Effect of post-heat treatment on the photocatalytic activity of titanium dioxide nanowire membranes deposited on a Ti substrate

Ying Chang, Chonggang Wu, Huihu Wang, Yan Xiong, Yuan Chen, Kai Ke, Yao He and Shijie Dong

Titanium dioxide nanowire membranes have been synthesized by a hydrothermal growth on the surfaces of Ti substrates in a 12 M NaOH aqueous solution at 160 °C for 24 h, followed by ion-exchange with 0.5 M HCl aqueous solution and subsequent heat treatment such as calcination or a second hydrothermal treatment. The as-prepared TiO₂ nanowires as well as their precursor were characterized by field emission scanning electron microscopy (FE-SEM), thermogravimetry-differential thermal analysis (TG-DTA), X-ray diffraction (XRD), the Brunauer–Emmett–Teller (BET) method, ultraviolet-visible (UV-Vis) spectrophotometry, transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectrometry. FE-SEM observations indicated that the TiO₂ nanowires were 50–250 nm in diameter and up to several dozens of microns in length. TG-DTA and XRD results demonstrated that the crystalline phases of the nanowires obtained from calcinations of their precursor at different temperatures above 350 °C consisted mostly of anatase. BET, UV-Vis, TEM and EDX results showed that the nanowires obtained upon calcination of their precursor at 550 °C had the greatest degradation efficiency for Rhodamine-B, and that, at the same temperature of 250 °C, the hydrothermal treatment process of TiO₂-precursor nanowires had a more significant effect on the photocatalytic activity of the resulting TiO₂ nanowires than the calcination.

Introduction

Due to economic disparity, rapid urbanization, industrialization, and population growth, there are growing concerns about water availability and the strategies necessary to deliver potable water with the growing demands for clean water sources. Industrial waste water is an extremely serious problem of water pollution, as it contains various compositions of constituent pollutants which are often unknown. Usually, these pollutants cannot be self-cleaned in the environment, the artificial treatment of which is complicated and costly.

TiO₂ is a wide-band semiconductor material with gaps of 3.2 eV for anatase and 3.0 eV for rutile. Degussa P25, a commercial TiO₂ polycrystalline nanopowder, is chemically inert and cost-effective, and exhibits satisfactory photocatalytic activity. Therefore, it has widely been used in photocatalytic water-treatment, although the separation of TiO₂ nanoparticles from the treated water has high energy costs. Recently, more focus has been directed to the technology of preparing TiO₂ nanowire/nanobelt thin membranes, which show superior performance to TiO₂ nanoparticles. For example, TiO₂ nanowires/nanobelts can minimize the release of nanomaterials into effluents during their self-assembled formation of membranes. As more and more studies are focused on this new technology, various methods to obtain TiO₂ nanowire/nanobelt membranes have been developing and improving. In the past decade, great efforts were focused on the effects of hydrothermal parameters on the compositions and morphologies and clarification of the sequential events in the formation process of titane nanotubes/nanowires/nanobelts. However, to our knowledge, nobody particularly investigated the preparation of TiO₂ nanowires via a second hydrothermal process.

In this work, we report the synthesis of TiO₂-precursor nanowires by a hydrothermal growth on the surfaces of Ti substrates, followed by the use of different heat-treatment methods (i.e. calcination and a second hydrothermal) on the synthesized precursor to obtain TiO₂ nanowires. Analysis of the experimental results demonstrates that the TiO₂ nanowires obtained upon the second hydrothermal treatment of their precursor possess higher photocatalytic activity than upon the calcination.

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**Experimental**

**Materials**

Titanium foil with purity greater than 99.5%, NaOH, HCl and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd, China and used as starting materials without further purification, and deionized water purified by ion exchange was used for solution preparation and synthesis.

