Photocatalytic Coating on Road Pavements/Structures for NOx Abatement

Presented to

Houston Advanced Research Center

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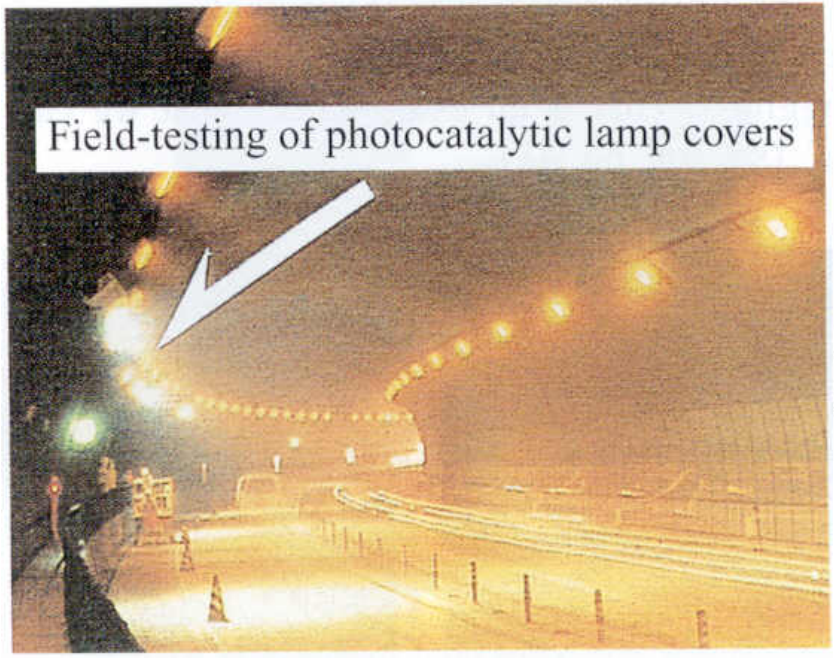
Lamar University, Beaumont, Texas

Photocatalysis is a Green Technology for Environmental Applications

Disinfection of Hospital Rooms (e.g., SARS viruses)



(Courtesy of Mitsubishi Paper Mills , Ltd.)

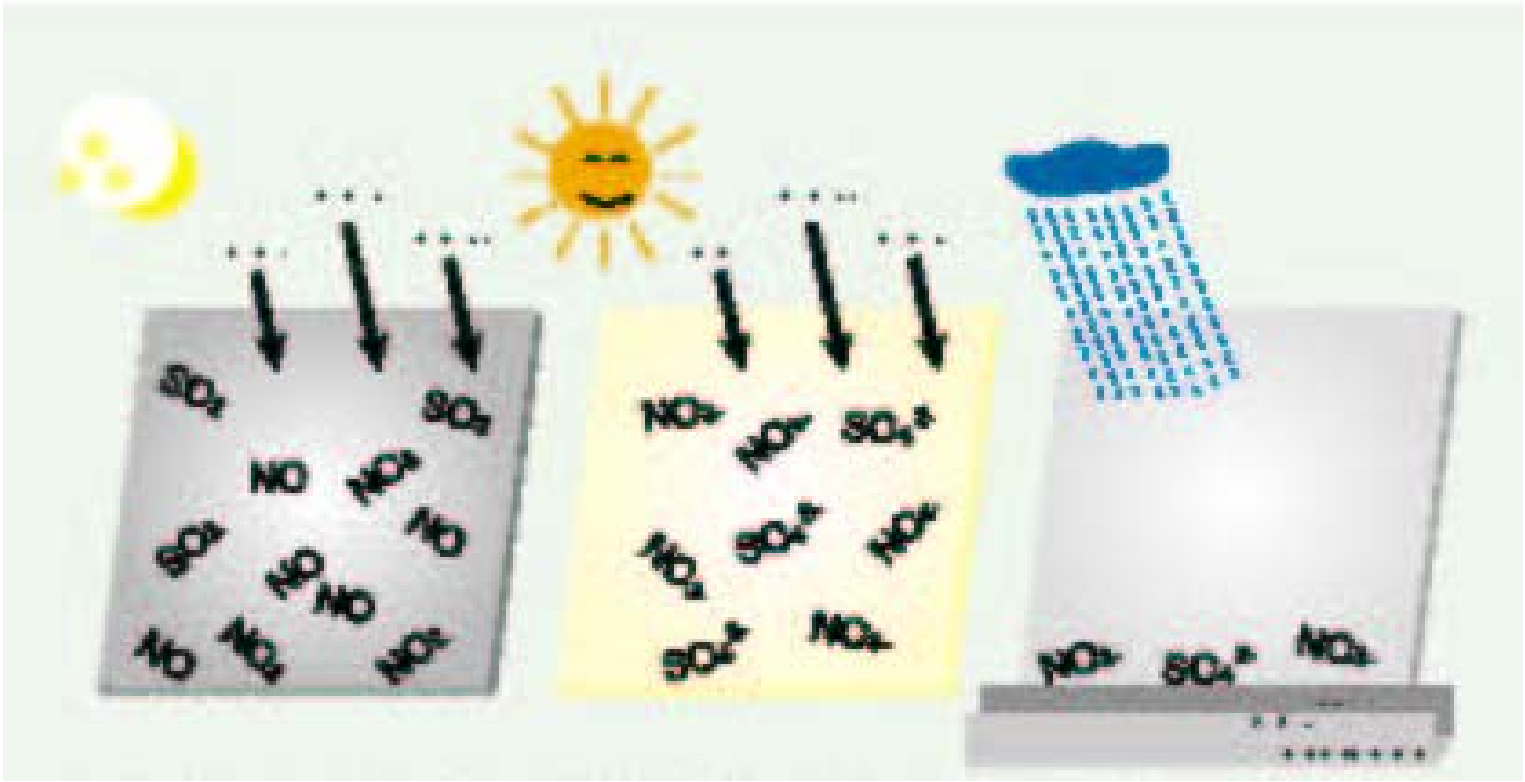
VOC oxidation into water, CO_2 and chlorides

