Simple hydrothermal preparation of nanofibers from a natural ilmenite mineral

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Abstract

Titrate nanofibers were synthesized by a simple hydrothermal method using a natural ilmenite mineral as the starting material. The chemical composition, crystalline structure, shape, size, and specific surface area of the prepared samples were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and the Brunauer–Emmett–Teller analysis (BET). The crystalline structure of the as-synthesized nanofibers demonstrated a layered titanate form, $\text{H}_2\text{Ti}_x\text{O}_{2x+1}$. The length of the prepared nanofibers ranged from 2 to 7 μm with diameters ranging from 20 to 90 nm. The as-synthesized nanofibers were solids with BET surface areas of approximately 50 m²/g. This synthetic method provides a simple route for the fabrication of one-dimensional (1-D) nanostructured materials from a low-cost natural mineral.

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1. Introduction

One-dimensional TiO₂ nanostructures including nanowires, nanorods, nanowhiskers, nanotubes and nanofibers have been intensively studied and researched due to their exceptional properties including chemical stability [1], biocompatibility [2,3], high photocatalytic reactivity [1,4], and cost-effectiveness. TiO₂ is one of the most attractive metal oxides for a versatile range of potential and novel applications [4–9], such as humidity sensors [10], optoelectronic devices [11], lithium ion batteries [12–14], hydrogen storage [15,16], dye sensitized solar cells (DSSC) [17–19], water treatment materials, catalysts, and gas sensors [20–25]. Low-dimensional TiO₂-related nanomaterials can be synthesized by various methods including electrospinning [26], hydrogen treatment [27], anodic porous alumina templating [28,29], carbon nanotube inner templating [30], supramolecular assembly templating [31], anodic oxidation of a titanium sheet [32], and hydrothermal NaOH (aq.) treatment [33,34]. Among these methods, the hydrothermal method for the synthesis of TiO₂ nanotubes, first proposed by Kasuga et al. [33,34], has been widely exploited for low-dimensional nanostructures [35–37]. The hydrothermal method is a straightforward synthesis that is cost effective and environmentally innocuous [38–41]. Furthermore, this technique can also be applied to the preparation of a wide range of low-dimensional TiO₂ nanostructures, such as nanoparticles [42], nanowires [43], nanofibers [38,39,41] and nanoribbons [43]. Ilmenite (FeTiO₃) is a natural source of low titanium content TiO₂ (usually approximately 50–60%) [44,45]. In our previous work, nanofibers were prepared by a simple hydrothermal method from a leucoxene mineral [41].

In this work, the direct synthesis of nanofibers from an ilmenite mineral is first reported. The nanofibers are prepared by the simple hydrothermal method using a low-cost ilmenite mineral as the starting material. Characterization of the prepared nanofibers is also reported.
2. Experimental

2.1. Synthesis

Titanate nanofibers are synthesized by the hydrothermal method using a natural ilmenite mineral (Sakorn Minerals Co., Ltd., Thailand) as the starting material. These materials are made from 5 g of the black granules of ilmenite mineral (used without purification) are placed in a Teflon-lined stainless steel autoclave. To the autoclave was then added 200 mL of 10 M NaOH (aq.), followed by heating at 120 °C for 72 h with stirring. This process resulted in the formation of solid nanowires and long nanofibers [41]. After the autoclave was allowed to cool to room temperature, the resulting product was washed several times with an HCl (aq.) solution and then several times with distilled water, followed by drying with hot air. The experimental procedure is schematically shown in Fig. 1.

2.2. Characterization

The chemical compositions of the as-synthesized samples are analyzed by X-ray fluorescence (XRF, Philips, PW-2404, 4 kW). The phase and crystallinity of the samples were characterized by X-ray diffraction (XRD, X'Pert PRO MPD model pw 3040/60, PANalytical) with Cu Kα (λ=0.154 nm) irradiation at a scan rate of 0.02° 2θ s⁻¹ and a 2θ range of 10-90°. The microstructure of the as-synthesized product was analyzed by scanning electron microscopy (SEM, JEM-6510, JEOL), with accelerating voltages of 5–20 kV and transmission electron microscopy (TEM, JEOL JEM-2010 Electron Microscope). The distribution of the sizes of the nanofiber diameters was analyzed by SEM. Nitrogen adsorption measurements (Quantachrome Instruments, Autosorb-1) are used to determine the Brunauer–Emmett–Teller (BET) specific surface area.

3. Results and discussion

The as-synthesized sample was brown, whereas the starting ilmenite mineral was black (Fig. 2). This result

![Fig. 1. Schematic representation of the experimental procedure.](image1)

![Fig. 2. Powders of (a) the starting ilmenite mineral and (b) the as-synthesized sample. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)](image2)
Table 1

