Titanium dioxide high aspect ratio nanoparticle hydrothermal synthesis optimization

Abstract: TiO$_2$-B (bronze) nanowires were synthesized via simple hydrothermal treatment of commercial titanium dioxide nanopowder in aqueous NaOH. The reaction temperature, calcination temperature, reaction time, NaOH concentration, autoclave filing fraction and precursor were systematically varied to optimize the nanowire morphology. The crystal structure, morphology and particle size were investigated by XRD, SEM and TEM. The morphology and structure are sensitive to experimental conditions. A reaction temperature of at least 150°C and NaOH concentration at least 10 M are essential, but reaction time from 24 to 72 h makes little difference. Nanowires obtained at 150°C were 60-180 nm wide and 2-4 µm long, while those after treatment at 200°C were thinner (40-100 nm) and longer (2-6 µm).

The relationship between reaction conditions and morphology is discussed and practical guidelines for titanium dioxide nanowire synthesis are suggested.

Keywords: titanium dioxide, nanowire, hydrothermal

DOI: 10.1515/chem-2015-0006
received September 17, 2013; accepted May 25, 2014.

1 Introduction

Nanostructured materials such as wires, rods, whiskers, belts and tubes attract great interest because unique mechanical, electrical, magnetic and optical properties result from special combinations of bulk and surface structures. Since the discovery of carbon nanotubes by Iijima in 1991 [1], much effort has been devoted to the development of one-dimensional nanomaterials. This soon embraced materials other than carbon, primarily sulfides [2] and oxides [3,4]. Among metal oxides, nanowire titanium dioxide has attracted particular attention because of its broad range of potential applications, including photocatalysis [5], solar cells [6], gas sensors [7], and drug delivery [8]. It also shows promise as a negative electrode material [9, 10] because its open mesoporous structure, efficient transport of lithium ions, and effective ion-exchange properties result in a high charge/discharge capacity, fast kinetics, robustness, and good safety characteristics.

TiO$_2$ nanowires can be synthesized by a sol-gel process [11], a template-assisted method [12], electrochemical anodic oxidation [13], or hydrothermal treatment [14]. Each method has advantages and disadvantages. For example, the template-assisted method employs an anodic aluminum oxide template to control the TiO$_2$ nanostructure but its removal is difficult; it may remain as an impurity. Kasuga et al. [15] first reported titanium dioxide nanotube hydrothermal synthesis by reacting TiO$_2$ particles with concentrated NaOH followed by acid washing. Armstrong et al. [16] found that as-synthesized nanotubes and nanowires are Na$_x$H$_{2-x}$Ti$_n$O$_{2n+1}$·$x$H$_2$O sodium hydrogen titanates. Acid washing results in ion exchange to produce H$_2$Ti$_n$O$_{2n+1}$·$x$H$_2$O hydrogen titanates; their dehydration yields nanostructured TiO$_2$. Hydrothermal synthesis of nanowires has many advantages, including solubility, diffusion and crystallization enhancements as well as control of morphologies, sizes and phase transformations at relatively low temperature.

Although many papers on hydrothermal titanium dioxide nanowire synthesis have been reported there has been no systematic study of the effect of reaction conditions on their crystal structure and morphology.

2 Experimental procedure

Titanium dioxide nanowires were synthesized via hydrothermal reaction of commercial TiO$_2$ powder (Degussa P25) in aqueous NaOH followed by ion exchange in aqueous HCl and calcination.
In our initial procedure 1 g of P25 powder was added to 15 M aqueous NaOH. After stirring for 1 h the resulting suspension was transferred to a Teflon-lined stainless steel autoclave and heated at 170°C for 72 h. The product was acid washed by stirring in 0.1 M HCl for 12 h. The material was then filtered and washed with distilled water or 0.1 M HCl until the filtrate became neutral. The dried, acid-washed samples were calcined at 400°C for 4 h in air. This procedure was optimized by varying the parameters in Table 1.

The products’ phase structures were investigated by X-ray diffraction (XRD) using a Philips PW 1050 diffractometer with CuKα irradiation (λ = 0.154056 nm). The texture and morphology were observed by scanning and transmission electron microscopy using Zeiss EVO 40 (SEM) and JOEL JEM 1200 EX (TEM) instruments.

### 3 Results and discussion

#### 3.1 Effect of reaction temperature

The starting commercial Degussa P25 TiO₂ powder is composed of small, irregular particles approximately 25 nm in diameter (Fig. 1). It is 75% anatase and 25% rutile. In the initial procedure the reaction temperature was 170°C. Four different temperatures were then tried with the other parameters unchanged. The reaction temperature influences the product nanostructure. Fig. 2 shows XRD patterns of TiO₂ treated for 72 h in 15 M NaOH at temperatures from 110 to 200°C. SEM and TEM images are in Fig. 3. Reaction below 130°C did not alter
the original morphology or structure. Increasing the reaction temperature to 150°C changed the morphology from particles to nanowires and the crystal structure changed to TiO$_2$-B (bronze). Further temperature increase did not change the structure or morphology but the aspect ratio increased. TiO$_2$ nanowires obtained at 150°C were 60-180 nm wide and 2-4 µm long, while those after treatment at 200°C were thinner (40-100 nm) and longer (2-6 µm).

