

TOWARD AN ACTIVE FABRIC-BASED AIR DECONTAMINATION SYSTEM

G. A. Gaddy^{1†*}, Matthew S. Bratcher^{1‡}, G. Mills², S. Huang³, B. L. Slaten³ and J. Debortoli³

¹United States Army Research Laboratory, [†]Sensors and Electron Devices Directorate, Adelphi, MD 20783

[‡]Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD 21005

²Auburn University, Department of Chemistry, Auburn, AL 36849

³Auburn University, Department of Consumer Affairs, Auburn, AL 36849

ABSTRACT

Heterogeneous semi-conductor photocatalysis of chloroform (CHCl_3) has been demonstrated on titanium dioxide (TiO_2) particles that were grafted on cotton fabric and on TiO_2 particles that were embedded in glass fabric. Modified TiO_2 particles were grafted onto cotton fabric and irradiated in the presence of CHCl_3 vapor. The synthesis of the system is described, and FTIR results of the decomposition of CHCl_3 are discussed. TiO_2 particles were also embedded in glass fabric and irradiated in the presence of CHCl_3 vapor. The embedding process is described, and the FTIR results of the decomposition of CHCl_3 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 TiO_2 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 TiO_2 and TiO_2 -based materials was measured using TiO_2 and TiO_2 -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 TiO_2 : 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 TiO_2 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 N_2 (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 Fe^{2+} by placing clean cotton fabric in a reaction vessel and covering the sample with 5.0 × 10⁻³ M FeSO_4 . The vessel was sealed and placed in a water bath at 45 °C while continuously degassing with N_2 . The fabrics were rinsed with DIW and dried.

ADMS-modified TiO_2 particles were suspended in acetone at 12.5% (w/w) and sonicated for 30 min. The modified TiO_2 particles were padded on the Fe^{2+} 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.

Fe^{2+} treated/ TiO_2 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 N_2 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 H_2O_2 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 N_2 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.

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE 00 DEC 2004	2. REPORT TYPE N/A	3. DATES COVERED -	
4. TITLE AND SUBTITLE Toward An Active Fabric-Based Air Decontamination System		5a. CONTRACT NUMBER	
		5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)		5d. PROJECT NUMBER	
		5e. TASK NUMBER	
		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) United States Army Research Laboratory, Sensors and Electron Devices Directorate, Adelphi, MD 20783; Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD 21005; Auburn University, Department of Chemistry, Auburn, AL 36849		8. PERFORMING ORGANIZATION REPORT NUMBER	
		10. SPONSOR/MONITOR'S ACRONYM(S)	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
		12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited	
13. SUPPLEMENTARY NOTES See also ADM001736, Proceedings for the Army Science Conference (24th) Held on 29 November - 2 December 2005 in Orlando, Florida.			
14. ABSTRACT			
15. SUBJECT TERMS			
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified	
19a. NAME OF RESPONSIBLE PERSON			

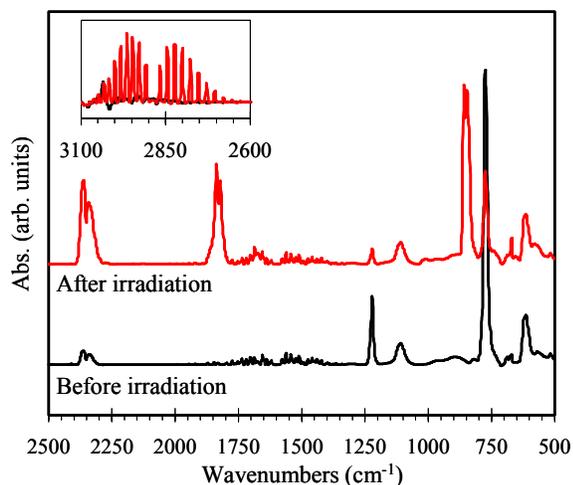


Figure 1: FT-IR spectra before and after 23 hrs irradiation of CHCl_3 (g) in the presence of ADMS-modified TiO_2 , PAN grafted cotton fabric.

