

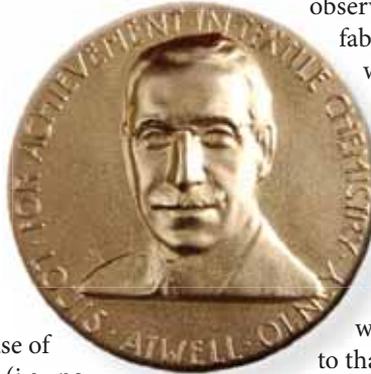


# Improving Personal Protection Through Novel Materials

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## Introduction

Chemical and biological protection is needed to reduce occupational exposure for individuals involved with the chemical industry, military, and emergency response. As well, chemically and biologically protective materials can be used to enhance the air quality in the built environment, in particular, hospital settings. Protection is provided by use of various mechanisms such as barrier (i.e., no permeation or penetration), repellency, adsorption, or a combination of these mechanisms. Basic mechanisms have been used to define novel approaches for chemical and biological protective clothing including microporous and nanofibrous membranes as well as self-decontamination materials.



observations of nonwoven and woven fabrics (0% to 100%).<sup>1,2</sup> No penetration was observed through the membranes when the challenge liquid had high surface tension (38 dynes/cm) and low viscosity (0.9 mPa·s). Polytetrafluoroethylene-based membrane materials with pore sizes smaller than 0.013  $\mu\text{m}$  had very low air permeability, but the water vapor transmission was similar to that observed for nonwoven and woven fabrics (20 g/m<sup>2</sup>/h).

## Membranes

The use of nonwoven materials for disposable protective garments has grown over the past few decades since they are relatively inexpensive, lightweight, and effective protection. These chemical protective materials are often used for body garments with monolithic polymer films as glove material. Penetration of chemical challenges through porous textile materials is governed by capillary size and structure, fabric finish, and fiber chemistry, as well as the surface tension and viscosity of the penetrating liquid.<sup>1,2</sup> There is an inverse relationship between chemical protection and air permeability that was used as a corollary to thermal comfort. Microporous materials laminated or in a layered system with other textiles have been used to provide more effective chemical protection, while providing a more acceptable level of thermal comfort.<sup>3</sup>

Performance of membranes and laminated membranes were compared to nonwoven and woven chemical protective materials (Fig. 1).<sup>4</sup> Chemical penetration through the membrane materials was much lower (0% to 8%) compared to previous

The majority of textile materials have a solid volume fraction of less than 0.5, and water vapor transport occurs primarily through the voids.<sup>5</sup> A slight downward trend in water vapor transport was observed with increase in solid volume fraction. Structural properties such as pore geometry, pore size, and the tortuosity of the passages through a material play a role in moisture vapor movement through a material.<sup>6</sup> Pore structure is quite complex; pore size varies along a single pore path and the material may contain closed or blind pores that terminate inside of the material, thus not contributing to flow. While fabrics could have very similar solid volume fraction, their water vapor transport could vary significantly. Nonwoven fabric and woven fabric with 0.4 solid volume fraction were evaluated for pore size and pore size distribution using capillary flow porometry. The woven fabric had through pore diameters in the range of 6.5  $\mu\text{m}$  to 115  $\mu\text{m}$ , while the nonwoven fabric that had the lower water vapor transport had through pore diameters in the range of 0.3  $\mu\text{m}$  to 6.2  $\mu\text{m}$ .<sup>5</sup> Therefore, it is possible to engineer the pore structure in membranes to achieve high chemical protection while maintaining higher comfort through higher water vapor transport.