### 3.2 Effect of calcination temperature

Calcination is necessary to remove water from intermediate hydrogen titanates and form pure crystalline TiO$_2$. The standard 400°C calcination temperature resulted in TiO$_2$-B nanowires. Calcination at 600°C caused the nanowires to aggregate into irregular anatase particles (Figs. 4, 5).
3.3 Effect of hydrothermal reaction time

Hydrothermal treatment of titanium dioxide at 170°C for different times (24, 48, 72 and 96 h) changes the morphology (Fig. 6). Nanowires appear after 24 h and do not change up to 72 h. After 96 h some nanoparticles appear to be attached to the nanowires. The nanowires are 40-180 nm wide and 2-6 µm long. Morphology, size, and structure (TiO$_2$-B) did not depend on the reaction duration (not shown).

3.4 Effect of NaOH concentration

The morphology is strongly affected by the NaOH concentration. Fig. 7 shows SEM and TEM images after hydrothermal treatment at 170°C for 72 h in 5, 10 or 15 M NaOH. In 5 M NaOH large irregular particles were formed. Closer inspection of the TEM image reveals that these are masses of nanorod-like particles. Increasing the NaOH concentration to 10 M results in nanowires with 40-120 nm diameter averaging about 2 µm long. Further NaOH concentration increase to 15 M leads to elongation of the nanowires up to 6 µm. The crystal structure was the same (TiO$_2$-B) irrespective of NaOH concentration (XRD not shown).

3.5 Effect of autoclave filling fraction

Surprisingly, the autoclave filling fraction had a strong impact on the product. In the initial procedure the autoclave was only 5% filled, yielding well defined TiO$_2$-B nanowires. Increasing the filling fraction to 10% led to well-developed TiO$_2$-B nanowires with small attached nanoparticles. When the volume fraction was raised to 50%, nanoparticles dominated the nanowires. The product exhibits a low crystallinity anatase structure (Fig. 8). Further filling fraction increase to 85% results in improved anatase crystallinity but the morphology changed to nanoparticles (Fig. 9).

Figure 5: SEM (left) and TEM (right) of TiO$_2$ nanowires calcined at 400 and 600°C.

Figure 6: SEM (left) and TEM (right) of samples prepared for different reaction times.
3.6 Effect of precursor

To determine whether different forms of TiO$_2$ can be used as precursors in hydrothermal nanowire synthesis TiO$_2$, nanorods and nanopowder were prepared following literature procedures [17,18]. The as-synthesized materials were added to 15 M NaOH and reacted at 170°C for 72 h. XRD patterns of the products are in Fig. 10 and SEM, TEM images are in Fig. 11. It seems that only commercial P25 TiO$_2$ powder yields the 40-120 nm wide and 2-5 µm long TiO$_2$-B wires. The TiO$_2$ nanorods were converted to single nanowires dominated by large, irregular particles. The anatase crystal structure remained unchanged. The titanium dioxide nanopowder precursor gave some thin (50-75 nm) and short (2 µm) nanowires with irregular particles and a TiO$_2$-B structure. Optimization of the synthesis parameters might improve the results.

The optimized reaction conditions for one dimensional TiO$_2$ nanoparticle formation are summarized in Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction temperature</td>
<td>150-200°C</td>
</tr>
<tr>
<td>Calcination temperature</td>
<td>400°C</td>
</tr>
<tr>
<td>Reaction time</td>
<td>24-72 h</td>
</tr>
<tr>
<td>NaOH concentration</td>
<td>&gt;10 M</td>
</tr>
<tr>
<td>Autoclave filling fraction</td>
<td>&lt;10%</td>
</tr>
<tr>
<td>Nanowires precursor</td>
<td>Degussa P25</td>
</tr>
</tbody>
</table>

Table 2: Optimum hydrothermal reaction conditions for TiO$_2$ nanowire preparation.
Figure 9: SEM (left) and TEM (right) of samples prepared with varied autoclave filling fraction.

Figure 10: XRD of TiO$_2$ materials synthesized using (a) commercial TiO$_2$ P25; (b) as synthesized TiO$_2$ nanorods; (c) as synthesized TiO$_2$ nanopowder.

Figure 11: SEM (left) and TEM (right) of samples prepared using different TiO$_2$ substrates.
4 Conclusions

We have identified hydrothermal synthesis conditions leading to TiO₂ nanowires. Reaction temperature and NaOH concentration are particularly important in controlling the nanostructure. Titanium dioxide nanowires can be readily synthesized hydrothermally using commercial Degussa P25 titanium dioxide nanopowder and highly concentrated (above 10 M) NaOH. TiO₂-B nanowires 60-180 nm wide and 2-6 µm long appear at the relatively low reaction temperature of 150°C after 24 h. Surprisingly, the autoclave filling fraction is crucial in nanowire formation; exceeding 10% changes the product to particles with a lower aspect ratio. Due to the low cost, procedural simplicity and facile morphology control, one dimensional TiO₂ can be manufactured on a large scale and considered for applications in solar cells, lithium batteries, hydrogen storage devices or biomedical applications where such materials have shown promise.

Acknowledgement: The work was supported by Wroclaw Research Centre EIT+ as part of the project “The Application of Nanotechnology in Advanced Materials” - NanoMat (POIG.01.01.02-02-002/08) co-financed by the European Regional Development Fund (Operational Program Innovative Economy, 1.1.2).

References