- Indoor Air Cleaning
- Process Vent /Groundwater Treatment

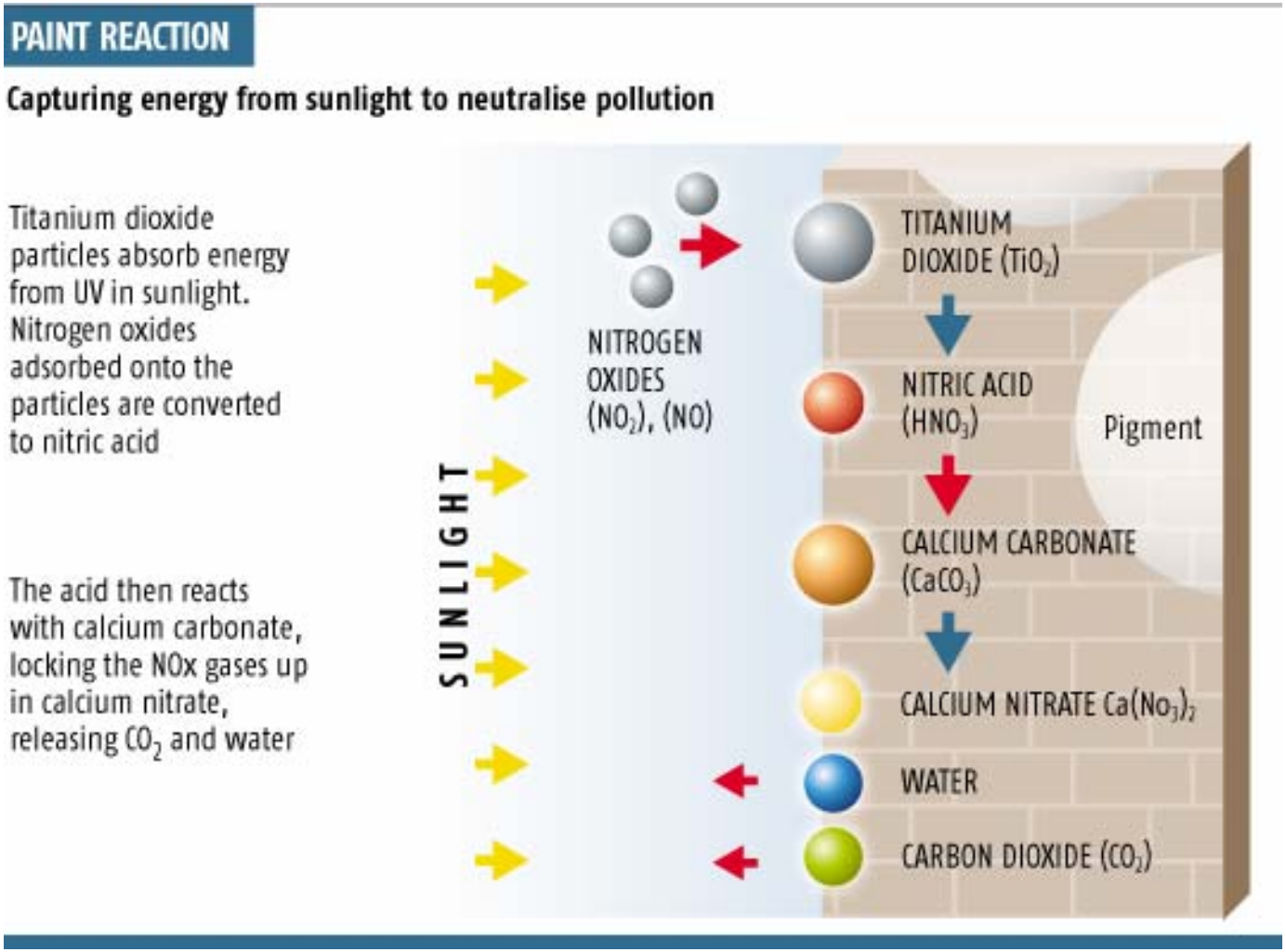
Self-cleaning photocatalytic lamp covers use photocatalysis under fluorescent light to oxidize grease/soot in urban traffic tunnels.

