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Abstract

Anatase porous TiO2 nanowires were synthesized via simple in situ hydrothermal treatment of the amorphous anodic TiO2 nanotubes in urea aqueous solution at 70 ºC. The morphology transformation process was also analyzed so that hydroxide induced dissolution-recrystallization mechanism was proposed. Due to the coarse surface and porous structure, the porous TiO2 nanowires possess a large surface area of 267.56 m2g-1, which is almost 4 times higher than that of amorphous anodic TiO2 nanotubes. The photocatalytic properties of the porous TiO2 nanowires towards MB, phenol and Rhodamine 6G were investigated. The porous TiO2 nanowires display better photocatalytic activity than that of TiO2 nanotubes or Degussa P25. The enhanced photocatalytic activity is attributed to the porous structure and the large specific surface area. Such porous TiO2 nanowires maybe considered as an ideal photocatalyst for the rapid photodegradation of organic pollutant in water. Furthermore, this facile, low-cost and environmentally friendly method is highly expected to innovate the design and fabrication of highly photoactive porous TiO2 nanowires, which have potential applications in photocatalysis and solar energy conversion.

Full Text

Preamble

Porous TiO Nanowires Derived from Nanotubes: Synthesis, Characterization, and Their Enhanced Photocatalytic Properties

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Abstract

Anatase porous TiO nanowires were synthesized via simple in situ hydrothermal treatment of amorphous anodic TiO nanotubes in urea aqueous solution at 70 °C. The morphology transformation process was analyzed, leading to the proposal of a hydroxide-induced dissolution-recrystallization mechanism. Due to their coarse surface and porous structure, the porous TiO nanowires possess a large surface area of 267.56 m^{2}g ^{1}, which is almost four times higher than that of amorphous anodic TiO nanotubes. The photocatalytic properties of the porous TiO nanowires toward methylene blue (MB), phenol, and Rhodamine 6G were investigated. The porous TiO nanowires display superior photocatalytic activity compared to TiO nanotubes or Degussa P25. The enhanced photocatalytic activity is attributed to the porous structure and large specific surface area. Such porous TiO nanowires may be considered ideal photocatalysts for the rapid photodegradation of organic pollutants in water. Furthermore, this facile, low-cost, and environmentally friendly method is highly expected to innovate the design and fabrication of highly photoactive porous TiO nanowires, which have potential applications in photocatalysis and solar energy conversion.

Keywords: TiO ; porous nanowires; structure transformation; dissolution-recrystallization; photocatalytic activity

1. Introduction

Titanium dioxide (TiO), as one of the most commonly used semiconductor materials, has attracted considerable attention due to its unique photoinduced activity for applications in photocatalysis, environmental pollution control, and solar energy conversion. Since these reactions typically occur on the TiO surface, the material properties are strongly related to surface area and local microstructures. Consequently, nanoscale TiO with large surface area and specific morphology has attracted great interest. To date, many methods—including anodization, template techniques, hydrothermal processes, and soft chemical processes—have been used to synthesize TiO nanomaterials with high photocatalytic activity. Among these synthesis strategies, the electrochemical anodization process has been widely utilized as a facile, inexpensive, and straightforward method for large-scale preparation of TiO nanotubes with controllable size and morphology. However, the smooth surface, relatively low surface area, and amorphous structure of the resulting anodic TiO nanotubes lead to low light utilization efficiency and poor photogenerated charge separation efficiency, thus resulting in poor photocatalytic activity.

Many efforts have been made to enhance the photocatalytic activity of anodic TiO nanotubes. For example, annealing anodic TiO nanotubes in air converts the amorphous TiO into anatase, which efficiently enhances photocatalytic performance. Decorating anodic TiO nanotubes with other materials, such as noble metals and other semiconductors, can also improve photocatalytic performance. However, these methods are expensive and energy-intensive. Recently, considerable efforts have shifted toward architecting one-dimensional TiO hierarchical nanostructures derived from TiO nanotubes. By adjusting the phase and microstructure of the anodic TiO nanotubes, desired high photocatalytic activity can be achieved. For instance, through a derivative anodic method, tube-in-tube TiO nanostructures possessing high surface area were synthesized, which showed enhanced photocatalytic performance. Hierarchical TiO nanotubes obtained via chemical etching of anodic TiO nanotubes exhibited high photocatalytic activity due to their good crystallinity. Despite these significant contributions from many groups, developing strategies for constructing anodic TiO nanotubes with high surface area and anatase phase remains an attractive ongoing task.