## Nanofibrous Membranes

Electrospinning is an effective technique for producing fibers of very small diameters that can be collected into an ultra-thin membrane web with



very small pore size.<sup>4,7,8</sup> Electrospun polyurethane nanofiber webs were layered on a conventional nonwoven fabric (Fig. 2).<sup>8</sup> Use of a very thin layer of nanofibers (1.0 and 2.0 g/m<sup>2</sup>) reduced the penetration of liquid pesticides through the layered system. Penetration through the nonwoven fabric alone was over 85%, while with the addition of the thin nanofibrous web, the penetration was reduced to below 25%. Water vapor transport was not changed by the addition of the nanofibrous web, but there was a decrease in air permeability by 30% to 50%.<sup>8</sup> However, air permeability was above 10 cm/sec/cm<sup>2</sup>, higher than most protective clothing materials currently in use.

Pore size distribution was influenced by the presence and area density of the nanofibrous web.<sup>7</sup> The nonwoven fabric had pore sizes ranging from 3 μm to 100 μm; the addition of 1 g/m<sup>2</sup> had pore sizes ranging up to 70 μm, with the largest frequency around 10 μm, while the addition of 2 g/m<sup>2</sup> reduced the range of pore sizes to under 2 μm with most pores under 0.5 μm.<sup>7</sup> Improved chemical protection and maintained thermal comfort were attained by layering electrospun nanofibrous webs on traditional nonwoven protective clothing materials

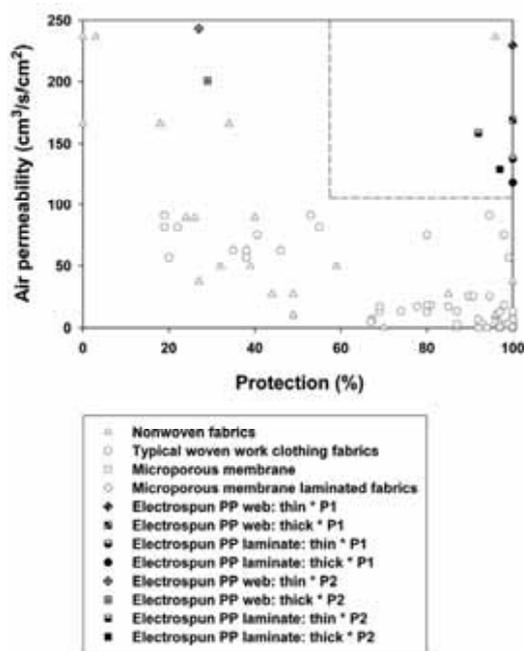


Fig. 1. Relationship between protection performance and air permeability for nonwoven, woven, microporous membranes and laminates, and electrospun polypropylene (PP) web/laminates, compared with penetration measured with two pesticide mixtures (P1 and P2).<sup>4</sup>

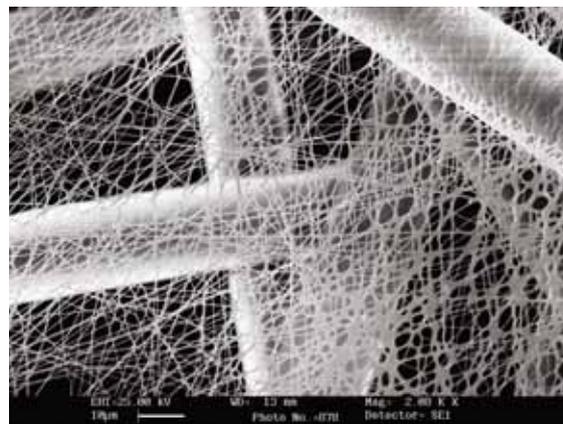


Fig. 2. SEM micrograph of electrospun polyurethane (PU) nanofiber web layered on a conventional nonwoven fabric.<sup>8</sup>

(Fig. 1).<sup>4</sup> Pore size and pore size distribution could be controlled by the level of web area density.