Nighttime and daytime processes of pollutant removal, and the regeneration of the TiO2- photocatalyst (Koji Takeuchi, Institute for Environmental Management Technology, Japan).

a) Adsorption of air pollutants especially during the night	b) removal of air pollutants by oxidation during the day	c) regeneration of catalyst by rainfall

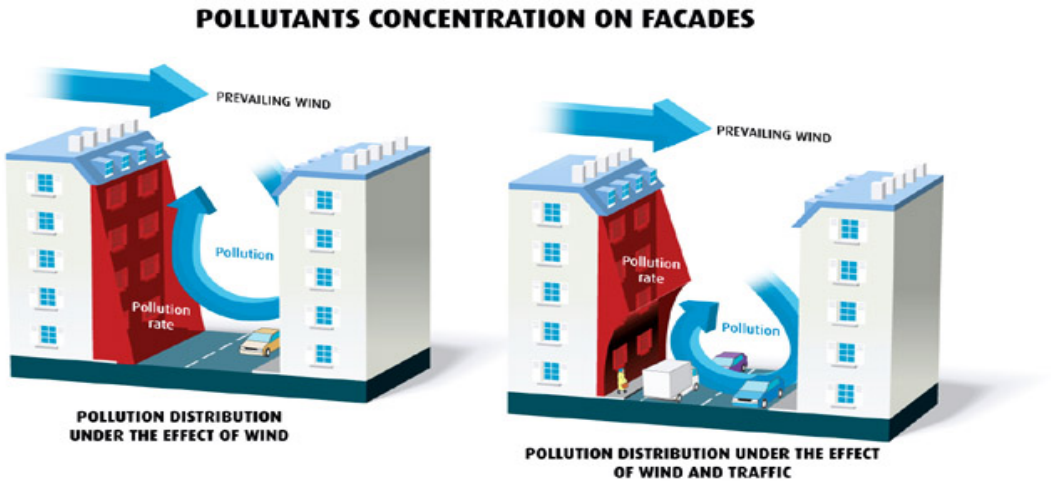


Pollutant-removal chemical reactions (courtesy of Hogan, New Scientist, February 2004



European Experience

- In 2002, 7000 square meters of road surface in Milan, Italy, were covered with a catalytic cement
  - Residents reported that it was noticeably easier to breathe - with the concentration of nitrogen oxides at street level cut by up to 60 %.
- More recently, Westminster borough of London cooperated with Mitsubishi Materials Corporation to pave roads with TiO_2 - containing paving stone (NOXER)
  - Under an intensity of UV light of 12 W/m^2, an 80% NO_x removal rate was achieved in the lab test (1 ppm NOx ; the UV intensity of direct sunlight in summer is 20-30 W/m^2, compared to 1 W/m^2 on a cloudy winter day).
- Euro PICADA (Photocatalytic Innovative Coverings Applications for De-pollution Assessment)
  - The 6-countries, 3.4 M€ PICADA project is testing photocatalytic concrete streets and walls in urban areas.



European Experience

TX Millennium brand (Italcementi Group)

In addition to pollution abatement, **photocatalytic white cement keeps architectural concrete clean and white (maintaining their aesthetic appearance unaltered in time)**

Japanese Experience

- The market for photocatalytic cements and paving slabs is growing
  - tested in Osaka, Chiba, Chigasaki & Saitama-Shintoshin
  - more than 50,000m^2 of such materials have been installed in Japan.