Herein, we demonstrate the synthesis of porous TiO nanowires composed of anatase TiO nanoparticles at low temperature via in situ hydrothermal treatment of amorphous anodic TiO nanotube arrays. Due to their coarse surface and porous structure, the porous TiO nanowires possess a large surface area of 267.56 m^{2}g^{1}, which is almost four times higher than that of amorphous anodic TiO nanotubes. The anatase porous structure and large surface area of the porous TiO nanowires lead to great enhancement in the photodegradation of organic pollutants. The photodegradation rate of the organic pollutant methylene blue (MB) under UV irradiation from the porous TiO nanowires is 4.5 times faster than that from amorphous TiO nanotubes and even higher than that from Degussa P25. In addition, the porous TiO nanowires exhibit high photocatalytic activity in degrading phenol and Rhodamine 6G (R6G) as well. This facile, cost-effective, and environmentally friendly method is anticipated to innovate the fabrication of highly photoactive porous TiO nanowires, which have potential applications in environmental remediation and solar energy conversion.

2. Experimental

All reagents were commercially available from Sinopharm Chemical Reagent Co., Ltd (China) with analytical grade and were used without further purification. Degussa P25 TiO (80% anatase and 20% rutile) was purchased from Guangzhou Huali Sen Trading Co., Ltd. The average particle size of P25 is 21 nm, and its specific surface area is 45.96 m^2/g.

The synthesis of porous TiO nanowires was divided into two steps. First, TiO nanotubes were fabricated by anodizing a pure Ti sheet as described previously. In brief, a high-purity (99.999%) titanium plate was anodized in a mixed electrolyte of ethylene glycol and ammonium fluoride (0.1 M) for 4 h. The anodizing voltage was 60 V, and the electrolyte temperature was maintained at 20 °C. Subsequently, the sample was rinsed with deionized water. Then, the as-fabricated TiO nanotubes were placed in a vessel containing 0.1 M urea solution (100 mL). After heating at 70 °C for 10 h, white plates were collected from the solution. The as-prepared porous TiO nanowires were washed with deionized water and dried in air.

Anatase TiO nanotubes were synthesized by annealing the as-prepared anodic TiO nanotubes at 500 °C for 2 hours.

The morphologies of the samples were examined by field-emission scanning electron microscopy (FE-SEM; FEI Sirion-200) and high-resolution transmission electron microscopy (HRTEM; JEM-2010). The crystal structure of the samples was determined by X-ray diffraction (XRD, Philips X' pert PRO) with Cu K radiation.

The photocatalytic activities of the various samples were evaluated based on the removal of simulated organic pollutants, such as methylene blue (MB), phenol, and R6G in solution. In a typical photocatalytic experiment, 50 mL of aqueous solution containing a certain amount of simulated organic pollutants and the as-synthesized product (30 mg) detached from Ti foil, as catalyst, was maintained in suspension by a magnetic stirrer. A 150 W high-pressure mercury lamp with maximum emission at 365 nm was positioned about 10 cm above the photoreactor. Prior to irradiation, the suspension was ultrasonicated for 3 min and magnetically stirred for 1 h in the dark to ensure adsorption-desorption equilibration. Then, UV light was turned on.

At given time intervals, 4 mL of solution was taken from the suspension and centrifuged at 10,000 rpm for 5 min to remove catalysts. The concentrations of MB, phenol, and R6G were monitored by UV-vis spectroscopy (CARY-5E).

