

State University of New York at Stony Brook

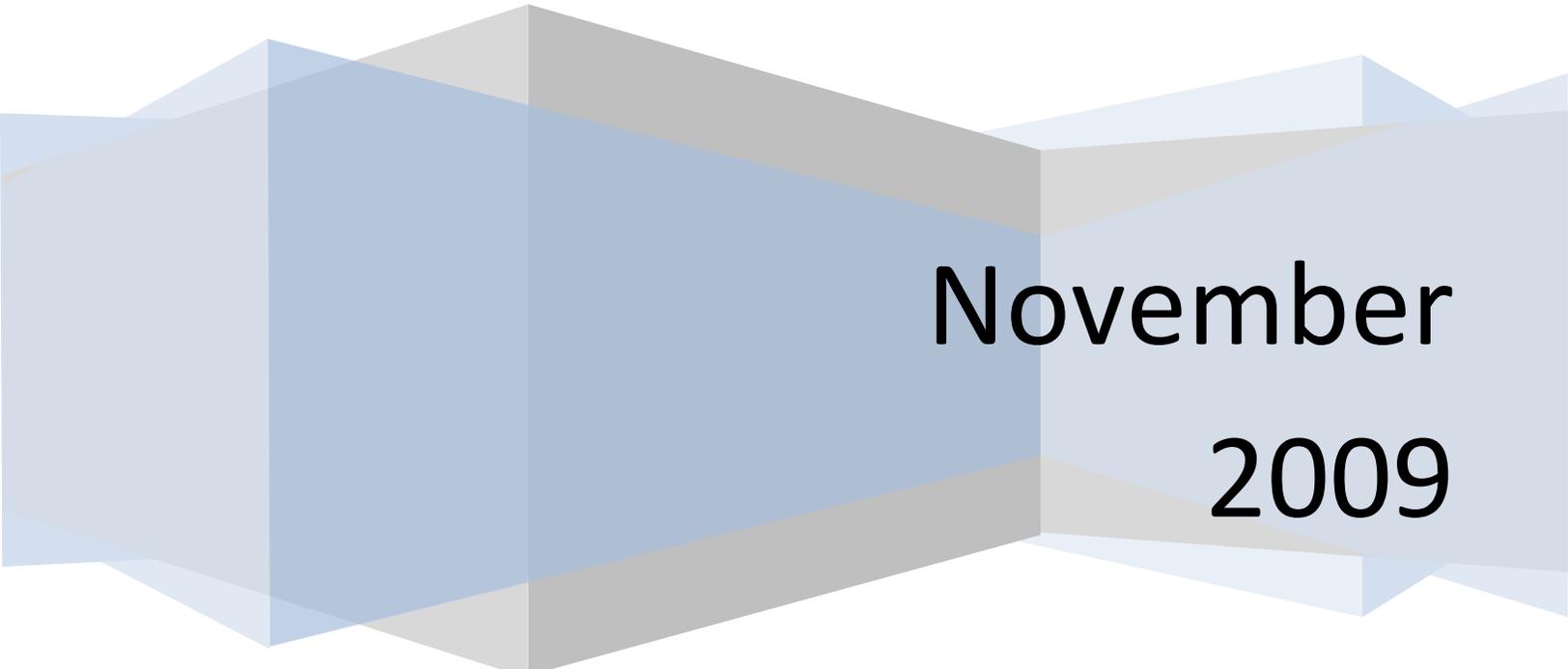
Materials Science and Engineering Department

Final Report

Self-cleaning coatings for environmental applications

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1. INTRODUCTION

Nitrogen oxides (NO and NO₂) emissions can cause various environmental and health problems. It contributes to formation of acid rain, atmospheric particles and various other toxic substances resulting in health problems, visibility reduction, eutrophication and global warming. One of the most prominent results of NO_x emissions is formation of ground level ozone, which is produced in the reaction of NO_x with volatile organic compounds (VOCs) in the presence of sunlight. When formed, it causes adverse effects such as damage to lung tissue and reduction in lung function. It is a significant nationwide problem millions of Americans live in areas that do not meet the health standards for ozone.

