Electrospun mesoporous titanium dioxide fibers

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Received 5 December 2003; accepted 27 December 2003

Abstract

There is growing interest in new ways to configure titanium dioxide (TiO2) as new applications emerge such as in photovoltaics and catalysis. A method has been developed for the preparation of mesoporous TiO2 fibers using electrostatic deposition. The mesoporous metal oxide fibers were prepared using Pluronic 123 as the template. The fibers contain anatase crystallized in the pore walls which transforms to rutile upon calcination above 800 °C. The electrospun fibers were evaluated for the photodecomposition of phenol and formic acid.

Keywords: Mesoporous molecular sieves; Titanium dioxide; Electrospinning; Fibers; Photocatalysis

1. Introduction

Titanium dioxide (TiO2) is widely studied for its potential applications in catalysis, sensors and high performance photovoltaics. Composites of TiO2 with efficient electron donor materials and dye sensitizers are widely used to increase the light harvesting capability of donor–acceptor systems [1–7]. For many of these applications, either commercially available crystalline TiO2 in the form of anatase is composited with desired photovoltaic material or titanium dioxide is prepared from its precursors. Dimensionality becomes a crucial factor in determining the properties of nanomaterials including surface area. Therefore, efforts have been made to decrease the particle size of porous or dense forms of titania [8–11].

Nanocrystalline TiO2 was prepared electrolytically from pure titanium in an acetylacetone and ethanol solution [8]. Nanocrystalline TiO2 powders have been produced at room temperature from poly-peroxotitanic acid gel. In addition to nanoparticles, there may be advantages for preparing TiO2 as high surface area fibers. Titania nanoribbons with a size range of 30–200 nm have been prepared hydrothermally from amorphous titania or titanium precursors in a basic medium [9]. Titania nanofibers have also been electrospun from titanium isopropoxide mixed with acetic acid and high molecular weight polyvinylpyrrolidone (PVP) to form amorphous titania nanofibers [12]. Amorphous titania films with micrometer sized pores has also been formed by electrostatic sol-spray deposition (ESSD) using titanium isopropoxide [13]. Although there has been progress in fabricating dense TiO2 in various configurations as explained above, there has been little reported regarding the morphogenesis of mesoporous TiO2 molecular sieves.

Transition metal oxides have been prepared in mesoporous forms using the amphiphilic surfactant templates such as triblock co-polymers, ionic surfactants such as cetyltrimethyl ammonium bromide (CTAB) and neutral amines [14–18]. The surfactant templated syntheses produce ordered periodic structures with thermally stable, high surface area porous frameworks. Mesoporous TiO2 has been prepared as bulk powders and films [14–21]. We have now combined the methodology for forming mesoporous TiO2 with the technique of electrospinning to produce mesoporous titanium...
dioxide fibers. Electrospinning involves the application of a high voltage to a viscous precursor gel which then traverses some distance to an oppositely charged conductive surface. As the resulting jet travels towards the grounded target, fibers form and deposit on the substrate of choice. This technique is well established for producing polymer fibers [22–26]. Only recently have we discovered how to apply this technique to the production of mesoporous SBA-15 and DAM-1 silica fibers [27] as well as molecular sieve/polymer composites [28]. Herein we report the preparation of mesoporous titanium dioxide fibers by electrospinning. These fibers have been fully characterized using microscopy and vibrational spectroscopy which indicate that the mesoporous TiO₂ fibers crystallize as anatase. These fibers can be converted to the rutile form upon heating with out loss in fiber structure.