3.1. Structure of the Porous TiO Nanowires

Figure 1a [Figure 1: see original paper] and 1b show the top-view and cross-sectional SEM images of the anodic TiO nanotubes. The open mouth and closed end of the tubes with approximately 165 nm outer diameters can be clearly observed. Moreover, the inner diameters of the nanotubes at the top side are larger than those at the bottom side, indicating the tapered hollow structure of the nanotubes. After urea treatment, the open mouth disappears, as shown in the top-view SEM image in Figure 1c, and the treatment causes formation of a rough surface, as shown in Figure 1d. The cross-sectional images of treated products in Figure 1e and 1f show disappearance of the tube-like structure.

TEM was also employed to characterize the samples before and after urea treatment. Figure 2a [Figure 2: see original paper] shows a typical TEM image of the anodic TiO nanotubes, demonstrating a diameter of 160 nm, which is in agreement with the SEM results. The corresponding selected area electron diffraction pattern (SAED) (the inset of Figure 2a) indicates the amorphous structure of the anodic TiO nanotubes. TEM images of urea-treated products are shown in Figure 2b. Surprisingly, it is very clear that the tube-like structure is transformed to rough porous nanowires after urea treatment. Furthermore, it can be observed that the obtained nanowires are composed of nanoparticles. The SAED pattern shown in the inset of Figure 2b presents series of concentric rings with different radii, indicating the polycrystalline nature of the porous TiO nanowires. The HRTEM image shown in Figure 2c shows that the fringe spacings are 0.47 nm and 0.35 nm, respectively, which match well with those of the lattice space of (002) and (101) of anatase TiO. Figure 2d shows the representative EDS spectra of porous nanowires.

The corresponding XRD pattern of the TiO nanotubes and porous TiO nanowires is also presented. For TiO nanotubes, no diffraction peak was observed, which is in agreement with the SAED result. However, all of the diffraction peaks should be indexed to TiO anatase (JCPDS File 89-4203) after urea treatment, and the amorphous TiO could be changed to crystalline TiO. More importantly, the tube-like structures are turned into anatase porous TiO nanowires. Previous reports indicated that amorphous anodic TiO nanotubes always need to be calcined at about 500 °C in air to achieve anatase polycrystalline structure. In contrast, the amorphous anodic TiO nanotubes can be conveniently transformed to anatase porous nanowires at a temperature as low as 70 °C in the present experiments.

3.2. Structure Change Mechanism

To study the morphological evolution from TiO nanotubes to porous TiO nanowires, time-dependent experiments were performed. Figure 3 [Figure 3: see original paper] shows the products prepared at different growth stages, with the left, middle, and right columns corresponding to top-side SEM images, lower-part SEM images, and TEM images, respectively. Initially, the TiO nanotubes as the precursor were added into urea solution at 70 °C. Figure 3a presents the morphology of TiO nanotubes, as described previously, in which the nanotubular structure and smooth surface wall can be clearly observed. Although the TiO nanotubes retain their nanotubular structure after 2 h, the open mouth becomes smaller both at the top side (left in Figure 3b) and lower part (middle in Figure 3b). As seen from the corresponding TEM image (right in Figure 3b), the smooth nanotubes turned into rough and porous nanotubes composed of nanoparticles. When the treatment time was prolonged to 4 h, the open mouths of the nanotubes at the top side could still be observed, but the diameter of the open mouths decreased (left in Figure 3c); at the lower part, the former open mouths were closed, indicating the formation of nanowires (middle in Figure 3c). Interestingly, the corresponding TEM image (right in Figure 3c) shows the combination of porous nanotube and porous nanowire structures. As the reaction time was further prolonged to 6 h, it can be found that at both the top side and lower part (left and middle in Figure 3d), the open mouths disappear, and the corresponding TEM image (right in Figure 3d) also illustrates the nanowire structure.