The primary sources of NO_x are summarized in Figure 1 (the EPA 1992 data). They include road vehicle emissions, electricity generation, non road equipment, fossil fuel combustion, industrial processes and various other sources. There are several conventional methods to deal with NO_x emissions, which include pollution prevention (e.g.

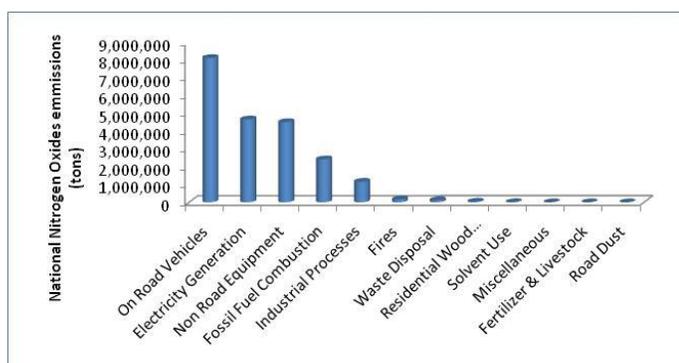


Figure 1: EPA data on NO_x Emission Sources 1992

optimization of combustion processes) and pollution removal, such as elimination

of NO_x by scrubbers and selective catalytic reduction. However, there is still a significant need to develop new methods of NO_x removal from the atmosphere, which remains an important environmental challenge of the 21st century.

For the last 20 years, photocatalytic oxidation (PCO) has been steadily gaining ground as one of the most innovative technologies to remove hazardous environmental pollutants. The PCO can provide an attractive alternative to more conventional methods, combining both functional (self-cleaning properties) and environmental benefits. This project is focused on evaluating the efficiency of NO₂ removal and self-cleaning efficiency by PURETi coatings under simulated environmental conditions.

2. EXPERIMENTAL SETUP

2.1 NO_x removal experiment

An experimental setup consisting of sealed reactor, NO₂ gas cylinder, air cylinder, UV lamp, humidity control, mass flow controllers, and NO_x analyzer has been designed for the project. The glass surfaces coated with PURETi product have been used to evaluate the environmental benefits of the coatings under simulated environmental conditions. Two sets of experiments were performed to determine the conversion strength of the PURETi coating. The first set had an initial concentration of NO₂ of ~480ppb, mimicking severely polluted industrial/urban environment. The second set had an initial concentration of NO₂ of ~240ppb, emulating an environment with lower pollution. The samples were tested under both UV radiation and dark conditions, to eliminate the experimental artifacts related to NO₂ adsorption of the reactor surfaces. The NO₂ concentration was measured by NO_x analyzer, which utilized the chemiluminescent method.