**Preparation**

TiO$_2$ nanowires were synthesized in a NaOH aqueous solution via hydrothermal growth on the surfaces of titanium foil (1 mm thick). In detail, a 20 × 20 mm$^2$ piece of titanium foil was washed sequentially with ethanol and deionized water, then placed in a 100 mL Teflon-lined pressure vessel filled with 50 mL of 12 M NaOH aqueous solution. After heating the vessel at 160 °C for 24 h, a thick, white-cotton-like membrane of sodium titanate nanowires was obtained on each side of the titanium foil surface. The nanowires were randomly oriented and entangled together (i.e. intertwined) to form macroporous structured membranes. The titanium foil covered with the nanowire membranes was washed in deionized water, and then immersed in a 0.5 M HCl aqueous solution at 50 °C for 12 h to effectively transform Na$_2$Ti$_3$O$_7$ nanowires into H$_2$Ti$_3$O$_7$ nanowires via ion-exchange of Na$^+$ with H$^+$. The membranes were then peeled off the Ti foil using a knife and again washed in deionized water until the pH value of the washing solution was neutral. Finally, both the TiO$_2$ precursor nanowire membranes obtained were air dried at 70 °C overnight (denoted as Sample A), and then heated with different post-heating treatments to obtain the resulting TiO$_2$ nanowire membranes. The different post-heating treatments included direct calcination at different temperatures (250, 350, 450, 550 and 650 °C) for 2 h (denoted as Samples B, C, D, E and F, respectively), and a second hydrothermal treatment at 250 °C for 2 h (denoted as Sample G) which was similar to the previous hydrothermal procedure except without NaOH.

**Characterizations**

Surface morphologies of the as-prepared H$_2$Ti$_3$O$_7$ precursor nanowires and of the TiO$_2$ nanowires upon the post-heats treatments of the precursor nanowires were analyzed on a FEI Quanta 450 field-emission scanning electron microscope (FE-SEM), operating at 7 kV. Data, obtained from a Shimadzu DTG-50H thermogravimetry-differential thermal analysis (TG-DTA) thermal analyzer, revealed the phase transformation temperature ranges required for designing the sintering program. Powder X-ray diffraction (XRD) patterns of TiO$_2$ nanowires as well as of their precursor nanowires were recorded on a Bruker, D8 Advance powder X-ray diffractometer with CuK$\alpha$ radiation (Si internal standard method), at a 2θ scan range of 5–60° and a scan speed of 2° min$^{-1}$. The specific surface areas of the samples were determined with Quantachrome instruments, NOVA 2200 specific surface area analyzer by the Brunauer–Emmett–Teller (BET) method using the N$_2$ adsorption data (as shown in Table 1). Absorption spectra of the samples were recorded with a Hitachi, U-3900 ultraviolet-visible (UV-Vis) spectrophotometer using BaSO$_4$ as a reflectance standard. High resolution transmission electron microscopy (HRTEM) observation and selected area electron diffraction (SAED) were carried out with a JOEL JEM 2100 microscope. To prepare the HRTEM specimens, the powder samples were first dispersed ultrasonically in acetone, and then one drop of the suspension was placed on a carbon-film-coated copper grid and allowed to dry in air before the specimens were finally transferred onto the microscope. An Oxford energy dispersive X-ray (EDX) spectrometer was used to analyze the elemental composition of the TiO$_2$ nanowire membranes prepared.

**Photocatalytic activity measurements**

The photocatalytic activity of the TiO$_2$ nanowire membranes was evaluated by monitoring the degradation efficiency of a Rhodamine-B (RhB) dye aqueous solution (20 mL of 5 mg L$^{-1}$). All the tests were performed using a 300 W Xenon lamp, which emits both ultraviolet (UV) and visible light; during the assay, 2 mL of the solution was extracted at 10 min intervals, the RhB concentration of which was then measured using a UV-Vis spectrophotometer (JASCO, V-560). The degradation efficiency was calculated as ($C_0 - C)/C_0$, where $C_0$ is the initial concentration of the RhB solution (i.e. 5 mg L$^{-1}$) and $C$ the remaining concentration of RhB upon degradation for 1 h.

