Hybrid Microporous Membranes Intended for Protective Clothing

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Competency: Chemistry

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GOAL

The research focuses on developing new membranes to provide enhanced personal protection and better meet the competing needs for thermal comfort and protection from liquid penetration by challenges such as bloodborne pathogens and pesticides in protective clothing for occupations where resistance to liquid penetration is needed, such as medical care and agricultural/chemical workers. Photocatalytic self-detoxification by coaxial electrospun nanofiber containing TiO2 nanoparticles were developed to use to enhance protections from toxic chemicals for military and occupational clothing.

Abstract

Electrospun nanofiber containing titanium dioxides (TiO2) was investigated as a self-detoxifying system. The material system was developed using polyacrylonitrile(PAN)-metal oxide composite fibers containing anatase TiO2. Fibers were prepared by uniaxial and coaxial electrospinning to compare the detoxification activities of the photocatalyst in different fiber morphologies. Monoaxial nanofibers were formed by conventional electrospinning of PAN/DMF solution containing TiO2 nanoparticles, while coaxial nanofibers had the metal oxide selectively placed in the sheath layer by electrospinning pure PAN solution and PAN/TiO2 solution as core and sheath layer, respectively. Location of nanoparticles relative to fiber morphology was determined by SEM and TEM. It was demonstrated that the coaxial approach resulted in location of nanoparticles in the sheath of the fibers rather than the uniform distribution obtained for monoaaxial fibers. Photocatalytic activity of the PAN/TiO2 fibers under UV irradiations was demonstrated by degradation of aldicarb, a carbamate pesticide, as measured by HPLC. In terms of degradation kinetics, surface distribution density of TiO2 nanoparticles on the electrospun fiber affected initial degradation rates while the final decomposition amounts did not differ for the submicron fibers.

1. Introduction

Photocatalysis, a partial oxidation of alkanes and olefinic hydrocarbons, was introduced and developed in 1970 [1]; these reactions took place at ambient temperature under ultra-violet irradiation. The nature of the reaction medium is heterogeneous being comprised of at least two phases: the solid (catalyst) and a fluid reagent (gas or liquid). Current research and development
activities use the application of photocatalysis as the basis for environmentally friendly technologies. Ollis and co-workers [3] demonstrated that the hydroxyl radicals produced during the sequence of light-induced redox reactions were responsible for the oxidative degradation of organic pollutants present in water and air with titania as photocatalyst. Within the past 30 years, semiconductor photocatalysis has been successfully used in the removal of over 1200 different organic toxicants in various media [4].

Titanium dioxide (TiO$_2$) as a photocatalyst has been investigated for almost four decades [2]. Photooxidation, one of the unique features of this metal oxide, is a mechanism suggested to define the driving force of strong oxidation by such metal based inorganic catalysts [5]. Titanium dioxide has been studied in various forms such as metal nanoparticle [6], cluster [7], encapsulated particle [8], thin film [9], aerogel [10] and nanofiber [11, 12] considering various applications such as highly efficient photocatalysis, solar energy conversion and self-cleaning ingredient. In this study, TiO$_2$ nanoparticles were employed to form a photocatalytic polymeric nanofiber substrate.

Coaxial electrospinning provides the technology to produce many different morphologies and nanofiber structures that were previously unattainable through simple monoaxial electrospinning [13]. Discovered around 2003 [14-16], it uses two different fluids flowing through concentric spinnerettes to generate nanofibers with a core-sheath structure [17]. Previous studies have indicated that while monoaxial nanofibers exhibit the capability to support catalytic nanoparticles and prevent their aggregation, if these nanoparticles are located at the center of the nanofiber there is a significant mass transfer limitation for the reactant to reach the catalytic particles thereby making any catalyst at the center virtually unavailable. Coaxial electrospinning can be used to tune the catalyst location in the shell or surface region of the nanofiber. In this work, TiO$_2$ nanoparticle was used a self-decontaminating catalyst in both monoaxial and coaxial electrospun nanofibers to study any photocatalytic differences due to fiber morphologies: randomly distributed nanoparticles by monoaxial electrospinning versus shell side embedded ones by coaxial.