Glass Fabric: Multi-filament glass fabrics with 20×20 filament counts and measuring $6 \times 11 \text{ cm}^2$ were coated with sodium silicate solution (14% NaOH, 27% SiO_2). The fabrics were placed in an oven at 90°C for 30 min until the samples became tacky. The fabrics were then padded with TiO_2 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 $\sim 50 \text{ mL}$ in volume and the top chamber $\sim 210 \text{ mL}$ in volume) airtight glass reaction vessel. The divider between the two chambers had a 1 cm diameter opening in the center.

The concentration of CHCl_3 (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/cm^2 . 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 TiO_2 and glass fabric with embedded TiO_2 systems, respectively. Both systems were irradiated in the presence of CHCl_3 vapor. In both systems, the degradation of CHCl_3 was observed as a result of heterogeneous photo-catalysis on TiO_2 .

The infrared spectra acquired after irradiation indicate the degradation of CHCl_3 due to the reduction

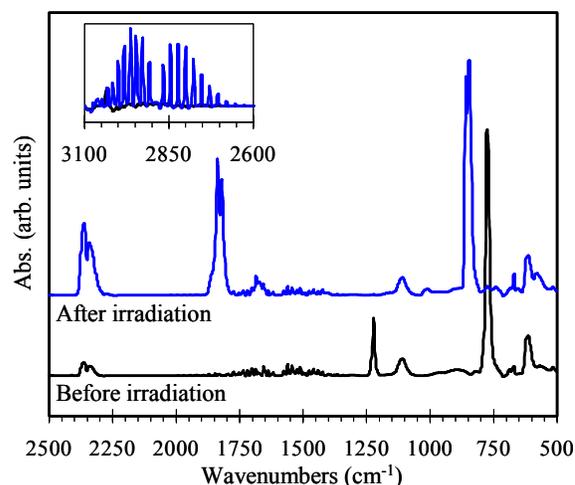
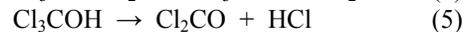
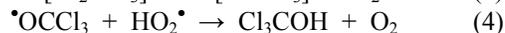
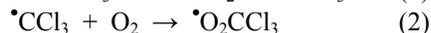


Figure 2: FT-IR spectra before and after 7 hrs irradiation of CHCl_3 (g) in the presence of TiO_2 embedded in glass fabric.

of the signals at 775 cm^{-1} and 1220 cm^{-1} which correspond to the $\nu_{\text{as}}(\text{C}-\text{Cl}_3)$ and the $\delta(\text{C}-\text{H})$ modes, respectively, of CHCl_3 . The spectra also show the appearance of signals at 850 cm^{-1} , 1820 cm^{-1} and 2890 cm^{-1} which correspond to the $\nu(\text{C}-\text{Cl}_2)$, $\nu(\text{C}=\text{O})$ and $\nu(\text{H}-\text{Cl})$ modes, respectively, of Cl_2CO . These results agree well with literature and give rise to the proposed mechanism for the photo catalytic oxidation of CHCl_3 vapor in these fabric-based systems:



4. DISCUSSION

The data clearly indicate the degradation of CHCl_3 in both the cotton fabric and glass fabric systems via heterogeneous photocatalysis on TiO_2 . 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

- Chio, Wonyong, Hoffmann, Michael R. *Environ. Sci. Technol.* **1997**, *31*, 89-95.
- Yang, Yu-Chu, Baker, James A., Ward, J. Richard. *Chem. Rev.* **1992**, *92*, 1729-1743.
- Hoffmann, Michael R., Martin, Scot T., Choi, Wonyong, Bahnemann, Detlef W. *Chem. Rev.* **1995**, *95*, 69-96.
- Panayotov, D. A., Paul, D. K., Yates, J. T. *J. Phys. Chem. B* **2003**, *107*, 10571-10575.