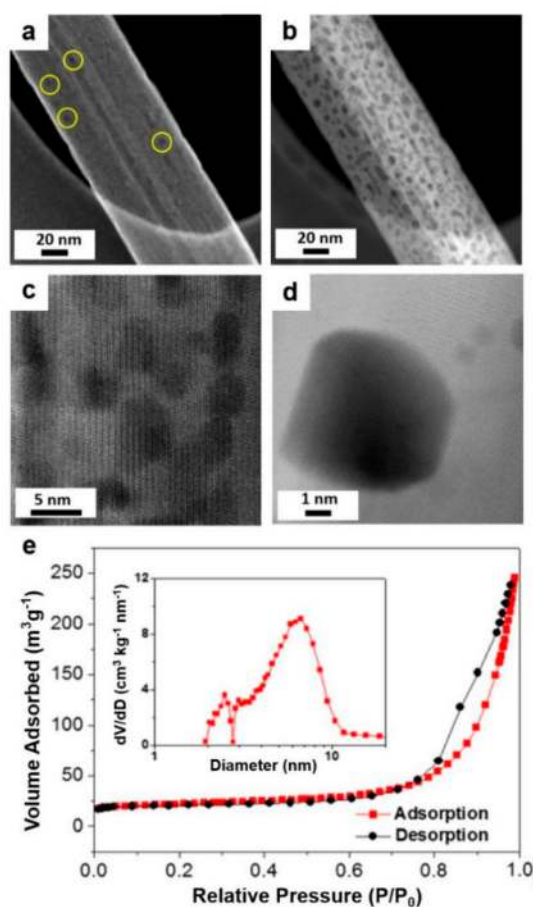


Figure 4. (a) High magnification SEM image, highlighting one single $\text{TiO}_2\text{-B}$ nanobelt with pores, (b) TEM image of mesoporous $\text{TiO}_2\text{-B}$ nanobelts, revealing homogeneous nanopores, (c) high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) image of single mesoporous $\text{TiO}_2\text{-B}$ nanobelt, (d) magnified pore image in (c), and (e) N_2 adsorption-desorption isotherm of the mesoporous $\text{TiO}_2\text{-B}$ nanobelts. Inset: the corresponding pore size distribution calculated by the Barrett-Joyner-Halenda (BJH) method from the adsorption curve.

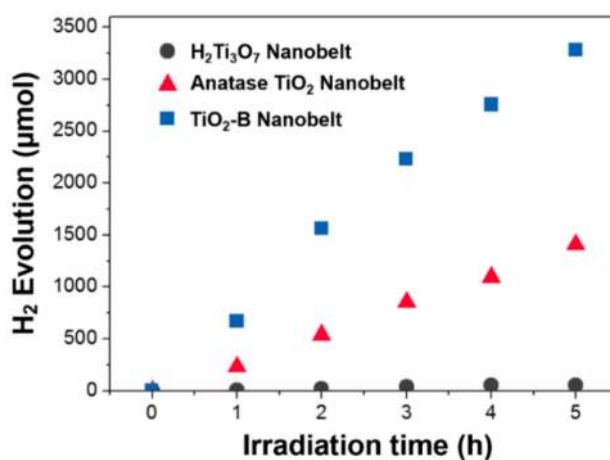


Figure 5. Comparison of photocatalytic water splitting tests of Pt-loaded (0.5%) $\text{H}_2\text{Ti}_3\text{O}_7$, anatase TiO_2 and mesoporous $\text{TiO}_2\text{-B}$ nanobelts samples with the same mass (70 mg) under UV-Visible light irradiation ($\lambda > 300$ nm).

4. Conclusions

We have designed and fabricated for the first time highly crystallized mesoporous TiO₂-B with high surface area (80.9 m² g⁻¹) and pore size of 6–8 nm. The obtained highly crystallized mesoporous TiO₂-B was used as photocatalyst, showing efficient water splitting for H₂ evolution (656.10 μmol h⁻¹), almost three times that of anatase TiO₂ nanobelts (282.06 μmol h⁻¹). It opens a new strategy for the design for photocatalyst of H₂ evolution reaction from H₂O.

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Conflicts of Interest: The authors declare no conflict of interest.

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