### Environmentally Responsive Membranes

Materials that are responsive to environmental stimuli including pH and temperature have been developed for protective clothing materials and biomedical applications. Surgical gowns and drapes are used as barriers to protect patients and to reduce the risk of exposure of healthcare workers to blood-borne pathogens. Membranes have been used to allow the passage of water vapor (~0.4 μm) while restricting passage of liquid droplet (~100 μm). While such microporous membranes have excellent water vapor transmission, water entry pressure is very low and capillary wicking of the challenging liquids cannot be avoided totally. Research has shown a direct correlation between wetting and

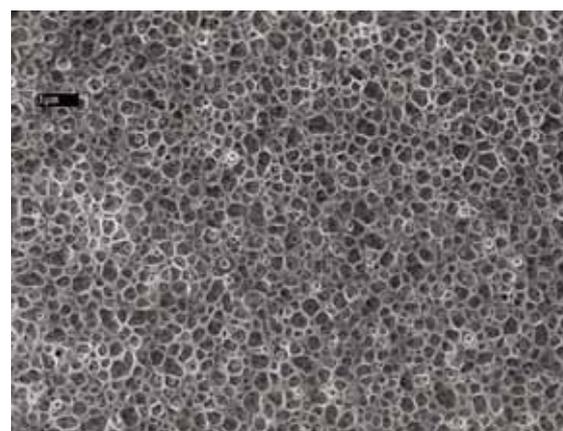


Fig. 3. SEM of microporous membrane.



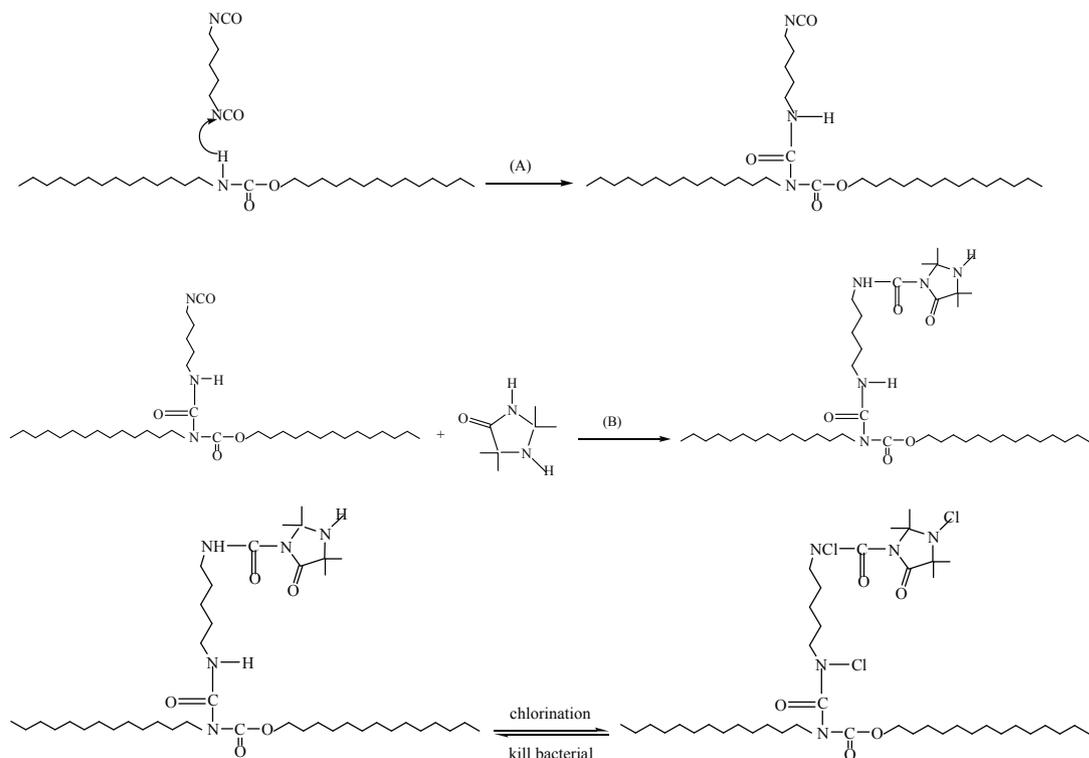


Fig. 4. Two-step reaction scheme of: (A) HMDI activation of PU membrane surface, and (B) surface grafting of TMIO, followed by chlorination of TMIO-modified PU membrane.