2. Experimental

2.1. Synthesis

The precursor gel for electrospinning TiO₂ fibers was prepared by the hydrolysis and condensation of Ti(OC₄H₉)₄ around the micelles formed by the triblock co-polymer surfactant P-123 (EO₉₀PO₇₀EO₉₀) (BASF) in the presence of concentrated hydrochloric acid. In a typical gel preparation, 2 g of pluronic P-123 was dissolved in 4 g of ethanol. In a separate beaker, 3.56 g of Ti(OC₄H₉)₄ (Chemat Inc.) was suspended in a solution of 2 g ethanol and 0.6 g concentrated HCl. This suspension was added to the ethanolic solution of P-123 followed by stirring at room temperature for ~15 min. The molar ratios of the gel were 0.0037 P-123:0.016 HCl:0.13 EtOH:0.01 Ti(OC₄H₉)₄. The clear, pale yellow precursor gel was heated at 45–50 °C for ~24 h to obtain a gel with a viscosity of 3750 cp optimum for electrospinning. The viscosity was determined at RT using a spindle speed of 1 rpm.

A 3 ml polypropylene syringe barrel, which is part of the nitrogen (~4 psi) driven fluid dispensing system (EFD 1500 XL), was charged with the precursor gel. A high voltage of 20 kV was then applied to a 22 gauge, flat tip needle and a jet formed resulting in fibers deposited on grounded aluminum foil target at a distance of 23 cm from the syringe. The fibers obtained were heated at 130 °C overnight to facilitate further condensation of the structure followed by calcination at 400 and 600 °C at a rate of 50 °C/h to remove the P-123 template. The fibers were further calcined up to 900 °C to evaluate the phase transformation from anatase to rutile.

The morphology and dimensions of the fibers were characterized by a Philips XL30 scanning electron microscope (SEM) using Au/Pd coated samples. X-ray diffraction (XRD) patterns were obtained using a Scin- tag XDS 2000 diffractometer with a Cu Kα radiation. The fibers were also characterized by Raman spectroscopy using a Perkin–Elmer FT-Raman GX spectrometer. A Brookfield digital viscometer was used to measure viscosity. Surface area measurements were made using a Quantachrome Autosorb-1.

2.2. Photocatalytic experiment

2.2.1. Differential reactor

The suspension for reaction was prepared by dispersing ultrasonically the mixture of 0.0650 g powdered Titania fibers (commercial Degussa P25 TiO₂ and Hombikat UV 100 TiO₂, used for comparison), 0.65 mmol phenol (Fisher, reagent grade) or 6.5 mmol formic acid (Fisher, 88%), and 650 ml distilled water for half an hour in an ultrasonic bath (Elma, Ultrasonic LC20H) and the suspension was stirred for half an hour afterwards.

The photocatalytic oxidation of phenol and formic acid in catalyst suspensions was carried out in a 445 mm-long 64 mm-in-outer-diameter annular borosilicate vessel (Ace Glass) with a quartz immersion well (Ace Glass, 49 mm O.D., 7854-27). The 6 mm-thick reaction zone can minimize the influence of light transfer resistance on the catalysts’ activities. The UV radiation source was a 450W medium-pressure mercury vapor quartz lamp (Jelight, J05PM1HGC2). A Pyrex filter (Ace glass, No. 7740) filtered out the far- and mid-UV bands (λ < 320 nm) of the lamp emission spectrum. The cooling water flowing through the double-walled immersion well eliminated the infrared spectrum of the light. The local light intensities at different locations along the outer wall of the reactor and the outer wall of the cooling jacket were measured for each catalyst with a detector (International Light, Inc., Model SED033 #3435) connected to a radiometer (International Light, Inc., Model IL 1700). The suspension temperature was maintained at 31.0±0.5 °C. The length of reaction zone was adjusted to 115 mm using aluminum foil on the Pyrex filter and black electric tape on the outer wall of the cooling jacket. The lamp was preheated for 5 min before each experiment for obviating the poor irradiation of the lamp in the first several minutes. The suspension was stirred magnetically and 500 ml/min of oxygen (Wright Brothers, 99.5%) was sparged into the solution from a gas distributor near the bottom of the reactor. The samples (5 ml) of reaction suspension were collected with a syringe at different intervals and filtered with Cameo 25P polypropylene syringe filters (OS-MONICS, Cat# DDP02T2550). At the same time, 5 ml original suspension was added to keep the volume of suspension in the reactor constant. The sample solutions were analyzed with a total organic carbon Analyzer (TOC-VCSH, Shimadzu).
2.2.2. Bulk reactor