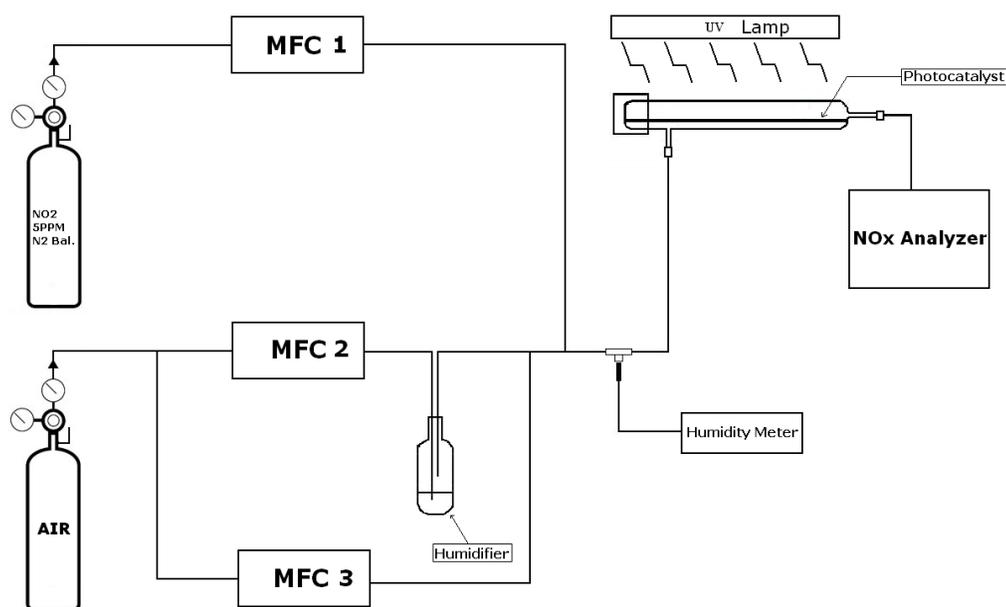


Figure 2: Schematic illustration of the photoreactor used for removal of NO₂ by TiO₂ photocatalysis.

Synthetic air and NO₂ flows from compressed gas cylinders were controlled by mass flow controllers (MFC). Given that water vapor is always present in the atmosphere, the mixture of air and NO₂ was humidified by passing part of the synthetic air from compressed air cylinders through a water bubbler. The relative humidity of air was controlled by varying the flow of dry and humid air. The resulting humidity was measured by a humidity probe (Vaisala HMP50 Humidity Probe) positioned downstream. The measured relative humidity was approximately 50% and the total gas flow rate through the reactor was 110 sccm (Standard Cubic Centimeters per Minute). The glass slides coated by were placed inside a sealed reactor and exposed to both humidified NO₂/air mixture and UV light. The UV lamps (Black light F15T8 and GE Company) used in all experiments provided UV-A radiation (also called “black light”) with a maximum wavelength of 360 nm. The intensity of the UV lights was measured

to be 0.94 mW. The NO₂ conversions were continuously measured by NO_x analyzer (Model 200E, Teledyne API Ltd) and recorded on computer hard drive through the data capture program.