**Results and discussion**

**Effect of post-heating treatment on specific surface area of TiO$_2$ nanowires**

Fig. 1 shows the FE-SEM images of the as-synthesized TiO$_2$-precursor nanowires (Fig. 1a) as well as of the TiO$_2$ nanowires obtained upon two different post-heating treatments (i.e. calcinations and hydrothermal) of the precursor at the same temperature and time (250 °C for 2 h). As expected, fibrous structures with a typical diameter of 50–250 nm and a length of several dozens of microns were observed for both the TiO$_2$ and its precursor nanowires. We found that the structure of both the TiO$_2$ nanowires underwent little changes after post-heating treatments of their precursor. Compared with the TiO$_2$ nanowires

<table>
<thead>
<tr>
<th>Samples</th>
<th>Specific surface areas (m$^2$ g$^{-1}$)</th>
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<tbody>
<tr>
<td>A</td>
<td>19.205</td>
</tr>
<tr>
<td>B</td>
<td>18.706</td>
</tr>
<tr>
<td>C</td>
<td>17.926</td>
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<tr>
<td>D</td>
<td>16.823</td>
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<tr>
<td>E</td>
<td>15.621</td>
</tr>
<tr>
<td>F</td>
<td>12.988</td>
</tr>
<tr>
<td>G</td>
<td>21.868</td>
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</table>
from ca. the DTA curve showed a significant exothermic peak ranging from ca. 60 to 145 °C (peaking at 130.5 °C). The rest of weight loss occurred between 145 and 700 °C, which may primarily be due to the decomposition of H₂Ti₃O₇ or further TiO₂ and hydrated water, followed by the crystallization of the TiO₂ nanowires. As the temperature was increased to ~503.2 °C, a weak exothermic peak was noted, probably representing the crystallization that led to the formation of the TiO₂-B phase. Furthermore, an exothermic peak appeared at 647.8 °C, which was likely caused by the formation of the crystal structure of anatase phase. More specifically, the TG curve clearly demonstrates that there was a noticeable weight loss between 145 and 300 °C during the decomposition process, which presumably resulted from the dehydration of H₂Ti₃O₇, as typically represented by eqn (1).

\[
H₂Ti₃O₇ \rightarrow 3TiO₂ + H₂O \tag{1}
\]

According to eqn (1), the weight loss due to the H₂Ti₃O₇ transformation into TiO₂ should be 6.7%; however, the actual weight loss from room temperature to 300 °C was ~9% measured from the TG curve, which means that the content of the adsorbed water evaporated between 60 and 145 °C was about 2.3% in the TiO₂-precursor nanowires. At higher temperatures above 300 °C, the TG curve nearly leveled off due to the negligible weight loss during crystal growth and/or transformation of TiO₂ nanowires.

To determine the structure of crystalline phase(s) of the H₂Ti₃O₇/TiO₂ nanowires, we performed XRD on the TiO₂ (Sample A) (Figs. 3a, 3b, and 3c). The XRD pattern of the TiO₂ nanowires is shown in Fig. 3a. The XRD pattern of the TiO₂ nanowires is shown in Fig. 3a. As shown in Fig. 3a, the XRD pattern of the TiO₂ nanowires is shown in Fig. 3a. All the peaks in the XRD pattern of the TiO₂ nanowires are due to the anatase phase, which is in good agreement with the DTA results. The XRD pattern of the TiO₂ nanowires is shown in Fig. 3a. The XRD pattern of the TiO₂ nanowires is shown in Fig. 3a. The XRD pattern of the TiO₂ nanowires is shown in Fig. 3a. The XRD pattern of the TiO₂ nanowires is shown in Fig. 3a. The XRD pattern of the TiO₂ nanowires is shown in Fig. 3a. The XRD pattern of the TiO₂ nanowires is shown in Fig. 3a. The XRD pattern of the TiO₂ nanowires is shown in Fig. 3a. The XRD pattern of the TiO₂ nanowires is shown in Fig. 3a. The XRD pattern of the TiO₂ nanowires is shown in Fig. 3a. The XRD pattern of the TiO₂ nanowires is shown in Fig. 3a. The XRD pattern of the TiO₂ nanowires is shown in Fig. 3a.