microorganism penetration.<sup>9</sup> Therefore, a membrane that is responsive to moisture could provide increased protection from blood-borne pathogens.<sup>10</sup>

A microporous polyurethane membrane was used as the host membrane to develop moisture responsive barrier membrane for use for biological protection of health care and medical workers (Fig. 3).<sup>10</sup> The membrane was modified by grafting poly(ethylene glycol) (PEG) onto polyurethane. A two-step grafting procedure was used. The first step used tin (II) as a catalyst to functionalize the polyurethane with hexamethylene diisocyanate (HMDI). The second step reacted the hydroxyl groups of PEG with the isocyanate end groups of HMDI that was grafted to the polyurethane in step one. Higher grafting yield was attained with PEG in the molecular weight range of 2,500 to 3,500. Grafting resulted in a membrane surface that was more hydrophilic than the original polyurethane membrane, and it reduced the polydispersity of the pore sizes and the number of larger surface pores. Image analysis and flow porometry analysis indicated grafting of PEG on the membrane surface and also within the pores on the pore surfaces. Flow porometry indicates that the

pore size of the modified membrane is less than 13 nm; this should prevent penetration of pathogens. Phi-X 174, used as a pathogen surrogate in testing of biomedical materials for barrier protection, is 27 nm. Data from water vapor transport experiments were consistent with exposure to high humidity causing the modified membranes to swell. The response time behavior of the modified membrane was attributed to swelling of the hydrophilic portion of the membrane as water was adsorbed resulting in reduction of the pore size. This reduction in pore size with increased moisture is expected to increase the protection from blood-borne pathogens, challenging liquids, and harmful particles.

## Antimicrobial Materials

### Antibacterial Membranes

Use of antimicrobial materials has increased to address growing public health awareness of disease transmission, cross-infection, and malodor caused by microorganisms. Special attention has been given to the use of these new materials in protective clothing for medical workers, first responders, in sportswear and under garments, and for other





health-related products. Various approaches have been used. The materials can be physically fabricated as monolithic polymer films or coatings that are impermeable to challenge microorganisms. Also, the fabrication process can control the pore size in a microporous membrane that can be used in clothing systems to restrict or block the penetration of pathogens and viruses. Antimicrobial materials can be chemically engineered by adding functional antimicrobial agents onto the surface or within the matrix to either kill or inhibit their growth.

Commonly-used antimicrobial agents that have been applied to textile materials include antibiotics, silver ions, quaternary ammonium, and N-halamines. Compounds containing nitrogen-halogen bonds that act as oxidizing agents are excellent biocides. Novel derivatives of imidazolidin-4-one have been studied for their antimicrobial properties; N-halamines or cyclic amines, such as oxazolidones and imidazolidinones have been used for water purification and incorporated into textile finishes.<sup>11</sup> Their biocidal mechanism is believed to be from a direct transfer of positive halogen from the N-halamine to biological receptors in the bacterial cells. After extensive use, antimicrobial activity can be reactivated by treatment with halogen-releasing agents such as NaOCl (common bleach).

To develop enhanced performance, an antimicrobial microporous membrane was developed using an N-halamine.<sup>12</sup> The moiety of 2, 2, 5, 5-tetramethyl-imidozalidin-4-one (TMIO) was grafted onto a microporous polyurethane membrane. Tin (II) was used as the catalyst to functionalize the polyurethane with hexamethylene diisocyanate (HMDI), followed with a reaction of TMIO with the HMDI-functionalized polyurethane membrane (Fig. 4). After chlorination, a total reduction of both Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* was observed after a 2-h contact period with the chlorinated TMIO modified membrane. Thus, a microporous membrane that is antimicrobial and possesses good barrier and water vapor transport was developed.