2. Experimental Methods

2.1 Materials

Polyacrylonitrile (PAN) (Mn ~150 kDa, Poly Science Inc., Warrington, PA), N, N-dimethylformamide (DMF) (98%, Fluka, Milwaukee, WI) and aldicarb (2-methyl-2(methylthio)propanal o-[(methylamino)-carbonyl] oxime, purity 99%, FW:190.26, Chem Service, West Chester, PA) were purchased commercially and anatase titanium dioxide (TiO$_2$) was kindly provided by Samsung Chemicals.

2.2 Coaxial Electrospinning

Solutions of N,N dimethylformamide with ten weight percent polyacrylonitrile (MW = 150 kDa) and various weight percent titania nanoparticles were prepared and heated at 100 °C for 24 h. Monoaxial nanofibers were generated using a syringe pump (Harvard Apparatus PHD 2000 Infusion) flowing at 0.03 mL/min through a 22 gauge needle (Hamilton N722). The electric field was generated by a 15 kV electric charge (HV ES3OP-5W Power Supply) and a 15 cm tip to collector plate distance. Coaxial nanofiber samples were generated using concentric needles,
inner of 24 gauge and outer of 18 gauge, with an inner/outer flow rate ratio of 2/3. The amount of components in each solution and the spinning conditions are listed in Table 1.

Table 1. Uniaxial (Uni) and Coaxial (Co) Electrospinning of PAN/TiO2 Solution

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>PAN / TiO2 (w/w)</th>
<th>Flow rate (mL/min)</th>
<th>Needle diameter (mm, I.D.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uni-0%-TiO2</td>
<td>1 / 0</td>
<td>0.03</td>
<td>0.41</td>
</tr>
<tr>
<td>Uni-20%-TiO2</td>
<td>1 / 0.2</td>
<td>0.03</td>
<td>0.41</td>
</tr>
<tr>
<td>Uni-33%-TiO2</td>
<td>1 / 0.5</td>
<td>0.03</td>
<td>0.41</td>
</tr>
<tr>
<td>Co-25%-TiO2</td>
<td>Core: 1 / 0 Shell: 1 / 0.3</td>
<td>Core: 0.010 Shell: 0.015</td>
<td>Core: 0.31 Shell: 0.84</td>
</tr>
<tr>
<td>Co-33%-TiO2</td>
<td>Core: 1 / 0 Shell: 1 / 0.5</td>
<td>Core: 0.010 Shell: 0.015</td>
<td>Core: 0.31 Shell: 0.84</td>
</tr>
</tbody>
</table>

2.3 Fiber Characterization

Electrospun fibers were mounted on aluminum microscopy stubs using carbon tape. The specimens were coated with gold-palladium (Au-Pd) for 30 s using an Edwards Auto 306 High Vacuum Evaporator (Edwards High Vacuum International, Wilmington, MA). Fiber morphology and TiO2 particle distribution were observed using a Field Emission Scanning Electron Microscope (FESEM) – Hitachi 4500 (Tokyo, Japan). Backscattered electron (BSE) imaging and subsequent energy dispersive X-ray (EDX) analyses were conducted using a Scanning Electron Microscope- JEOL model XA-8900R superprobe (JEOL Ltd., Tokyo, Japan) equipped with a Tracor Northern Flextran Series-II Energy Dispersive X-ray Analyzer (Middletown, WI). All the electron microscopy images were obtained with an accelerating voltage of 10 KeV. The specimen current in backscattered electron imaging was 5.0 nA.

It was necessary to use EDX analysis to identify TiO2 in the fiber mat. By putting the X-ray spot probe on a location of interest for 30 s with respect to the energy at 4.5 KeV of Ti. Analysis of these data allowed comparisons of TiO2 nanoparticles at different locations on fiber.

2.4 Photodegradation of Aldicarb Solution

Photo-oxidation experiments were conducted with the electrospun PAN nanofibers containing varying amounts of TiO2. A toxic solution for the decontamination test was made with 2 mM aldicarb, a carbamate pesticide chemical, in HPLC grade water. A nanofiber mat around 3 mg was submerged in each 5 mL-aqueous aldicarb solution. After sonication in an ultrasonic bath for 5 min. to distribute the fibers uniformly and remove air bubbles from solutions, test tubes
containing contaminated solution with electrospun fiber were placed in an ultra-violet chamber and exposed to UV radiation for 1, 2 and 3 h. The chamber has 8 UV lamps (350 nm wavelength, 4 watt, 3 inch tall) and a rotating sample plate exposed specimens with 2.5 cm distance between lamp and specimen.