Effect of post-heat treatment on crystalline structure of TiO₂ nanowires

To optimize the calcination temperature in the post-heat treatment, TG-DTA combined analysis was performed on the TiO₂ precursor nanowires, which are shown in Fig. 2. The initial weight loss until ca. 145 °C in the TG curve might be attributed to the evaporation of adsorbed water onto H₂Ti₃O₇; accordingly, the DTA curve showed a significant endothermic peak ranging from ca. 60 to 145 °C (peaking at 130.5 °C). The weight of nanowires remained nearly constant up to 250 °C in the TG curve nearly leveled off due to the negligible weight loss during crystal growth and/or transformation of TiO₂ nanowires. At higher temperatures above 300 °C, the TG curve nearly leveled off due to the negligible weight loss during crystal growth and/or transformation of TiO₂ nanowires. To determine the structure of crystalline phase(s) of the H₂Ti₃O₇/TiO₂ nanowires, we performed XRD on the TiO₂ (Sample A) (Fig. 3a), as well as on the TiO₂ nanowires obtained from calcinations of the TiO₂ precursor at 350 °C (Sample C), 450 °C (Sample D), 550 °C (Sample E) and 650 °C (Sample F) (Fig. 3b–e, respectively), as shown in Fig. 3. Fig. 3a indicates that the main crystallite of the precursor was the layered H₂Ti₃O₇ structure(s), which could be converted to a TiO₂ polymorph (TiO₂-B) upon post-heat treatments as shown in Fig. 3b; further, the broadening of the diffraction peaks of the TiO₂-precursor nanowires in Fig. 3a was presumably due to the small nanometer size of their crystallites, and/or to the bending of some atomic crystallographic plane(s) of the nanowires. Two new broad peaks emerged at 2θ values of 28.5° and 43.8°, revealing the collapse (i.e. destruction) of the layered structure(s) of hydrogen titanates and the formation of TiO₂-B (Fig. 3b and c). Compared with Fig. 3b and c, there

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**Fig. 1** Morphologies observed by FE-SEM of (a) the as-synthesized H₂Ti₃O₇ (precursor of TiO₂ nanowires) and the TiO₂ nanowires prepared from (b and d) the calcination and from (c and e) the hydrothermal treatment of the TiO₂ precursor nanowires at 250 °C for 2 h.

**Fig. 2** Typical TG-DTA curves of the H₂Ti₃O₇ (precursor of TiO₂) nanowires.
appeared a pronounced new peak at $2\theta = 37.721^\circ$ in Fig. 3d, which, matching the (004) lattice planes of anatase, indicates the transformation from TiO$_2$-B to anatase.$^{25,26}$ In addition, the obvious diffraction peaks at 25.221°, 36.861°, 37.721° and 38.641° in Fig. 3d, respectively, corresponded to the (101), (103), (004) and (112) lattice planes of anatase, indicating the coexistence of TiO$_2$-B and anatase at 550°C. These agree well with the TG-DTA observation (from Fig. 2) where a small exothermic peak located at 503.2°C occurred in the DTA curve, which is characteristic of the TiO$_2$-B crystal formation. Finally, with the further development of phase transformation upon an increase in the sintering temperature, as shown in Fig. 3e, the sharpened peak at 25.221° was attributable to the strongest reflection from lattice-plane (101) of the TiO$_2$-anatase phase, which suggests that Sample F primarily contained highly crystalline anatase.