Antimicrobial nanofibrous membranes were developed using N-halamine additives in electrospinning solutions.<sup>13</sup> N-halamines generally have one or more imide, amide, or amine halamine bonds. Research has shown that the antimicrobial power of the N-halamines are in the order of imide

> amide > amine.<sup>14</sup> A series of structurally different N-halamines were used as additives in an electrospinning dope of nylon 6 using 88% formic acid as the solvent. N-halamines were chlorinated 5,5-dimethylhydantoin (CDMH) with both imide and amide halamine groups, chlorinated 2,2,5,5-tetramethyl-imidozalidin-4-one (CTMIO) with both amide and amine halamine groups, and chlorinated 3-dodecyl-5,5-dimethylhydantoin (CDDMH) with an amide halamine group and long alkyl chain. The N-halamine additives were uniformly distributed in the nanofibrous membrane with fibers ranging in diameter from 500 nm to below 100 nm; this resulted in a total reduction in both *E. coli* (Gram-negative bacteria) and *S. aureus* (Gram-positive bacteria) after short contact times of 5 to 40 min based upon the specific N-halamine and the related active chlorine content. At the same chlorine content, CDMH resulted in the shortest time for total reduction. With an increase in N-halamine concentration in the electrospinning dope, the active chlorine content increased, resulting in higher antimicrobial rate and larger antimicrobial reduction. While slight leaching with methanol was observed with CDMH and CTMIO, no observable leaching occurred for CDDMH during a 24-h period.

Incorporation of N-halamines into electrospun nanofibrous membranes offers several advantages. This one-step process, with an additive to the spinning dope, is low in additional cost to gain the added antimicrobial functionality. Incorporation of the N-halamines as an additive in the fiber allows the chlorine content to be increased beyond that feasible with a fiber-surface treatment. Embedding N-halamine into the polymer matrix can provide a reservoir to deliver antimicrobial power over the wear life of the material.

### Antifungal Membranes

Effects of indoor air quality on health are of increasing concern; indoor air pollutants come from many sources including heating/cooling systems and molds. Common indoor molds that effect air quality are *Penicillium*, *Cladosporium*, *Aspergillus*, *Alternaria*, and *Mucor*. They produce volatile metabolites that elicit respiratory syndromes such as asthma, bronchitis, and rhinitis. Further, in a hospital environment, invasive aspergillosis is a life-threatening infection in immunocompromised patients. *Aspergillus* spores are involved in lethal pulmonary infections in these patients. Reduction





Fig. 5. *Aspergillus niger* spores on cotton fibers.

in air contamination in hospital isolation areas has been achieved through elimination of facility sources and through air filtration systems. Research has demonstrated the role of clothing in spore transport and release; important factors governing the retention and release of spores from clothing were fiber surface morphology, moisture content, and available fiber surface area per fabric area.<sup>15</sup> The most unusual propensity for storage and release of spores was seen in cotton fabrics. The physical structure of cotton allows the fiber to act as a storage device for spores (Fig. 5).

Approaches to improve indoor air quality and infection control include control of the source, dilution of the pollutant, or use of antimicrobial materials/processes. Antifungal properties can be developed using eco-friendly approaches such as plant derived natural antimicrobial products as additives for finishes and coating or for inclusion in manufactured fibers. Saponin, an antifungal agent, was used as an additive in an electrospinning dope of cellulose acetate to fabricate an antifungal nanofibrous cellulose membrane.<sup>16</sup> Quillaja saponin from the soapwort plant is a major family of second-