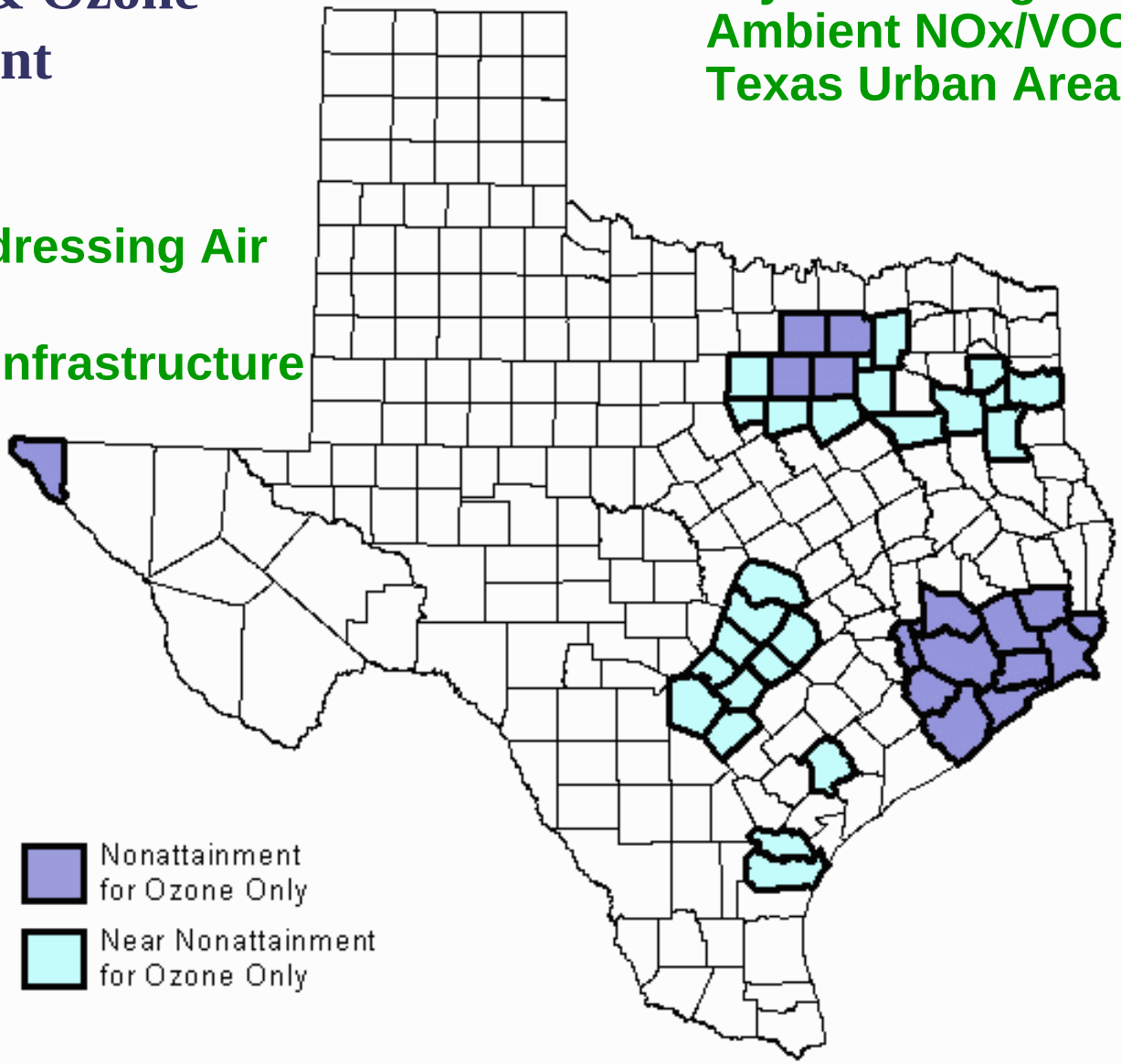
Work of Nature

- **Nearly Maintenance-Free**
  - **Only requires Sunlight, Rainfall, and Natural Air Movement.**
- Air turbulence is constantly carrying the gases over the surface for deposition
- The simulated vertical NO concentration profile on an urban model road showed **the highest concentration occurs on the road surfaces (~800 ppb)**

Air Quality & Ozone Nonattainment

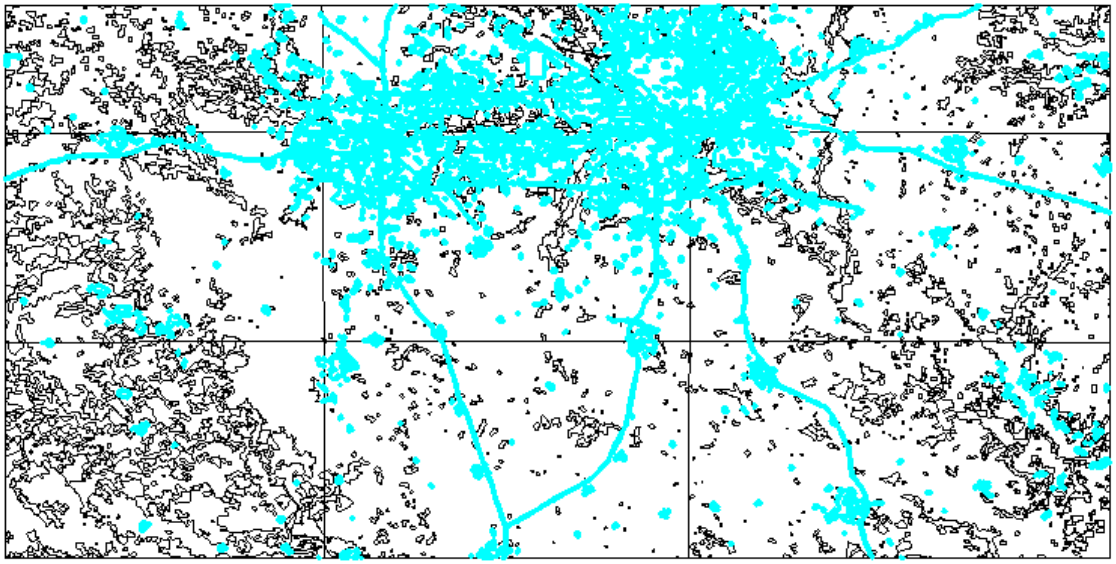
Catalytic Coatings Combat Ambient NOx/VOCs in Texas Urban Areas