In addition, Fig. 4 shows XRD patterns a and b of the TiO$_2$ nanowires prepared from different post-heat treatments (calcination and hydrothermal, respectively) of the TiO$_2$ precursor at 250°C for 2 h. The sharper diffraction peaks in Fig. 4b demonstrate that, in comparison to the calcination (Fig. 4a), the hydrothermal treatment was more favorable for the formation and growth of anatase crystals.

**Effect of post-heat treatment on UV-Vis absorption**

Fig. 5a shows the UV-Vis absorbance spectra of Samples C, D, E and F. The band gap energy ($E_g$) for direct gap semiconductors can be evaluated by using the Tauc equation,$^{27,28}$

$$ (\alpha E_p)^{0.5} = k(E_p - E_g) $$  \hspace{1cm} (2)

where $\alpha$ is the absorption coefficient, $E_p$ the discrete photon energy ($h\nu$), and $k$ absorption constants for indirect transitions.$^{29,30}$ Plots of $(\alpha E_p)^{0.5}$ versus $E_p$ for the TiO$_2$ nanowire membranes are shown in Fig. 5b; the corresponding $E_g$ values were 2.98, 2.94, 2.90 and 2.93 eV, respectively. When the temperature was increased from 350 to 550°C, the absorbance of UV and visible light was steadily enhanced (Fig. 5a). As shown in Fig. 3, the major crystalline phase of the TiO$_2$ nanowires prepared from calcination of the TiO$_2$ precursor at 350–550°C was TiO$_2$-B phase, with a small amount of anatase phase, and the content of anatase increased with an increase in the sintering temperature. Therefore, the increase in the absorption intensities of the TiO$_2$ nanowires can be attributed to the increase in the content of anatase phase, which is consistent with other studies.$^{2,5–8,15}$ With a further increase of the calcination temperature from 550 to 650°C, Sample F against Sample E possessed a significantly higher level of anatase (cf. Fig. 3e vs. d), nevertheless with a relative reduction in its specific surface area.
which results in decreases in the UV-Vis absorption intensities as shown in Fig. 5a (550°C vs. 650°C). Given that a higher calcination temperature induces an increase in the content of anatase while a decrease in the specific surface area, we can come to the conclusion that the higher UV-Vis absor- bances of Sample F than Sample E may be determined by the interactions of the two competing effects: that is, the effect of specific-surface-area decrease predominated over that of anatase-content increase.

The UV-Vis absorption spectra (Fig. 6a) were taken of the TiO2 nanowires obtained by the different post-heat treatments of the TiO2 precursor at 250°C, with Spectrum 1 representing the calcination and Spectrum 2 the hydrothermal treatment, from which the band-gap energy profiles were calculated (as shown in Fig. 6b). It is seen that, compared to the calcination method, the hydrothermal treatment of the TiO2 precursor resulted in a stronger light-absorption ability (Fig. 6a) and a narrower band gap (Fig. 6b) of the TiO2 nanowires, which could be attributed to a higher content of their highly crystalline anatase phase (Fig. 4) as well as their higher specific surface area (Fig. 1 and Table 1).