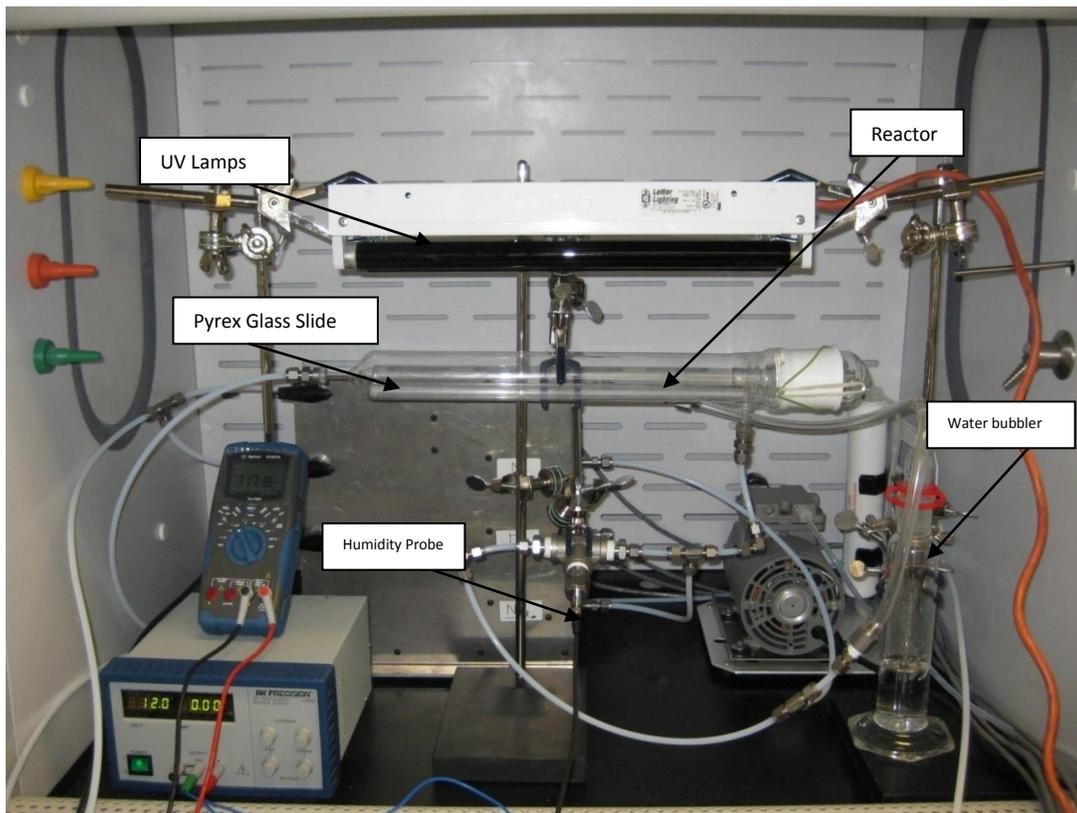


Figure 3 : Experimental setup detailing the key parts of the lab scale gas feeding and reaction system.

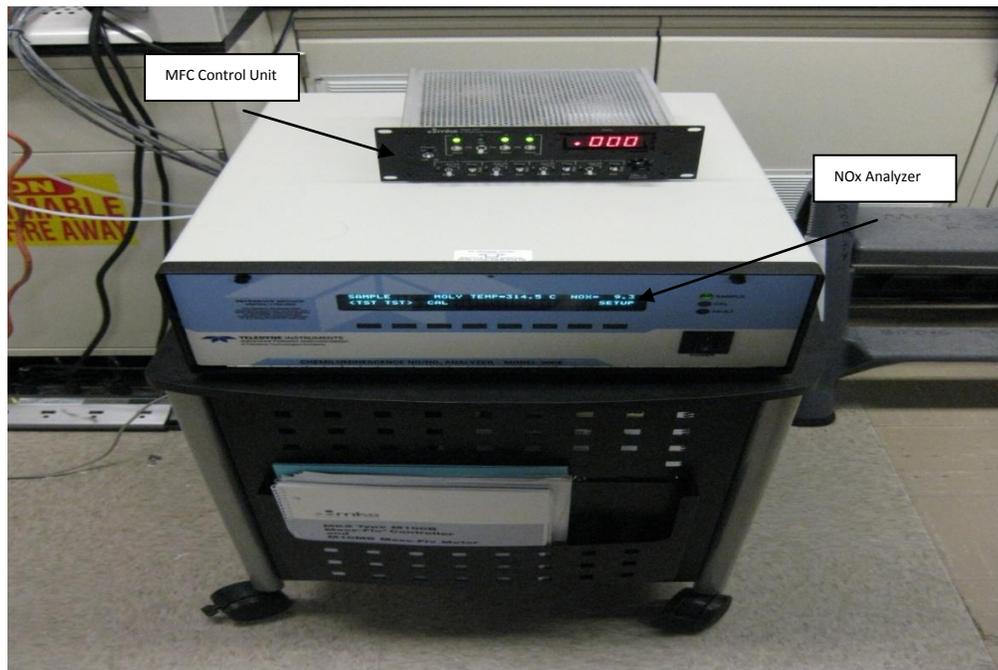


Figure 4: The MFC control unit and NO_x Analyzer

2.2 Self-cleaning properties

The stearic acid of 97 % purity was obtained from Acros Organics through Alfa Aesar. The solvents used for preparation of the solutions were ultra-pure water from Direct-Q 3 Millipore system and absolute ethanol from SDS. The UV Source was a BLAK-RAY Model 100 B UV 100W lamp with an emission spectrum ranging from 200 to 600nm with the maximum output at 365nm. The glass substrate used for the experiment was Pyrex glass.