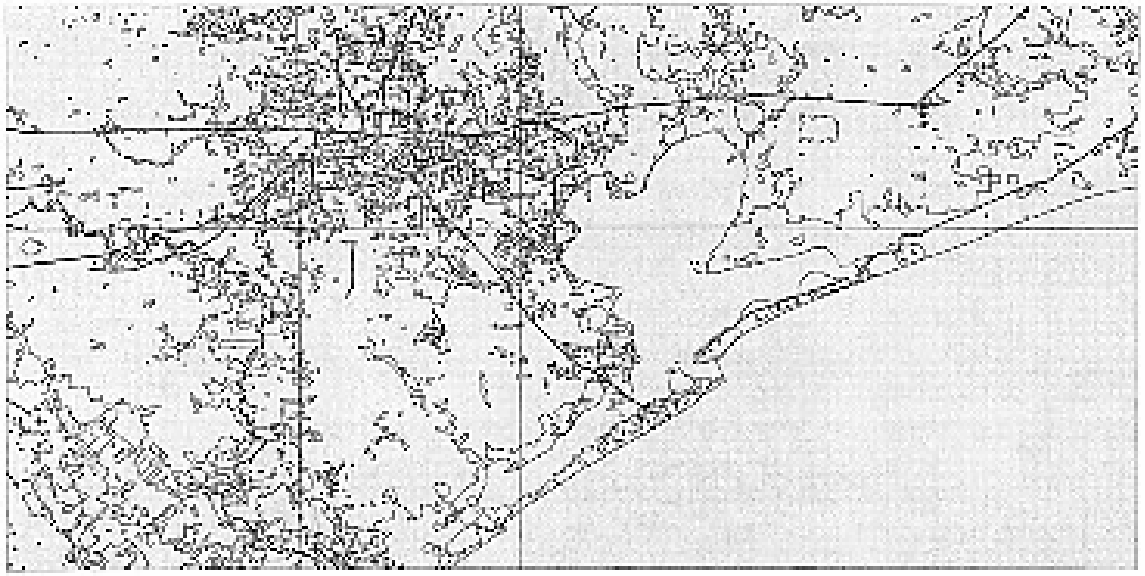
Technology Addressing Air Quality through Transportation Infrastructure



http://www.tnrcc.state.tx.us/gis/metadata/nonatain_met.html

DFW built-up area
= 12200 (km)^2





HGB built-up area = 10040 (km)^2

City Planning & Green Architecture

- This technology will give architects and town planners a new weapon in the fight against pollution.
- This green construction technology has the potential to **reduce the number of high ozone days in the DFW or HGB areas.**
- Texas' large urban areas (DFW & HGB) with plenty of sunshine provide an ideal setting for developing and testing the photocatalytic coating technology to facilitate sustainable economical growth in Texas.

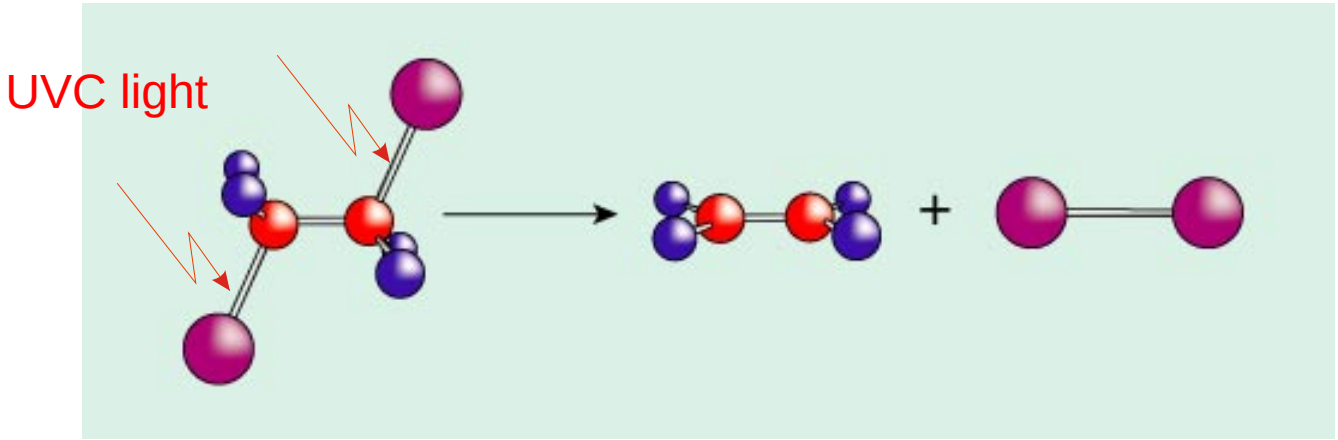
TiO_2 Catalytic Coatings as Noted by TCEQ

- http://www.tceq.state.tx.us/assets/public/implementation/air/sip/miscdocs/area_8-31-05.pdf
- **Area - Potential Control Strategies for DFW Attainment Demonstration**