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Ilmenite mineral (wt%)</th>
<th>As-synthesized sample (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>66.99</td>
<td>76.21</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>24.01</td>
<td>21.80</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.38</td>
<td>0.12</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.11</td>
<td>0.30</td>
</tr>
<tr>
<td>MnO</td>
<td>0.82</td>
<td>0.68</td>
</tr>
<tr>
<td>ThO₂</td>
<td>0.64</td>
<td>0.01</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.62</td>
<td>0.12</td>
</tr>
<tr>
<td>MgO</td>
<td>0.27</td>
<td>0.09</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.26</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>PbO</td>
<td>0.25</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.15</td>
<td>0.05</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>0.09</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.21</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>0.24</td>
<td>0.15</td>
</tr>
<tr>
<td>CaO</td>
<td>0.16</td>
<td>0.08</td>
</tr>
</tbody>
</table>

indicates that a large portion of Fe impurities were removed by the NaOH (aq.) hydrothermal treatment and the neutralization/washing processes [38]. The chemical compositions of the ilmenite mineral and of the as-synthesized samples found using X-ray fluorescence are shown in Table 1. During the hydrothermal process, the quantities of impurities, such as Fe₂O₃, Al₂O₃, SiO₂, and MnO, decreased while the TiO₂ content increased from 66.99 to 76.21 wt%. This may be due to higher solubility of the impurities in the NaOH and HCl aqueous solutions during the preparation process [46,47]. The doping of Fe³⁺ in the nanofiber matrix leads to a significant red shift in the optical response toward the visible spectrum caused by a reduction in the band gap energy [48], resulting in the brown-color of the as-synthesized samples. The nanofibers doped with Fe³⁺ could be an alternative, economically efficient material used as a photocatalyst in hydrogen production, dye-sensitized solar cells and the decomposition of organic dyes.

The XRD patterns of the starting ilmenite mineral and the as-synthesized sample are shown in Fig. 3. The crystalline structure of the starting ilmenite mineral appears to be of the rutile phase, while the crystalline structure of the as-synthesized nanofibers demonstrated a layered titanate \( H_2Ti_xO_{2x+1} \) structure, most likely trititanate \( H_2Ti_3O_7 \), indicating the existence of hydrogen in the prepared nanofibers [38-41]. No diffraction peaks of other impurities (such as starting rutile and NaCl) are observed. This result is due to the reduction of the Na content in the nanofibers from repeated HCl leaching and water washes [36,49]. However, when compared with titanate nanotubes, the nanofibers contain more residual Na ions under the same ion exchanging conditions because of the geometry of the nanofibers, i.e., their solid and thicker structure. In addition, alkali-metal hexatitanates (\( A_2Ti_6O_{13}, A=Na, K, \) and Rb) tend to form stable solid fibrous structures that do not leach out easily during aqueous HCl treatments at room temperature [38]. An SEM image of the starting ilmenite mineral is shown in Fig. 4; this illustrates the granular structure of the material, with grain sizes of 150-200 μm. After the hydrothermal treatment, the as-synthesized sample exhibited a uniform fiber-like morphology (Fig. 5). To confirm the formation of nanofibers, TEM analysis was used, and a representative image can be seen in Fig. 6. From the TEM images, it can be observed that the as-synthesized nanofibers are solid rather than hollow.

The nanofibers tend to form bundles; thus some of the nanofibers look thicker than others. The prepared nanofibers had lengths from 2 to 7 μm with diameters of 20-90 nm (Fig. 6). The nano-fiber formation can be explained by the coarseness of the ilmenite granules, which retarded their dissolution in the NaOH solution, suppressing nucleation and assisting preferential crystal growth along the 010 direction of the trititanate [38]. The diameters (Fig. 7) of the as-prepared nanofibers were found to
In summary, titanate nanofibers are synthesized by a hydrothermal method using a low-cost ilmenite mineral as the starting material. After the hydrothermal synthesis, solid nanofibers showed an increased TiO\textsubscript{2} content were obtained. Analysis of the crystalline structure of the as-synthesized nanofibers exhibit a significant enhancement in the wavelength region of 300–500 nm due to the natural Fe-doping characteristic of the ilmenite mineral. Further studies on the synthesis and characterization of this material are currently being performed.

4. Conclusion

In summary, titanate nanofibers are synthesized by a hydrothermal method using a low-cost ilmenite mineral as the starting material. After the hydrothermal synthesis, solid nanofibers showed an increased TiO\textsubscript{2} content were obtained. Analysis of the crystalline structure of the as-synthesized nanofibers exhibit a significant enhancement in the wavelength region of 300–500 nm due to the natural Fe-doping characteristic of the ilmenite mineral. Further studies on the synthesis and characterization of this material are currently being performed.
Table 2
The BET specific surface area of the starting ilmenite mineral and the as-synthesized nanofibers.

<table>
<thead>
<tr>
<th></th>
<th>Bet surface area (m$^2$/g)</th>
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</thead>
<tbody>
<tr>
<td>Starting ilmenite mineral</td>
<td>0</td>
</tr>
<tr>
<td>As-synthesized</td>
<td>~49</td>
</tr>
</tbody>
</table>

Fig. 8. UV-vis absorbance spectra of the as-synthesized nanofibers and commercial grade TiO$_2$ nanoparticles (ST-01).

as-synthesized nanofibers demonstrated a layered titanate H$_2$Ti$_7$O$_{21}$+4 structure, most likely in the form of trititanate (H$_2$Ti$_3$O$_7$). The prepared nanofibers showed lengths of 2-7 μm with diameters of approximately 20-90 nm and a corresponding BET specific surface area of approximately 49 m$^2$/g. These Fe$^{3+}$ doped nanofibers may show utility as a novel photocatalyst material for hydrogen production, dye-sensitized solar cells and the decomposition of organic dyes.

Acknowledgments

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