The suspension for reaction was prepared by sonicating a mixture of 0.180 g of the powdered Titania fibers or the comparison TiO₂ catalysts, 0.100 g phenol, and 800 ml distilled water with the same procedure as above. The photocatalytic experiments were carried out in a traditional annular quartz liquid-phase photocatalytic reactor (Ace glass, Inc., No. 7840) with the same quartz immersion well as above. The immersion-type UV radiation source was a 200 W medium-pressure mercury vapor quartz lamp (Jelight, J05PM1HGC1). The suspension was stirred magnetically and the reactor was put in a water bath, which maintained the suspension temperature at 32.5 ± 0.5 °C. 500 ml/min of oxygen was sparged into the solution from a gas distributor near the bottom of the reactor. The pH of the reaction suspension was not adjusted. The samples of reaction suspension were taken, filtered, and analyzed in the same way as above.

3. Results and discussion

The preparation of the precursor gels for electrosprinning can be a challenge because ideally one would like to have a clear viscous gel. Many of the metal oxide precursors begin to hydrolyze in the gel and start to precipitate. So for example in the case of TiO₂, the possible precursors titanium isopropoxide, titanium ethoxide and titanium chloride were too difficult to work with because solids would precipitate before the gel could be electrospun. Therefore, we employed the less reactive titanium tetrabutoxide as the source of titania. Additionally, the metal alkoxide was dispersed in an ethanol/HCl solution versus just water to better control the rate of hydrolysis. In the present study we employed the triblock co-polymer pluronic P-123 as a template. This is the same template employed to make the mesoporous molecular sieve SBA-15. Once a clear viscous gel was obtained it was transferred to a syringe with an electrical contact made to the needle. Another electrode is established at a distance of 23 cm from the needle. This can be almost any conductive surface but typically aluminum foil works fine. When an electrical potential is applied to the precursor gel, the gel starts to form a Taylor cone which further elongates and starts to whip (move in a zig-zag path towards the target) owing to the instability of the jet. This cone eventually reaches the target by constantly increasing the perimeter of the cone, ultimately depositing as a mesh of fibers on the target. Interestingly, the TiO₂ fibers formed so well that webs of fibers were generated almost everywhere in close proximity to the aluminum foil as shown in Fig. 1. This digital image of TiO₂ fibers, recorded after electrosprinning for only a few minutes, reveals that mesoporous TiO₂ spider webs are formed that can actually be handled with a pair of tweezers.

At RT temperature the condensation of the TiO₂ molecular sieves is only partially complete. Therefore, the fibers are generally heated at 130 °C to improve the degree of condensation. This heat treatment does not alter the appearance of the fibers. The fibers were also calcined at 400 and 600 °C to remove the Pluronic P-123. Fig. 2a shows the SEM images of the fibers before calcination. The average diameter of the fibers was ~600–700 nm. After calcination at 400 °C (Fig. 2b) the fibers remained intact but there was a slight decrease in the diameter reflecting further condensation and loss of template.

Powder X-ray diffraction patterns were taken from the fibers at low angle to assess the mesopore structure and at higher angles to evaluate the wall crystallinity, after calcination. The XRD pattern of the fibers heated to 350 °C at low angle shows a very weak peak corresponding to a \( d_{(100)} \)-spacing of 119 Å (Fig. 3). The quality of this XRD pattern may suggest that the mesoporous TiO₂ is not highly ordered. A mesoporous titania thin film prepared using P-123 as the surfactant was reported to have \( d \)-spacing up to 107 Å with the mesostructure stable up to 250 °C [14]. So it is possible that there was some collapse of the pore structure upon calcination. Heating the fibers to 400 °C results in a surface area of 199 m²/g and a pore size of 3.7 nm as shown in Fig. 4. Heating the fibers further to 600 °C reduces the surface area to 32 m²/g which shows that the framework is not stable to high temperature calcinations. Another report of mesoporous TiO₂ using P-123 as the surfactant and titanium tetra ethoxide as the titanium source suggested a worm hole type of pore structure with anatase present in the films [16]. Therefore, it is possible that wormholes are also present in these fibers.