Following the photoreaction, the specimens were centrifuged at 5000 rpm for 3 min; the supernatant was filtered through a disk type syringe filter (Alltech Assoc. Inc., Deerfield, IL) with 25 mm diameter consisting of 0.2 μm-pore size nylon membrane in order to remove impurities and then placed a 2-mL HPLC vial. Photodegradation activities of the electrospun fibers were measured by analyzing the concentration of aldicarb in each treatment solution of 1.5 mL using HPLC (Agilent 1100, Santa Clara, CA) with method conditions: 15 °C, C18 column, 60% acetonitrile / 40% water (pH-3 using H₃PO₄), 220/4 detector (DAD), flow rate 1 mL/min, with detection for 15 min.

3. Results and Discussion

3.1 Fiber Characterization

Both uniaxial and coaxial PAN fibers containing TiO₂ nanoparticles were prepared by electrospinning (Figure 1).

![Figure 1. PAN Nanofiber Containing TiO₂ Nanoparticles](image)

The coaxial electrospun fibers were prepared to have the TiO₂ located in the sheath of the fiber. X-ray microanalysis was used to confirm that the sheath-core structure was an anticipated (Figure 2). Spot probes in the sheath area of the fibers showed the presence of titanium while for spots in the core of the fiber did not have any detected titanium. The gold that was detected was in the sputter coating used in the preparation of the specimens for electron microscopy.
Figure 2. Electron Microprobe Analysis in Cross-section of Coaxially Electrospun PAN-TiO$_2$ Fiber; Point 1, 2 and 5: surface area, Point 3 and 4: center area (Accelerating Voltage: 10 kV)
3.2 Photocatalytic Degradation

Photocatalytic degradation by fibers containing TiO$_2$ has been shown to follow the pathway in Figure 3. Three compounds shown in Table 2 were found in the LC/MS analysis.

Figure 3. Oxidation Scheme of Aldicarb

Table 2. Chemical structure and Molecular Weight of Aldicarb and the Oxidized Derivatives [18]

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.W.</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldicarb</td>
<td>190</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Aldicarb sulfone</td>
<td>222</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>2-propenal, 2-methyl-, O-[(methylamino) carbonyl] oxime</td>
<td>142</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>

The degradation of aldicarb with the uniaxial and coaxial electrospun fibers is shown in Figure 4. Increase in the amount of TiO$_2$ increased the degradation of aldicarb for both types of fibers. For the coaxial fibers, the rate of degradation was faster (Figure 4 b). The rate of degradation is an importance in performance of the material to provide human protection.
Figure 4. Photocatytic Activities (a) Uniaxially electrospun fiber mat; (b) Coaxially electrospun fiber mat; (c) Uniaxial vs Coaxial
4. Conclusions

- Co-axial electrospinning formed fibers with core-sheath structure.
- TiO₂-containing fibers possess self-decontaminating properties.
- Surface density of nanoparticles distribution in fibers affects the degradation rate.
- This metal oxide-fiber system has potential for use in protective clothing.

References


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PROJECT WEB SITE http://www.ntcresearch.org/projectapp/?project=C05-CR01
PERSONAL WEBSITE http://www.human.cornell.edu/che/bio.cfm?netid=sko3
C05-CR01 A10

PROJECT STATISTICS:
# graduate students involved in the research: 9
# postdoctoral associates: 4
# undergraduate students involved in the research: 1
# theses completed: 3
# presentations: 28
# publications: 18
# papers submitted: 2
# contact with others/government: 2 [The National Personal Protective Technology Laboratory (NPPTL) of NIOSH, Natick Soldier Center; TNO Defense, Security, and Safety the Netherlands]
# contact with academic (non NTC): 7 [Oklahoma State University, University of Minnesota, University of Missouri, University of Maryland Eastern Shore, Seoul National University, Iowa State University, Chungnam National Univ., Hong Kong Polytechnic University]