TOWARD AN ACTIVE FABRIC-BASED AIR DECONTAMINATION SYSTEM

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ABSTRACT

Heterogeneous semi-conductor photocatalysis of chloroform (CHCl3) has been demonstrated on titanium dioxide (TiO2) particles that were grafted on cotton fabric and on TiO2 particles that were embedded in glass fabric. Modified TiO2 particles were grafted onto cotton fabric and irradiated in the presence of CHCl3 vapor. The synthesis of the system is described, and FTIR results of the decomposition of CHCl3 are discussed. TiO2 particles were also embedded in glass fabric and irradiated in the presence of CHCl3 vapor. The embedding process is described, and the FTIR results of the decomposition of CHCl3 are discussed.

1. INTRODUCTION

In order to satisfy the requirements of the Army Future Combat System (FCS) the Army requires improved Nuclear Biological Chemical (NBC) protective clothing for personnel and protection for equipment. This summary describes research into a possible solution for the Army’s need for protective materials as counter measures against chemical warfare.

Titanium dioxide is widely recognized as a powerful photo-oxidation catalyst.1-3 Research groups have shown TiO2 to be an effective decontaminant in the presence of UV light (350 nm) for blister agent simulants: 2-chloroethyl ethyl sulfide (2-CEES) and diethyl sulfide (DES).4 Although these research groups showed promising results, the materials used in the experiments do not lend themselves well to implementation. In previous reports, the photocatalytic performance of TiO2 and TiO2-based materials was measured using TiO2 and TiO2-based materials pressed into small pellets.4

The research reported in this summary is directed at developing a system that is more amenable to implementation. Successful demonstration of titanium photo-catalysis on fabrics would aid in fostering the transition of this technology into service. Possible applications include protective clothing for personnel, individual filtration media, vehicle ventilation system decontamination and decontaminating textiles and composites.

2. EXPERIMENTAL

Allyl Chlorodimethylsilane Modified TiO2: A round bottom flask containing 150 mL DMF and a stir bar was pre-heated at 80 °C in a water bath for 30 min. 15.0 g TiO2 and 3.0 mL dry pyridine were added to the reaction flask. After that, the reaction vessel was sealed with a septum and degassed with N2 (vented with a needle). During the degassing, occasional stirring was needed to maintain the uniformity of the reaction system. After 30 minutes of degassing, 4.0 mL of allyl chlorodimethylsilane (ADMS) was injected into the reaction vessel and stirred. The reaction system was kept in the water bath at 80 °C for 12-15 hours.

Cotton Fabric: Bleached and mercerized cotton print cloth fabric samples with 80 × 80 yarn count measuring 15 × 30 cm2 were impregnated with Fe2+ by placing clean cotton fabric in a reaction vessel and covering the sample with 5.0 × 10⁻³ M FeSO4. The vessel was sealed and placed in a water bath at 45 °C while continuously degassing with N2. The fabrics were rinsed with DIW and dried.

ADMS-modified TiO2 particles were suspended in acetone at 12.5% (w/w) and sonicated for 30 min. The modified TiO2 particles were padded on the Fe2+ impregnated cotton fabric (6 × 11 cm2) using a 1.0” paintbrush. The padded fabrics were dried in a vacuum oven at 30 Torr and RT for 120 min. This process was repeated, if necessary until a 10-20% weight increase of the fabrics was obtained.

Fe2+ treated/TiO2 padded fabrics were placed in a vessel along with 550 ml distilled water and 46.0 mL acrylonitrile. The vessel was sealed and degassed with N2 for 20 min. The vessel was then placed in a water bath at 60 °C for 15 minutes. Then, 2.5 mL of degassed 0.11 M H2O2 was injected into the reaction vessel. The vessel was kept in the water bath at 60 °C for 90 additional minutes under continuous degassing. The vessel was then removed from the water bath and allowed to reach RT under N2 degassing. The modified fabric was removed from the vessel and rinsed with distilled water. DMF was used to remove unreacted species. The fabrics were laundered 10 times and then vacuum dried at 30 Torr.
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Glass Fabric: Multi-filament glass fabrics with 20 × 20 filament counts and measuring 6 × 11 cm² were coated with sodium silicate solution (14% NaOH, 27% SiO₂). The fabrics were placed in an oven at 90 °C for 30 min until the samples became tacky. The fabrics were then padded with TiO₂ particles suspended in acetone at 12.5% (w/w) that had been sonicated for 30 min. The fabrics were then cured at 150 °C for 1 hour.

Method: The photolysis experiments were performed in a 260 mL dual chambered (bottom chamber ~ 50 mL in volume and the top chamber ~ 210 mL in volume) airtight glass reaction vessel. The divider between the two chambers had a 1 cm diameter opening in the center. The concentration of CHCl₃ (l) used in all the experiments was 107 ppm and was injected into the bottom chamber which contained a triangular stir bar. The system was allowed to equilibrate before each FTIR analysis by placing the vessel on a stir plate for 15 min.

The system was irradiated using 350 nm light generated from a Rayonet photochemical reactor with an average light intensity of 10 mW/cm². FTIR analysis was obtained using a Bruker Equinox 55 spectrophotometer.

3. RESULTS

The FTIR spectra in Figures 1 and 2 correspond to cotton fabric with PAN grafted ADMS modified TiO₂ and glass fabric with embedded TiO₂ systems, respectively. Both systems were irradiated in the presence of CHCl₃ vapor. In both systems, the degradation of CHCl₃ was observed as a result of heterogeneous photocatalysis on TiO₂.

The infrared spectra acquired after irradiation indicate the degradation of CHCl₃ due to the reduction of the signals at 775 cm⁻¹ and 1220 cm⁻¹ which correspond to the νₚₐₛ(C-Cl₃) and the δ(C-H) modes, respectively, of CHCl₃. The spectra also show the appearance of signals at 850 cm⁻¹, 1820 cm⁻¹ and 2890 cm⁻¹ which correspond to the ν(C-Cl₂), ν(C=O) and ν(H-Cl) modes, respectively, of Cl₂CO. These results agree well with literature and give rise to the proposed mechanism for the photo catalytic oxidation of CHCl₃ vapor in these fabric-based systems:

\[
\begin{align*}
\mathrm{TiOH}^+ + \mathrm{CHCl}_3 & \rightarrow \mathrm{TiOH}_2^+ + \cdot \mathrm{CCl}_3 \\
\cdot \mathrm{CCl}_3 + \mathrm{O}_2 & \rightarrow \cdot \mathrm{O}_2 \mathrm{CCl}_3 \\
2[\cdot \mathrm{O}_2 \mathrm{CCl}_3] & \rightarrow 2[\cdot \mathrm{OCCl}_3] + \mathrm{O}_2 \\
\cdot \mathrm{OCCl}_3 + \mathrm{HO}_2^+ & \rightarrow \mathrm{Cl}_2 \mathrm{COH} + \mathrm{O}_2 \\
\mathrm{Cl}_2 \mathrm{COH} & \rightarrow \mathrm{Cl}_2 \mathrm{CO} + \mathrm{HCl} \\
\mathrm{Cl}_2 \mathrm{CO} + \mathrm{H}_2 \mathrm{O} & \rightarrow \mathrm{CO}_2 + 2\mathrm{HCl}
\end{align*}
\]

4. DISCUSSION

The data clearly indicate the degradation of CHCl₃ in both the cotton fabric and glass fabric systems via heterogeneous photocatalysis on TiO₂. Although the degradation is relatively slow, this research shows the feasibility of fabrics as photocatalysis substrates for U.S. Army applications. Efforts are underway to optimize the systems to increase reaction rates.

REFERENCES