In the case of electrospun SBA-15 and DAM-1, as the gel exits the syringe needle, the self assembled regions in the gel start to dry as nanosized clusters which have well

![Fig. 1. Digital image of TiO₂ fibers during electrostatic deposition.](image-url)
aligned pores or wormholes. As the jet containing these nanoclusters begins to whip back and forth the clusters lose registry but condense further. Then as they deposit on the target, fibers form that are composed of these randomly ordered clusters possibly with some amorphous material intermixed. Preliminary TEM results (not shown) indicate that these clusters appear to be on the order of 5–10 nm.

Unlike the mesoporous silica molecular sieves, the TiO\textsubscript{2} compositions tend to exhibit crystallinity in the pore walls. Fig. 3b shows the XRD patterns recorded at higher angles for the electrospun fibers as well as a commercial sample of anatase (Aldrich). The observed reflections at d-spacings of 3.54, 2.38, and 1.89 for the fiber samples correspond well to the (101), (004), and (200) reflections of anatase respectively. Therefore, one might conclude that anatase is crystallized in the mesopore walls. However, one cannot rule out the possibility that some dense TiO\textsubscript{2} crystals are also present. Raman spectra were also obtained for the fibers and commercial anatase which confirm the presence of anatase in the fibers. Fig. 5 shows the Raman spectra obtained for pure anatase and the TiO\textsubscript{2} fibers which match quite well.

The fibers were calcined to 900 °C to further evaluate the stability and the possible phase transformation of anatase. Fig. 6a shows the XRD patterns of the calcined sample at different temperatures and the evolution of the rutile phase beyond 700 °C. After calcination at 800 °C the intensity of (101) and (200) peaks belonging to anatase can be seen to decrease with the slow evolution of rutile. Beyond 800 °C the major portion of the sample is converted to rutile with a small residual (101) peak for anatase. These new reflections can be indexed to (110), (101), (200), (111), and (210) reflections of the rutile form of TiO\textsubscript{2}. Unfortunately, the fibers appear to have lost the mesoporosity. However, the TiO\textsubscript{2} fiber morphology was maintained even after the high temperature treatment. Fig. 6b shows an SEM image of the fibers after calcining at 900 °C. The fibers appear to have a roughened surface but otherwise there is no evidence of cracking. So it may be possible to prepare both anatase and rutile fibers by this electrospinning method.

One of the potential applications for the mesoporous TiO\textsubscript{2} fibers is photocatalysis. As a measure of reactivity the photooxidation of phenol and formic acid were evaluated using the powdered electrospun fibers and two different commercial TiO\textsubscript{2} samples (Degussa P25 and...
Hombikat UV 100) with a differential and traditional bulk reactor. Degussa P25 has both anatase and rutile forms in the ratio of 3–4:1, which exist separately [29]. It is frequently used as a benchmark for photocatalysts although its high activity is still not well understood [30]. Its BET surface area is around 50 m²/g and its primary particle size is about 25 nm [31] Hombikat UV 100 is a pure anatase TiO₂ with a primary crystal size less than 10 nm and a surface area of 334 m²/g [32]. The TiO₂ fiber sample evaluated here was calcined at 600 °C. Although, the calcined fibers exhibit a low surface area (32 m²/g) indicating some loss in porosity, there is no evidence of residual carbon in these samples. Additionally, the surface area of the fiber sample is not significantly different from that reported for P25. The plots for total carbon concentrations (TOC) versus time using titania fibers (fiber), Hombikat UV 100 TiO₂ (HK) and Degussa P25 TiO₂ (P25) catalysts in phenol and formic
acid photodecomposition with the differential reactor are shown in Figs. 7 and 8. The plot of TOC curve in phenol photodegradation with the bulk reactor is shown in Fig. 9. The conditions of all the above experiments and the corresponding kinetic reaction rates are summarized in Table 1. In all three cases, P25 is the most active; the titania fibers are ranked last in performance where the margin of error is only 2–3%. The marginal performance of the titania fibers compared with HK may reflect the size and surface area of the calcined sample, because the recombination rate of the electron and hole created upon UV irradiation in a bigger TiO₂ particle is larger [33]. The light intensities (Table 1) measured on the outer wall of the reactor reflect the ability of light absorption by the catalysts. The three series of experiments indicate that the absorption by the titania fibers is weak, although a weak absorption does not necessarily mean a bad performance. The light absorption difference between P25 and titania fibers may