**Effect of post-heat treatment on photocatalytic activity of TiO2 nanowires**

The degradation curves (Fig. 7a), as well as kinetic curves (Fig. 7b) analyzed from Fig. 7a, of the TiO2 nanowires were measured by monitoring the photocatalytic degradation of the RhB aqueous solution with Samples C, D, E and F, respectively, as the photocatalysts. Prior to the measurements, the solution containing the catalyst sample was stirred at room temperature in the dark for 10 min to establish an adsorption/desorption equilibrium between the RhB-dye and the sample surfaces, and the photo-degradation efficiencies of the samples were found to be 44%, 50%, 85% and 64%, respectively. The kinetic analysis by Fig. 7b indicates that the photocatalytic reaction of Samples C, D and F followed a pseudo-first-order reaction, and the rate constants of RhB degradation by them were estimated to be 0.01127 min⁻¹, 0.01515 min⁻¹, and 0.03228 min⁻¹, respectively. It is notable that the photocatalytic activity of Sample E, exhibiting a maximum in the degradation efficiency, did not follow a pseudo-first-order mechanism. According to the previous studies, the photocatalytic activity of TiO2 can be identified as significant for aqueous pharmaceutical solutions interacting with nanomaterials through surface adsorption and photocatalytic degradation of the former by the latter; further, the surface adsorption for most of pharmaceuticals follows a pseudo-second-order model, whereas the photocatalytic degradation complies with a pseudo-first-order model. As held by the researchers, adsorption by TiO2 nanomaterials actually is not only surface adsorption behavior, which also depends on complicated factors such as surface charge of nanomaterials, adsorbent masses, ambient pH values, etc.; generally, the adsorptive capacity of TiO2 nanomaterials is nearly saturated during 30 min. But notably, the time intervals of adsorption/desorption equilibrium between the RhB-dye and the surfaces of Samples C, D, E and F were invariably 10 min in this study,

![Fig. 6](a) UV-Vis absorption spectra and (b) plots of $(\omega h \nu)^2$ vs. $h \nu$ for the TiO2 nanowires obtained by (1) the calcination and (2) the hydrothermal treatment of the H2Ti3O7 (precursor of TiO2) nanowires at 250°C for 2 h.

![Fig. 7](a) Degradation curves and (b) kinetic curves of a RhB aqueous solution of 5 mg L⁻¹ that is photocatalytically degraded by the TiO2 nanowires prepared from the calcinations of the H2Ti3O7 (precursor of TiO2) nanowires for 2 h at different temperatures of 350 (Sample C), 450 (Sample D), 550 (Sample E) and 650 °C (Sample F).
which indicates that it was possible for some kinds of samples (Samples C, D and F) to obtain an adsorption/desorption equilibrium in the 10 min, whereas that the other sample (Sample E) did not. Due to its unsaturated adsorptive capacity, the photocatalytic activity of Sample E after the treatment in the dark for 10 min might probably be determined by a coupling of the surface adsorption (ruled by the pseudo-second-order model) and the photocatalytic degradation (ruled by the pseudo-first-order model). The synergistic decoloration of the RhB aqueous solution by both the surface adsorption and the photocatalytic degradation resulted in the inappropriateness to plot linearly as a pseudo-first-order model. However, the data beyond 30 min shown in Fig. 7b, which reflects the near saturation of adsorptive capacity of Sample E, can be well fitted by the pseudo-first-order formula.

Again, degradation curves (Fig. 8a), and kinetic curves (Fig. 8b) obtained from Fig. 8a, were plotted to compare RhB degradation efficiencies by the TiO₂ nanowires obtained by the different post-heat treatments (calcinations vs. hydrothermal) of the TiO₂ precursor at 250 °C. Similarly, the hydrothermal kinetic plot of Sample G (Fig. 8b) was apparently nonlinear, the rationale behind which was also the synergistic decoloration of the RhB aqueous solution through both the surface adsorption and the photocatalytic degradation of RhB by Sample G. Compared to the calcination at 250 °C, the hydrothermal treatment at the same temperature led to a higher RhB degradation efficiency (60% vs. 38%), which was comparable to that (64%) of Sample F that was formed from calcination of the precursor at 650 °C. This probably is due to the fact that the sample treated with the hydrothermal method (Sample G) had a higher proportion of anatase phase (cf. Fig. 4) as well as a higher specific surface area (cf. Fig. 1 and Table 1), which favored an enhancement of photocatalytic activity relative to the calcinated sample (Sample B) (cf. Fig. 8).