TiO_2 Catalytic Coating: Cost-Effectiveness

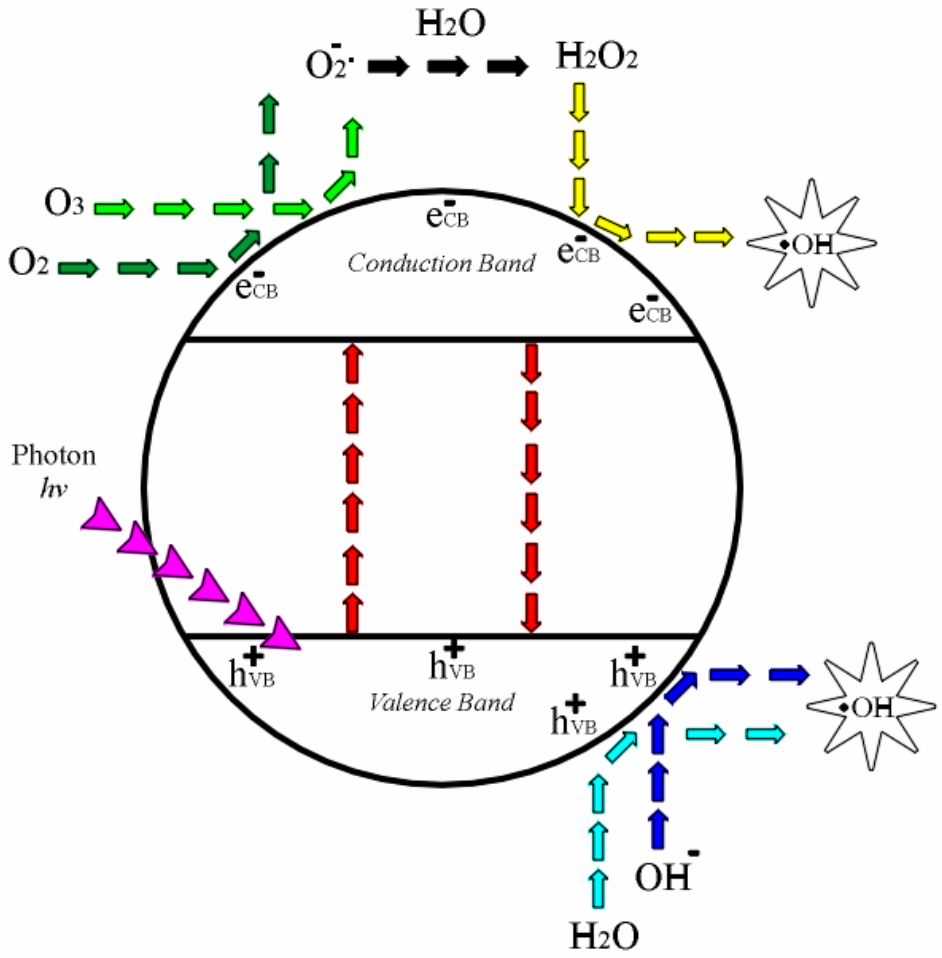
- **Even though the chemistry works for both NOx and VOCs, the current project will focus on NOx only.**
- **The preliminary estimate of NOx removal is very promising (50,000 ton/yr or 28% for Harris County at a cost of $200/ton assuming pavements last for 5 years).**

Photolysis: High Energy Photons



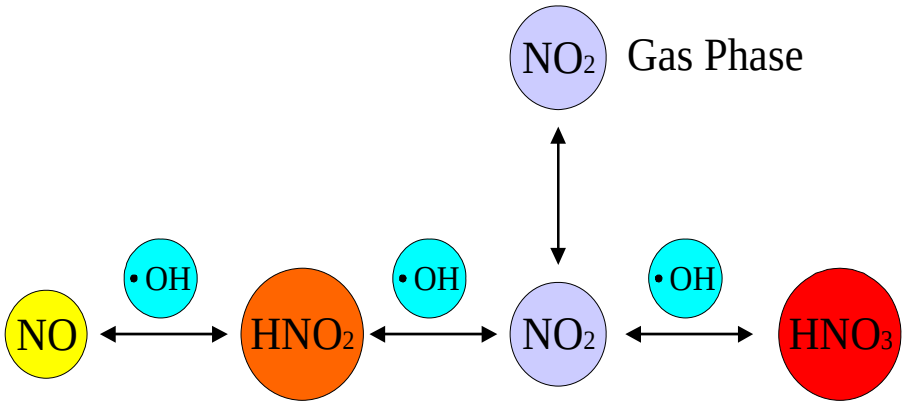
UVC can break the chemical bonds

Photocatalysis: Lower Energy Photons



- **Potential to use sunlight**
- **Ambient T & P**
- **Light-induced electron-hole pairs generating free radicals to start redox reactions**