Nicolet 6700 FTIR (Thermo Scientific Inc) was used in transmission mode for quantitative analysis of stearic acid degradation. The spectral range used for analysis was from 4500 to 450 cm^{-1} with 32 scans with spectral resolution of 4 cm^{-1} . The degradation rate was calculated by integrating the absorbance of stearic acid between 2800 and 2965 cm^{-1} . This range corresponds to the signals of the symmetric and asymmetric CH stretching mode of the CH_2 groups at 2849 and 2916 cm^{-1} and to asymmetric stretching mode of the CH_3 group at 2953 cm^{-1} .

Stearic acid solution (10 g/L in absolute ethanol) was deposited on the glass substrate by spin coating method. Approximately 60 μL of solution was deposited on 2.8 x 2.8 cm^2 glass substrate. The spin coating parameters were as following:

- Time of rotation: 60 s
- Speed: 750 rpm
- Acceleration: 400 rpm/s

Glass substrate was irradiated by UV just before the stearic acid deposition to eliminate any potential surface contamination. After stearic acid deposition and collection of background spectra the measurements were taken every 8 minutes during the course UV exposure. The distance between the glass substrate and the UV source was 21 cm. The experiments were repeated 3 times for 3 different PURETi samples.

3. RESULTS

3.1 *NO_x removal experiment*

The glass slides coated with PURETi product exhibited a significant activity in eliminating the NO_2 from the gas phase. The coating has removed almost 80% of NO_2 in both sets of experiments under the experimental conditions employed in our study, with the results adjusted for the control experiments (unadjusted total conversion of NO_2 was 98.76% and 97.81% for initial concentrations of $\sim 480\text{ppb}$ and $\sim 240\text{ppb}$ resp.). In comparison, the conversion of NO_2 by UV alone for the uncoated samples was only 19.25% and 16.73% for the two sets of experiments. The NO_2 conversion in the absence of PURETi coating can be attributed to the direct photolysis of NO_2 under UV radiation, which follows the reaction: $\text{NO}_2 + h\nu$ (290-430 nm) $\rightarrow \text{NO} + \text{O} (^3P)$. The results of our experiments are summarized in Figure 5.