Moreover, TEM and HRTEM were also used to study the fine structure of Sample G as shown in Fig. 9a and b, respectively. Fig. 9a unveils a typical morphology of the TiO₂ nanowires: the average diameter of the nanowire sample was approximately 60 nm; and the corresponding SAED (the inset in Fig. 9a) reveals that the TiO₂ nanowires had a near single crystal anatase structure, which was consistent with the XRD result (Pattern b of Fig. 4). Furthermore, the near single-crystalline structure was further confirmed by the HRTEM image (shown in Fig. 9b): Fig. 9b shows that the distance between adjacent lattice fringes was ca. 0.35 nm, which could be assigned to the interplanar spacing of the TiO₂ anatase (101).
planes; this corroborates the formation of anatase TiO$_2$ nanowires in our experiments.

In addition, as shown in Fig. 10, Sample G against Sample B had a remarkably higher ratio of the Ti and O combined content to the Na level; this suggests that the hydrothermal method, making the Na$^+$-ion impurity diffuse effectively into the water phase, increased the purity of the formed TiO$_2$ nanowires, which also contributed to the increase of their photocatalytic activity.

Conclusions

This work has detailed the synthesis of TiO$_2$ nanowires (membranes) on a titanium foil substrate via a three-step route: (1) hydrothermal growth of Na$_2$Ti$_3$O$_7$ from Ti substrate in a concentrated NaOH aqueous solution; (2) exchange of Na$^+$ ions with H$^+$ to form H$_2$Ti$_3$O$_7$; and (3) post-heat treatment (i.e. annealing) of the H$_2$Ti$_3$O$_7$ precursor by calcination at different temperatures (250, 350, 450, 550 and 650 °C) or by hydrothermal treatment (250 °C).

Morphological characterizations by the FE-SEM have revealed that the TiO$_2$ nanowires synthesized from the hydrothermal have a significantly smaller diameter and hence a higher specific surface area than those from the calcination. The TG-DTA, TEM and XRD results have indicated that a calcination temperature of ca. 550 °C maximally contributes to the formation and growth of anatase crystals with a relative reduction in the specific surface area of the TiO$_2$ nanowires, and that the hydrothermal favors an enhancement of TiO$_2$-nanowire crystallinity, especially for the anatase phase. UV-Vis absorption spectra and their associated band-gap energy profiles have uncovered that the TiO$_2$ nanowires, prepared from calcination of the TiO$_2$ precursor at 550 °C, have maxima in UV-Vis absorption intensities as well as the narrowest band-gap among those calcinated at the other temperatures. EDX spectrometry has demonstrated that, due to the diffusion of Na$^+$-impurity into the water phase, the hydrothermal forms much purer TiO$_2$ nanowires than the calcination.

The photocatalytic degradation of an RhB aqueous solution has been investigated by the TiO$_2$ nanowires synthesized from the calcination and the hydrothermal methods. Assays have demonstrated that the TiO$_2$ nanowires obtained by calcination at an optimum temperature of 550 °C exhibit a maximum in photocatalytic activity compared with the other TiO$_2$ nanowires calcinated at 350, 450 and 650 °C, presumably owing to a combination of the effects of anatase-content increase and of specific-surface-area decrease with increasing the calcination temperature. At the same temperature of 250 °C, the hydrothermal produces TiO$_2$ nanowires of markedly higher photocatalytic activity than the calcinations, primarily due to their significantly higher specific surface area, degree of crystallinity, and purity (from a much decreased Na$^+$-impurity content).

Acknowledgements

The authors gratefully acknowledge the financial support for this work from the State Key Development Program for Basic Research of China (Contract no. 2010CB635107), the National Natural Science Foundation of China (NSFC) (Contract no. 51004046, 51202064 and 51302073), the National Science Foundation of the Hubei province of China (Contract no. 2010CD05806), the Wuhan Youth Chenguang Program of Science and Technology (Contract no. 2013070104010016) and Middle-aged and Young program of Educational Commission of Hubei Province (Q20101409).

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