NOx photocatalytic oxidation

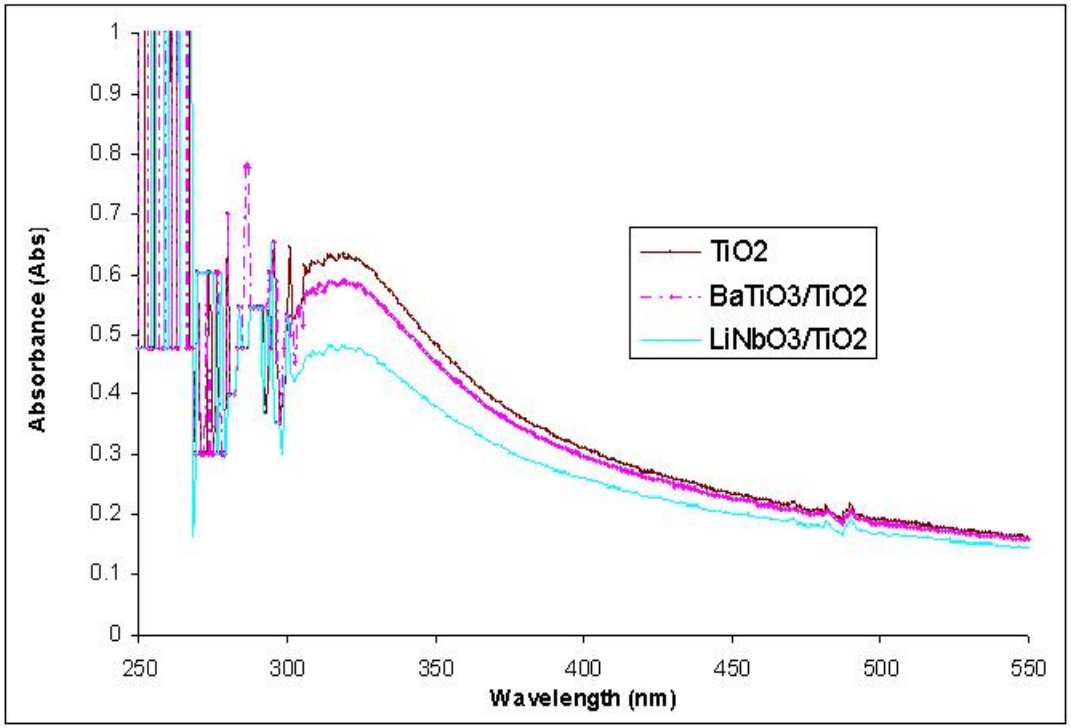


$$HNO_3 + CaCO_3 \leftrightarrow Ca(NO_3)_2 + H_2O + CO_2$$

Proposed Tasks

- Technology Update and Preliminary Impact Study
  - Latest developments in removal rate estimate & cost data
  - Estimation of coatable road surfaces (including pavement, sound barrier, road sign, etc.) using GIS
- Lab Investigations
  - Ferroelectric Optical Additive
  - Visible-Light-Responsive Catalyst
  - Advanced Photocatalytic Composite Materials

Lab Investigation (1): Ferroelectric Optical Additives

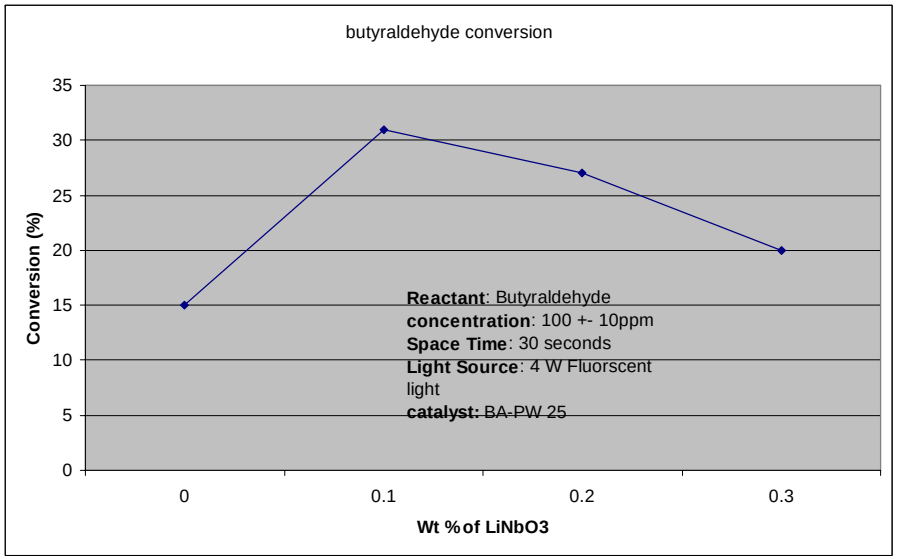


Lamar University has pioneered the use of wide band gap, high transmittance, ferroelectric crystals such as $LiNbO_3$ and $BaTiO_3$ as additives to utilize UV/visible light more efficiently.