3.3. Growth Mechanism

Based on the above experimental results and analysis, we propose that the morphology evolution of the porous TiO nanowires could be attributable to a dissolution-recrystallization process, as shown in Figure 4 [Figure 4: see original paper]. It is well known that TiO is an amphoteric oxide; besides acid solution, it can also slightly dissolve in alkaline solutions. In our case, the TiO nanotubes were immersed into urea solution (shown in Figure 4a). When the solution was heated at 70 °C, hydroxyl ions could be generated because of hydrolysis of the urea, resulting in alkalization of the solution. In heated solutions, the surface atoms of TiO nanotubes would first react with hydroxyl ions to form TiO^{2}, as described in Equation 1. As the dissolution of TiO nanotube walls continues, the OH inside the nanotube is consumed faster than that outside the nanotube because the OH inside the nanotube is difficult to exchange with that outside the nanotubes due to confinement by the nanoscaled hole of the nanotube. When the concentration of OH inside the nanotube decreases to a certain value, TiO^{2} undergoes a hydrolytic reaction to transform into TiO, as shown in Equation 2. The recrystallized TiO spontaneously nucleates onto the residual nanotube frame, which can provide many high-energy sites for nanocrystallites (shown in Figure 4b, 3b). As the etching proceeds, more and more TiO nuclei can be formed and grow within the nanotubes. As a result of the etching of the TiO frames and the formation and growth of TiO nanocrystallites, the inner space of the nanotube was gradually occupied by TiO nanocrystallites, and the diameter of the nanotube gradually decreased. As described previously, the as-prepared TiO nanotubes possess a tapered hollow structure; thus, the narrow part at the bottom would be fully occupied by TiO nanocrystallites and would first transform to porous nanowires while the upper part remains nanotubular morphology (as shown in Figure 4c, 3c). However, the reaction will not stop in that TiO prefers to nucleate and grow on the upper part after the bottom part is fully occupied. With increasing reaction time, the upper part of TiO nanotubes would become filled with TiO nanocrystals, and the whole nanotube would finally transform into nanowires composed of TiO nanocrystals (Figure 4d, 3d).

$TiO + 2OH \rightarrow TiO^{2}$

3.4. N Adsorption-Desorption Analysis

The microstructure of the porous TiO nanowires was further characterized using N adsorption/desorption isotherms. Figure 5a [Figure 5: see original paper] and 5b present the nitrogen adsorption-desorption isotherms and BJH pore size distribution curves of the TiO nanotubes and porous TiO nanowires. Both samples exhibited a type IV isotherm with a type H3 hysteresis loop (according to IUPAC classification), typical of mesoporous materials. The pore size distribution of the TiO nanotubes shows a bi-modal size distribution, with smaller sizes peaking at 20 nm and larger sizes at 100 nm. The smaller mesopores can be related to pores formed between stacked nanotubes, while larger mesopores reflect the hollow structure of the nanotubes. The pore size of the porous TiO nanowires also exhibits two distributions, with smaller sizes peaking at sub-2 nm and larger sizes at 20 nm. The larger mesopores can also be related to pores formed between stacked nanowires, and the smaller mesopores would be attributed to the stacking of nanoparticles within nanowires. The nanoholes within nanotubes are occupied by nanoparticles due to the urea treatment. As a result, the pore size peak at 100 nm within porous TiO nanowires vanishes while a peak at 10 nm appears, which further confirms the SEM and TEM results. The BET specific surface area and pore volume of the porous TiO nanowires are determined to be 267.56 m^{2}g ^{1} and 0.31 cm^{3}g ^{1}, respectively, which are significantly higher than the values of porous TiO nanowires (70.28 m^{2}g ^{1} and 0.12 cm^{3}g ^{1}). Hence, the porous TiO nanowires could be considered a promising photocatalytic candidate for water treatment thanks to their high BET surface area, high pore volume, and ideal pore size distribution.