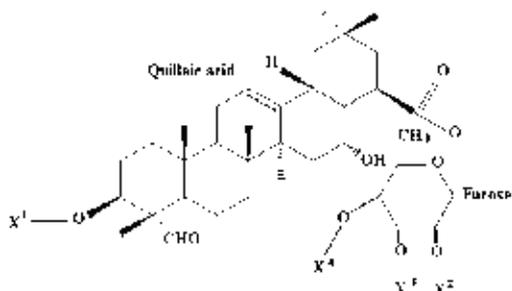


Fig. 6. Common chemical structure of Quillaja saponin.

ary metabolites that have strong biological activities including antimicrobial and insecticidal effects (Fig. 6). Saponin (1.5 wt%) was added to a solution of cellulose acetate in acetone/dimethylformamide/water that was used to electrospin nanofibers. These cellulose acetate nanofibrous webs were deacetylated using 0.05 M NaOH in methanol to form cellulose nanofibrous membranes loaded with Quillaja saponin. Antifungal activities of the electrospun membranes were evaluated against both *Penicillium roquefortii* and *Aspergillus ochraceus* showing a reduction of 84.6% and 53.4% respectively after 24 h. The results show that saponin-loaded fabric has high potential for household applications and could be evaluated further for medical applications.

### Self-Detoxifying Materials

Chemicals may enter the body through a variety of routes including ingestion on food or in drinking water, inhalation, and absorption through the skin. Dermal absorption, rather than inhalation or ingestion, is the primary route for occupational chemical exposure. Toxic chemicals may contaminate clothing and skin directly in the field or by indirect contact with contaminated surfaces. Elevated temperatures with perspiration and other dermal secretions increase the potential for transfer of pesticides to clothing and skin. Pesticides adsorbed on personal protective equipment can be transferred with friction when donning and doffing a contaminated garment. Chemical detoxifying properties of materials offer the potential of increased protection for workers or military personnel exposed to occupational toxins. Using textile treatments that provide self-decontamination properties can reduce the toxicity of contaminants through oxidation or destructive adsorption. These self-decontaminating properties could reduce the toxicity of chemicals, thus increasing the protection.

Photocatalytic oxidation is one of the most effective ways to decompose alkenes and other volatile organic compounds. Titanium dioxide, TiO<sub>2</sub>, is a well known metal oxide with photocatalytic properties that has been incorporated into fabrics to aid in degradation of organic compounds. Cotton fabrics that were treated with aqueous TiO<sub>2</sub> in a silicone finishing solution aided in the decomposition of gaseous ammonia<sup>17</sup> and mixed pesticides including methyl parathion.<sup>18</sup> In the outdoor environment, with the combination of elevated temperatures during the summer growing season, direct sunlight,



and moisture, these self-decontaminating properties of textiles may be effective in increasing personal protection.

Anatase TiO<sub>2</sub>/PAN and SiO<sub>2</sub> fibers were prepared by a sol-gel process and electrospinning technique under low temperature conditions.<sup>19</sup> Anatase TiO<sub>2</sub> containing nanofibers were obtained by hydrolysis of the titanium component of the as-spun composite fibers in acidic solution. The diameters of the prepared anatase TiO<sub>2</sub>/PAN fibers were less than 1 μm. The photocatalytic activity of the TiO<sub>2</sub>/PAN fibers was measured using malachite green, aldicarb, and toluene; their degradation under UV irradiation showed high photocatalytic activity of the anatase TiO<sub>2</sub>/PAN fibers.<sup>20</sup> HPLC results show that PAN/TiO<sub>2</sub> (2:1) nanofiber exposed to UV irradiation reduced the aldicarb concentrations. While the higher concentration solution (0.02 M) decreased to 0.016 M after 2 h, the other pesticide solution (0.002 M) decreased to 0.0011 M in 2 h. Three oxidation products were observed including aldicarb sulfoxide and aldicarb sulfone. The third degradation product, 2-propenal-2-methyl-O-[(methylamino) carbonyl] oxime may have reduced toxicity relative to aldicarb, aldicarb sulfoxide, and aldicarb sulfone.<sup>21</sup> While questions remain about toxicity of the specific degradation compounds and the kinetics of photocatalytic degradation, we have confirmed that aldicarb was decomposed by nanofibers containing titania.