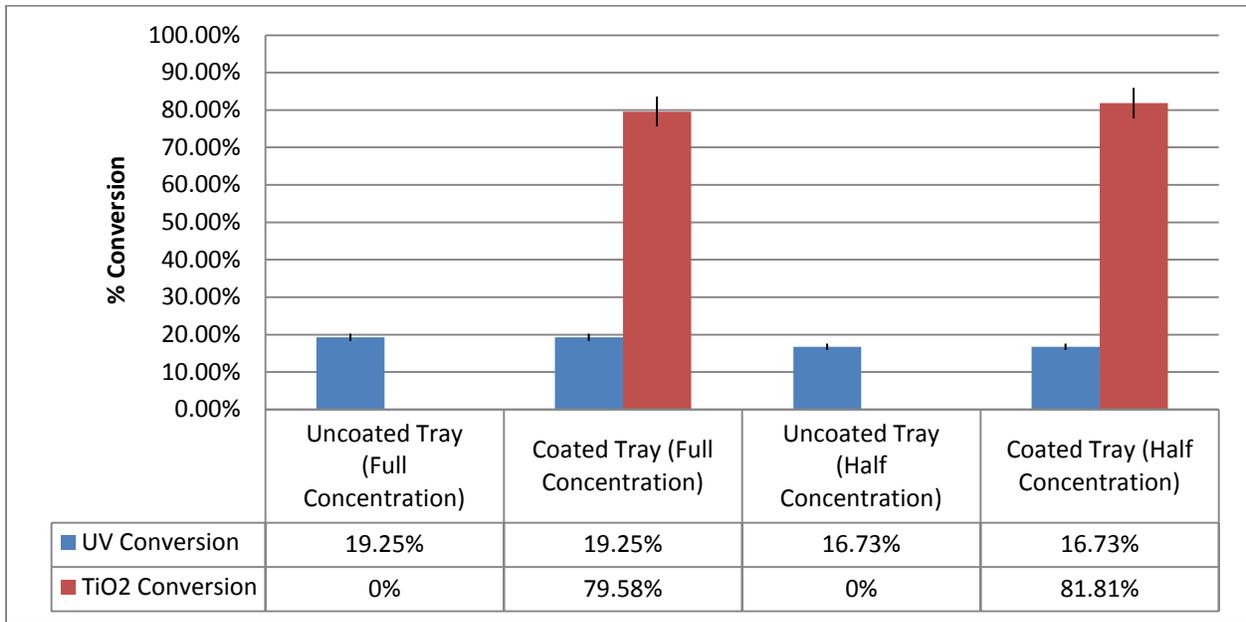


Figure 5 : NO₂ conversion comparison between the uncoated and coated pyrex trays

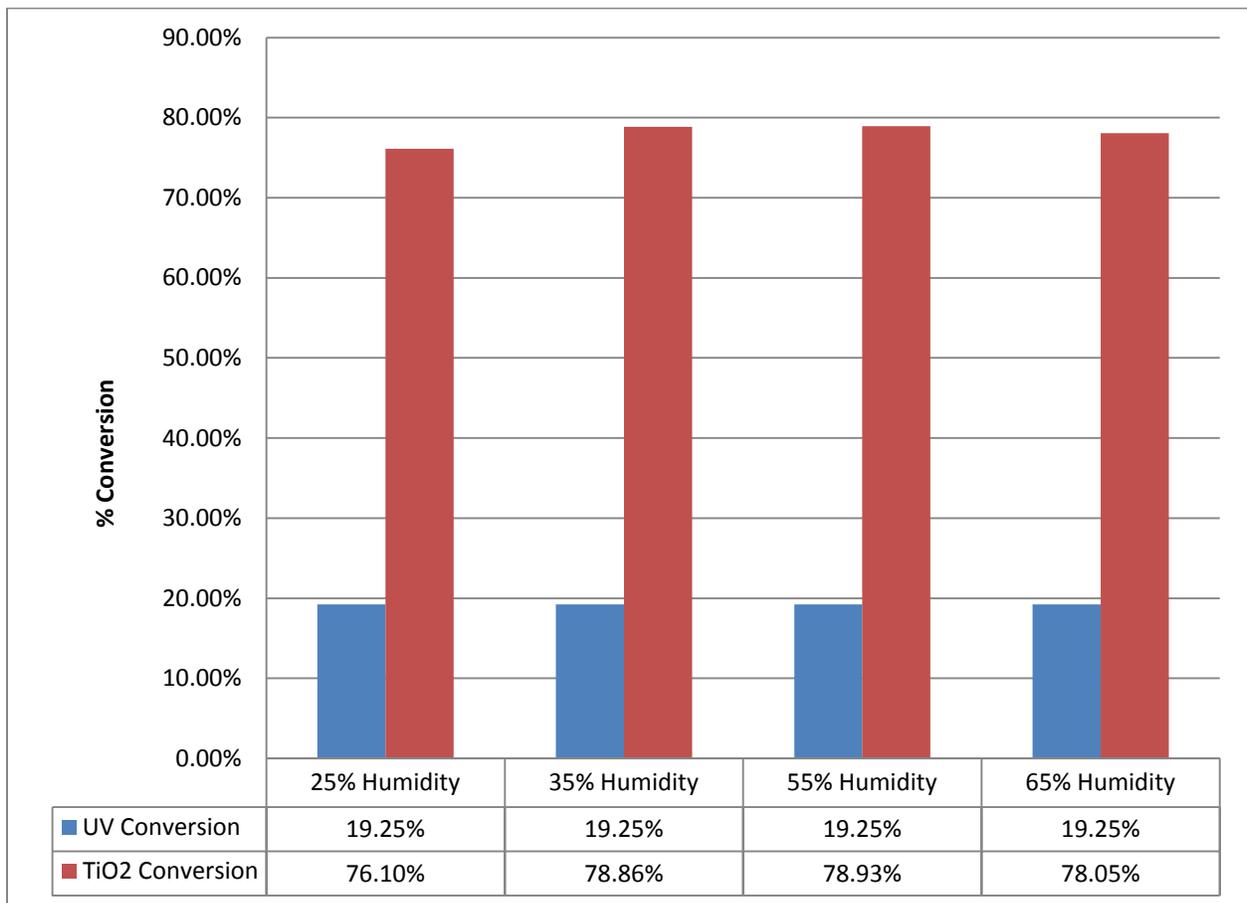


Figure 6: Conversion with variable humidity

The maximum NO₂ conversion by direct photolysis is represented by the red bars. The blue bars represent the NO₂ conversion by TiO₂ coated trays, adjusted for direct photolysis. These results also indicate that there is no significant dependence of conversion on NO₂ concentration, given that conversion at 240 ppb was only few percent higher than that at 480 ppb.

Figure 6 shows the dependence of the NO₂ conversion on humidity. It can be seen that a difference in NO₂ conversion at various level of humidity is negligible with the maximum conversion occurring at 55% and the minimum one at 25%.

3.2 Self-cleaning properties

The photocatalytic activity of the PURETi coating was assessed by disappearance of stearic acid, which is commonly used to determine self-cleaning properties of various substrates. Figure 7 shows the stacked FTIR spectra of the stearic acid as a function of UV exposure. Based on this information we can conclude that stearic acid is substantially decomposed under UV radiation as indicated by significant reduction in intensity of absorbance over the course of UV exposure.