3.5. Optical Properties

The optical properties of the porous TiO nanowires and TiO nanotubes were investigated by UV-vis diffuse reflectance spectra (Figure 6 [Figure 6: see original paper]). It can be seen that there is a small peak at 474 nm within the spectrum of the TiO nanotubes, while no peak can be observed for the porous TiO nanowires, indicating the color change from brown to white. Furthermore, compared to TiO nanotubes, the porous TiO nanowires showed higher UV light absorption. Obviously, the UV-vis absorption is considerably affected by the morphological changes, and the rough surface and porous structure of the porous TiO nanowires can allow multiple reflections of UV light, which enhances light-harvesting and thus increases the quantity of photogenerated electrons and holes available to participate in the photocatalytic decomposition process.

3.6. Photocatalytic Activity

As far as TiO photocatalyst is concerned, the anatase phase and surface area are the most important criteria. High photocatalytic efficiency of the porous TiO nanowires could be expected due to the anatase phase and high surface area. To demonstrate the functionality of the as-fabricated porous TiO nanowires, their photocatalytic activity was evaluated based on the removal of methylene blue (MB) dye in aqueous solution. For comparison, the photocatalytic activities of amorphous TiO nanotubes, anatase TiO nanotubes, and P25 particles were also investigated. Figure 7a [Figure 7: see original paper] displays the variation of photocatalytic activity of different samples determined at the maximal absorption wavelength of MB (664 nm) with irradiation time. As expected, the porous TiO nanowires exhibit superior photocatalytic performance compared to other photocatalysts. MB is almost completely photodegraded by the porous TiO nanowires within 80 minutes, while 40%, 75%, and 90% of MB are removed by amorphous TiO nanotubes, anatase TiO nanotubes, and P25, respectively.

As shown in Figure 7b, the MB photodegradation kinetics of various photocatalysts were also investigated. After plotting the natural logarithm of residual phenol concentration versus UV irradiation time, the linear relationship of ln(C /C) versus time shows that the photoelectrocatalytic degradation of MB follows pseudo-first-order kinetics: ln(C /C) = kt, where C /C is the normalized MB concentration, t is the reaction time, and k is the apparent reaction rate in min ^{1}. The apparent photodegradation rate constant by the porous TiO nanowires is 0.0426 min ^{1}, which is 4.35 times greater than that of amorphous TiO nanotubes (0.0098 min ^{1}), 2.18 times greater than that of anatase TiO nanotubes (0.0195 min ^{1}), and 1.26 times greater than that of P25 (0.0337 min ^{1}). Besides MB, phenol and R6G with a concentration of 15 mg L ^{1} were also employed to evaluate the photocatalytic activity of the porous TiO nanowires. From Figure 8a [Figure 8: see original paper] and 8b, it is clear that toward phenol and R6G, the porous TiO nanowires also exhibit higher photocatalytic performance than other samples. Both phenol and R6G can be completely photodegraded by the porous TiO nanowires within 30 minutes. Such dramatic enhancement of catalytic activity can be attributed to synergistic effects of morphology and structure transformation. First, the anatase structure of porous TiO nanowires facilitates electron transfer from bulk to surface, thus inhibiting their recombination with photoinduced holes and leading to higher quantum efficiency. Meanwhile, the porous TiO nanowires possess much higher BET surface area than TiO nanotubes, and the increased surface area can provide more active catalytic sites.

Furthermore, the porous structure of TiO nanowires with smaller textural mesopores and larger pore volume would provide transport pathways for reactant substances of different sizes compared to those in an open medium, and expedite mass transportation. In addition, the compact stacked nanoparticles within porous TiO nanowires can allow multiple reflections of UV light, which enhances light-harvesting and thus increases the quantity of photogenerated electrons and holes available to participate in the photocatalytic degradation of organic pollutants. These factors are beneficial for forming more surface hydroxyl radicals to enhance the photocatalytic degradation of phenol. Additionally, based on the well-known fact that anatase phase TiO possesses higher photocatalytic activity than amorphous TiO , the anatase phase characteristics of the present porous TiO nanowires after urea treatment exhibit superior photocatalytic behavior. Therefore, it can be concluded that porous TiO nanowires can serve as excellent photocatalysts.