Photocatalytic activity of TiO<sub>2</sub> also can be used to reduce the volatile organic compounds (VOC) in the built environment and improve indoor air quality. Therefore, we studied the decomposition of a

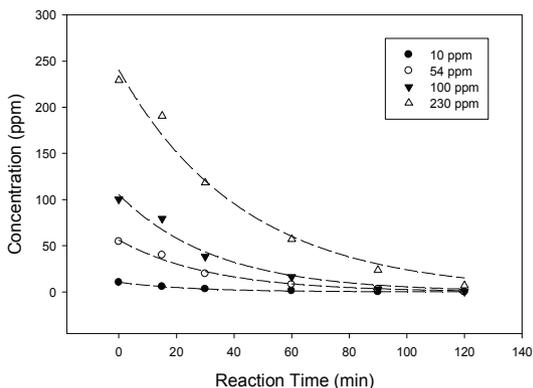


Fig. 7. Degradation of toluene in air with reaction time in the presence of UV and TiO<sub>2</sub> nanofiber; FTIR absorbance at 730 cm<sup>-1</sup>. The equation of degradation kinetics is  $y = y_0 e^{-0.03t}$ , where  $y_0$  is initial concentration (ppm) and  $t =$  time (min).

toluene-air mixture by the anatase TiO<sub>2</sub>/PAN fibers with UV irradiation.<sup>20</sup> Previous research has shown that the photocatalytic oxidation of toluene results in the formation of degradation products such as benzaldehyde, benzoic acid, and cresol.<sup>22</sup> We studied the interaction of toluene with the TiO<sub>2</sub> photocatalyst using FT-IR. Toluene gas demonstrated peaks from 3100-2800 cm<sup>-1</sup>, 1610-1360 cm<sup>-1</sup>, and at 730 cm<sup>-1</sup> due to CH stretching or ring stretching. Since FTIR absorbance is proportional to the concentration of toluene, photodegradation of toluene-air mixtures having different concentrations could be monitored over exposure time (Fig. 7). The mixture with the greater toluene content required the longest time to achieve total degradation. Toluene at all concentrations was observed to decompose due to photocatalytic reaction of anatase TiO<sub>2</sub> in the nanofiber.

Nanocrystalline materials, such as MgO, CaO, and Al<sub>2</sub>O<sub>3</sub>, exhibit enhanced surface chemical reactivity toward incoming adsorbates including polar organics such as aldehydes and ketones.<sup>23,24</sup> The chemical reactivity of adsorbates on the nanoparticles has been shown to follow a two-step surface stoichiometric decomposition mechanism; adsorption of the toxic agent on the surface by means of physisorption is the first step, followed by chemical decomposition. Magnesium oxide MgO in nanocrystalline form (particle size ≤ 8 nm, aggregate size = 3.3 μm) has a large reactive surface area due to polyhedral shapes and high proportion of corner/edge sites compared to typical polycrystalline material.<sup>25</sup> The surface morphology of the MgO structure is very important—higher number of defects and corners of small nanoparticles provide high surface reactivity. High surface area combined with high surface reactivity gives these materials great potential for use in decontamination of toxic substances by dissociative chemisorptions termed “destructive adsorption.”

Magnesium oxide (MgO) has been shown to degrade organophosphate including dimethyl methylphosphonate (DMMP), a chemical agent stimulant,<sup>23</sup> and paraxon.<sup>26</sup> It can be added to textile materials either as a fabric finish or an additive in fiber formation. Cotton fabric was treated with an aqueous slurry of these nanoparticles, alone and combined with starch. The fabric treatments containing the MgO nanoparticles resulted in enhanced adsorption of the pesticide aldicarb as well as self-decomposition.<sup>27</sup>





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