**Table 1**

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactor</th>
<th>TiO₂</th>
<th>Reactant</th>
<th>Reaction rate, a (mg carbon/min/l)</th>
<th>Max. light intensity, b (10⁻² W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Differential</td>
<td>0.0650 g P25</td>
<td>Phenol</td>
<td>0.359 ± 0.006</td>
<td>2.69</td>
</tr>
<tr>
<td>2</td>
<td>Differential</td>
<td>0.0650 g HK</td>
<td>Phenol</td>
<td>0.142 ± 0.001</td>
<td>3.43</td>
</tr>
<tr>
<td>3</td>
<td>Differential</td>
<td>0.0650 g fiber</td>
<td>Phenol</td>
<td>0.023 ± 0.002</td>
<td>4.20</td>
</tr>
<tr>
<td>4</td>
<td>Differential</td>
<td>0.0650 g P25</td>
<td>Formic acid</td>
<td>0.506 ± 0.008</td>
<td>2.88</td>
</tr>
<tr>
<td>5</td>
<td>Differential</td>
<td>0.0650 g HK</td>
<td>Formic acid</td>
<td>0.379 ± 0.004</td>
<td>3.70</td>
</tr>
<tr>
<td>6</td>
<td>Differential</td>
<td>0.0650 g fiber</td>
<td>Formic acid</td>
<td>0.074 ± 0.002</td>
<td>4.40</td>
</tr>
<tr>
<td>7</td>
<td>Bulk</td>
<td>0.1800 g P25</td>
<td>Phenol</td>
<td>0.926 ± 0.026</td>
<td>0.15</td>
</tr>
<tr>
<td>8</td>
<td>Bulk</td>
<td>0.1800 g HK</td>
<td>Phenol</td>
<td>0.309 ± 0.002</td>
<td>0.60</td>
</tr>
<tr>
<td>9</td>
<td>Bulk</td>
<td>0.1800 g fiber</td>
<td>Phenol</td>
<td>0.067 ± 0.002</td>
<td>2.16</td>
</tr>
</tbody>
</table>

Initial reactant concentration: 1 mM phenol; 10 mM formic acid; 100 mg/l phenol.

a The total carbon curves in decompositions of both phenol and formic acid follow zero-order decay kinetics. Reaction temperature: 31.0 ± 0.5 °C (1–6); 32.5 ± 0.5 °C (7–9).

b The light intensity on the outer wall of the reactor.
be due to the existence of some rutile form of TiO₂ in P25 [32] and that between HK and titania fibers may be because of their particle size difference. The room temperature photocatalytic oxidation of 4-chlorophenol in a cylindrical reactor using visible light generated by a 450 W medium-pressure mercury vapor quartz lamp was also evaluated, however, the titania fibers exhibit essentially no activity. The photocatalytic activity of the calcined fibers is somewhat disappointing. However, we plan to evaluate fibers heated below 350°C as well as prepare nanofibers (<100 nm) in an effort to better mimic the Degussa P25 nanosized TiO₂.

4. Conclusion

Electrospinning is an easy and effective technique for producing mesoporous transition metal oxide fibers based on titanium. The extension of this electrospinning process to other mesoporous metal oxide compositions is also currently in progress. The photocatalytic properties of the calcined TiO₂ fibers fall well below those of commercial catalysts. Nevertheless, there are several parameters including fiber size and porosity that can be tuned in an effort to improve reactivity. The TiO₂ fibers are also being evaluated for photovoltaic applications.

Acknowledgements

We thank the Robert A. Welch Foundation and the US Air Force for support of this work.

References