The renewable photocatalytic activity must be investigated because reuse performance is also a key factor for the applications of photocatalytic materials. The result is presented in Figure 9 [Figure 9: see original paper], from which we can see that the photocatalytic activity of the porous TiO nanowires is very stable. Even after 5 cycles under UV irradiation, more than 90% of MB was degraded within 80 min, indicating that the porous TiO nanowires are stable and effective for the removal of organic pollutants in water. Obviously, the porous TiO nanowires prepared in our experiments are a promising photocatalyst due to their excellent activity and good recycling performance.

4. Conclusions

In conclusion, anatase porous TiO nanowires have been produced spontaneously from anodized amorphous TiO nanotubes in urea solution at a temperature as low as 70 °C. The phase and morphology transformation process of the TiO nanotubes were characterized, and a mechanism of hydroxide-induced dissolution and recrystallization is proposed. Due to the hydrolysis of urea, the amorphous TiO nanotube walls can be gradually etched by hydroxyl ions and dissolved. When the concentration of OH inside the nanotubes decreases to a threshold value, the dissolved TiO can recrystallize from solution and nucleate onto the residual nanotube frame and grow within the nanotubes. During the dissolution-recrystallization process, more and more TiO nuclei are formed and grow within the nanotubes, finally filling the inner space of nanotubes to yield anatase porous TiO nanowires. The surface area of porous TiO nanowires reaches 267.56 m^2g^{1}, which is almost four times higher than that of TiO nanotubes. The photodegradation rate of the organic pollutant methylene blue (MB) under UV irradiation by the porous TiO nanowires is 4.35 times higher than that of the TiO nanotubes and much higher than that of Degussa P25. Besides degrading MB, the porous TiO nanowires also exhibit high photocatalytic activity in degrading phenol and R6G. The enhanced photocatalytic activity achieved from the porous TiO nanowires is ascribed to the porous structure and large surface area. The results demonstrate a facile and practical route for designing and architecting highly photoactive one-dimensional TiO -based porous functional materials, which have potential use in photocatalysis and solar energy conversion.

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Figures

Figure 1. SEM images of TiO nanotubes and porous TiO nanowires: (a, b) top-view of the anodic TiO nanotubes, (b) cross-section and surface view of the bottom side of the anodic TiO nanotubes, (c) top-view of the porous TiO nanowires, (d) cross-section images of the porous TiO nanowires (the inset is the enlarged image), (e) high and (f) low magnification cross-section and surface view of the porous TiO nanowires.

Figure 2. (a) TEM image of a single TiO nanotube (inset is the corresponding SAED), (b) TEM image of the porous TiO nanowires (inset is the corresponding SAED), (c) HRTEM image of the porous TiO nanowires, (d) EDS of the porous TiO nanowires, (e) XRD pattern of the TiO nanotubes and porous nanowires.

Figure 3. Morphology transformation from the TiO nanotubes at different reaction times: (a) 0 h; (b) 2 h; (c) 4 h; (d) 6 h. The left and middle columns show the SEM images of the top and lower part, while the third column shows the corresponding TEM images of TiO nanostructures.

Figure 4. Schematic illustration of the morphological transformation from the TiO nanotubes to the porous nanowires.

Figure 5. (a) N adsorption-desorption isotherm of the TiO nanotubes and porous TiO nanowires, and (b) the corresponding pore size distribution.

Figure 6. UV-vis absorption spectrum of the TiO nanotubes and porous TiO nanowires.

Figure 7. (a) The variation of photocatalytic degradation ratio of MB over the porous TiO nanowires, amorphous TiO nanotubes, anatase TiO nanotubes, P25, and self-fading, (b) the pseudo first-order kinetic rate plots for the photodegradation of MB.

Figure 8. The variation of photocatalytic degradation of phenol (a) and R6G (b) over the porous TiO nanowires, anatase TiO nanotubes, amorphous TiO nanotubes, P25, and self-degradation with time of irradiation.

Figure 9. Cyclic degradation of MB by porous TiO nanowires.

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