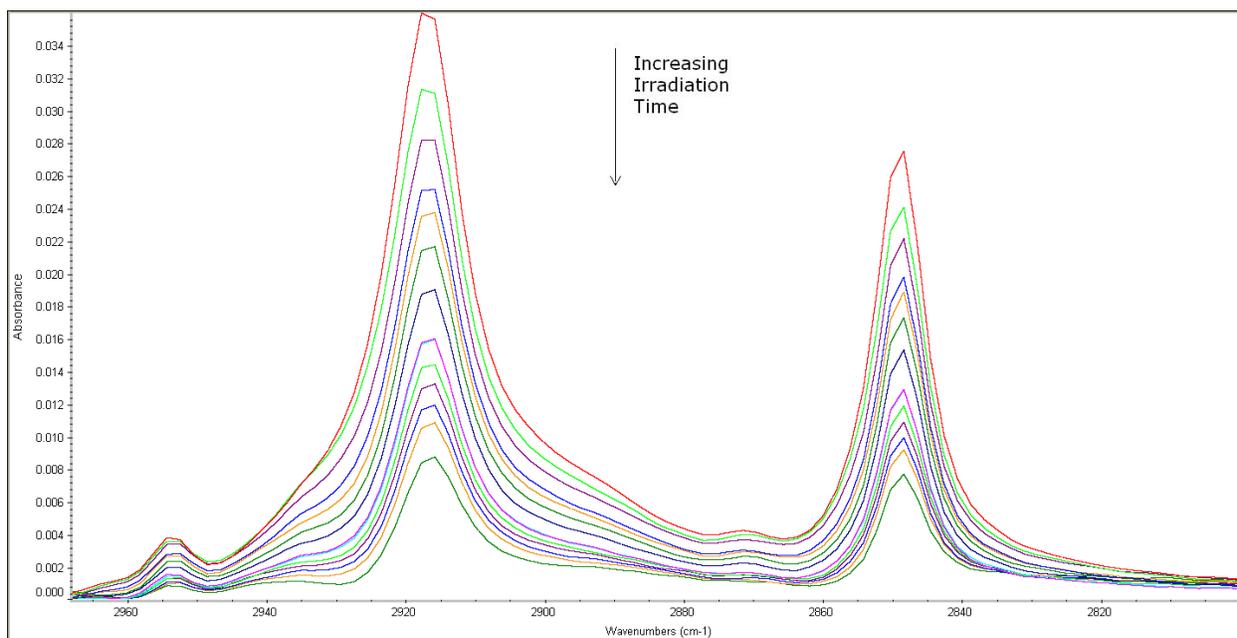


Figure 7: FTIR spectra of stearic acid for increasing UV-irradiation time.

The rates of stearic acid degradation were analyzed by integrating the area under the peaks (between 2800 and 2975cm⁻¹). The results are shown in Fig 8. The y-axis represents the stearic acid concentration as a function of time normalized for initial concentration. The x-axis represents the time of exposure, or more specifically, a number of UV exposures, each lasting for 8 minutes. The error bars are given for 90% confidence intervals. Figure 8 indicates that almost 80 % of stearic acid disappeared within 104 minutes of exposure. It can be concluded that PURETi coating is very effective for decomposing the stearic acid, which can serve as a good approximation of self-cleaning properties of the samples tested.

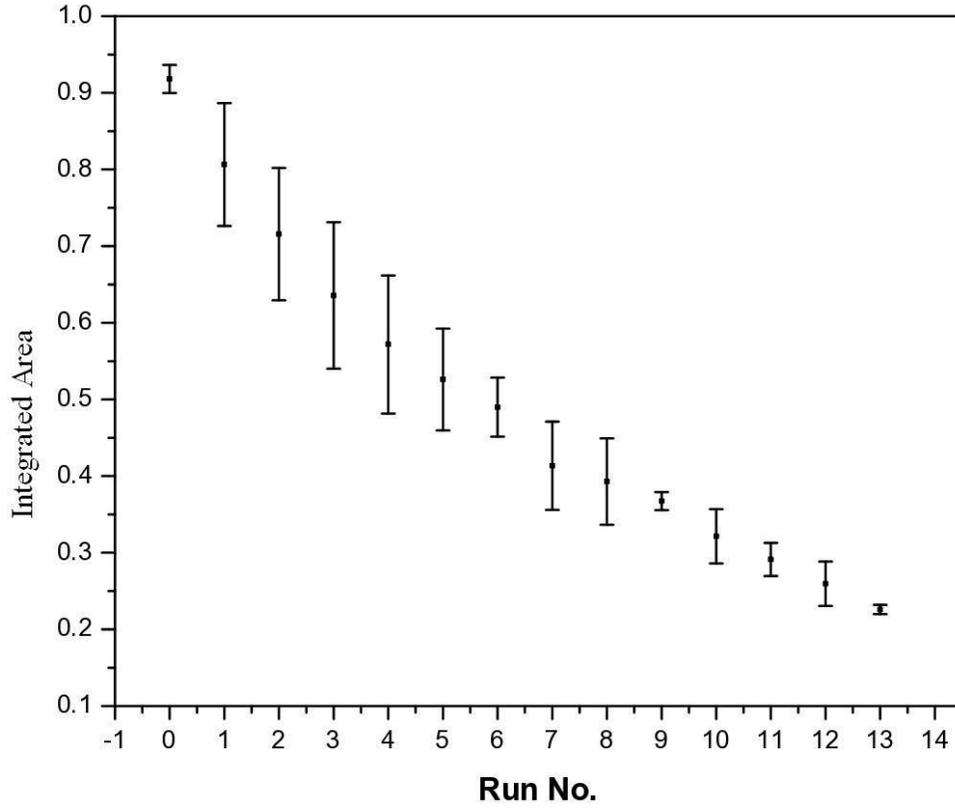


Figure 8: Integrated area vs. number of runs (each run consists of 8mins) for stearic acid degradation

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