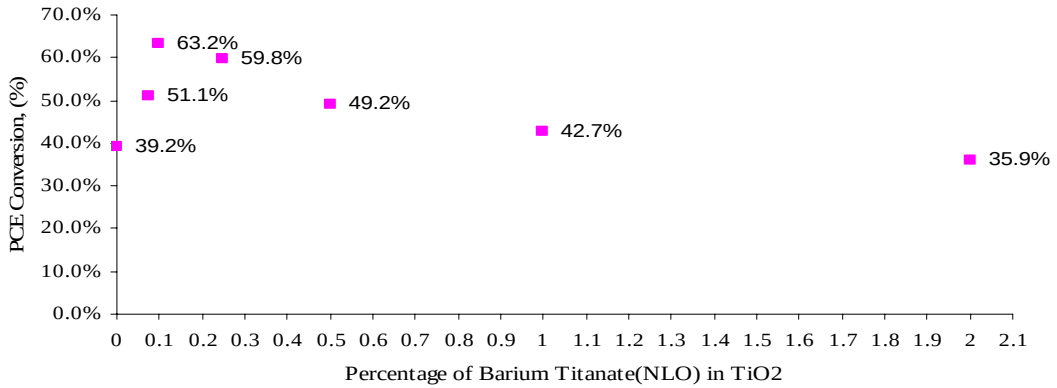
The ferroelectric opticals can guide UV/Visible light into the catalyst interiors, enhance scattering, and stabilize the electron-hole pairs

Both $BaTiO_3$- and $LiNbO_3$- modified TiO_2's absorb less in the UVA/Vis. region (300-550nm) compared to Degussa P-25 TiO_2.

Enhancements with $LiNbO_3$ and $BaTiO_3$ Additives



0.10% (w/w) $LiNbO_3$ shows a 16% increase in butyraldehyde conversion using visible-light-responsive BA-PW25



0.1% (w/w) $BaTiO_3$ shows a 24% increase in PCE conversion using P-25 TiO_2

Lab Investigation (2)

- Test visible-light-responsive catalysts (e.g., BA-PW 25, TiO_xN_y, TaN) vs. regular UVA light titania (e.g., P-25)
- Lab investigation using **photocatalytic concrete composite materials** for NOx removal

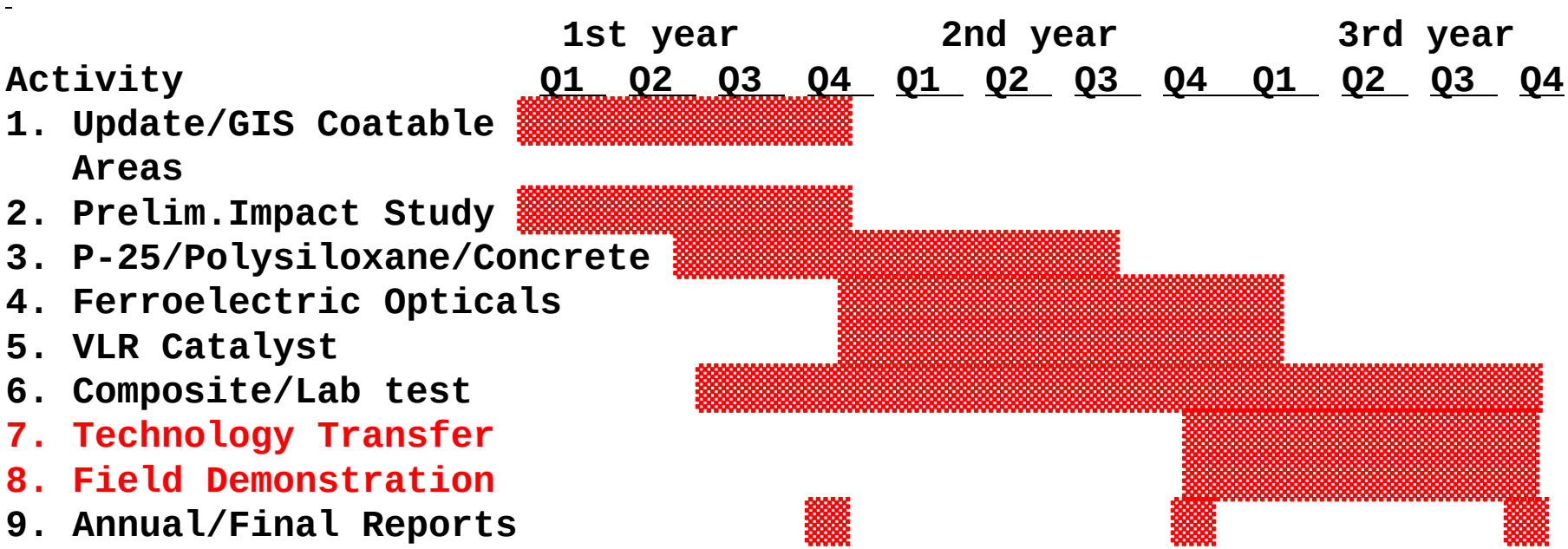
Technology Transfer Partners

- Concrete & Coating companies
  - **Few Ready Mix Concrete Co., Jasper, Texas.**
    http://concreteproducts.com/mag/concrete_few_ready_mix/
  - **Italcementi Group's subsidiary:Essroc**
  - **Green Millennium**

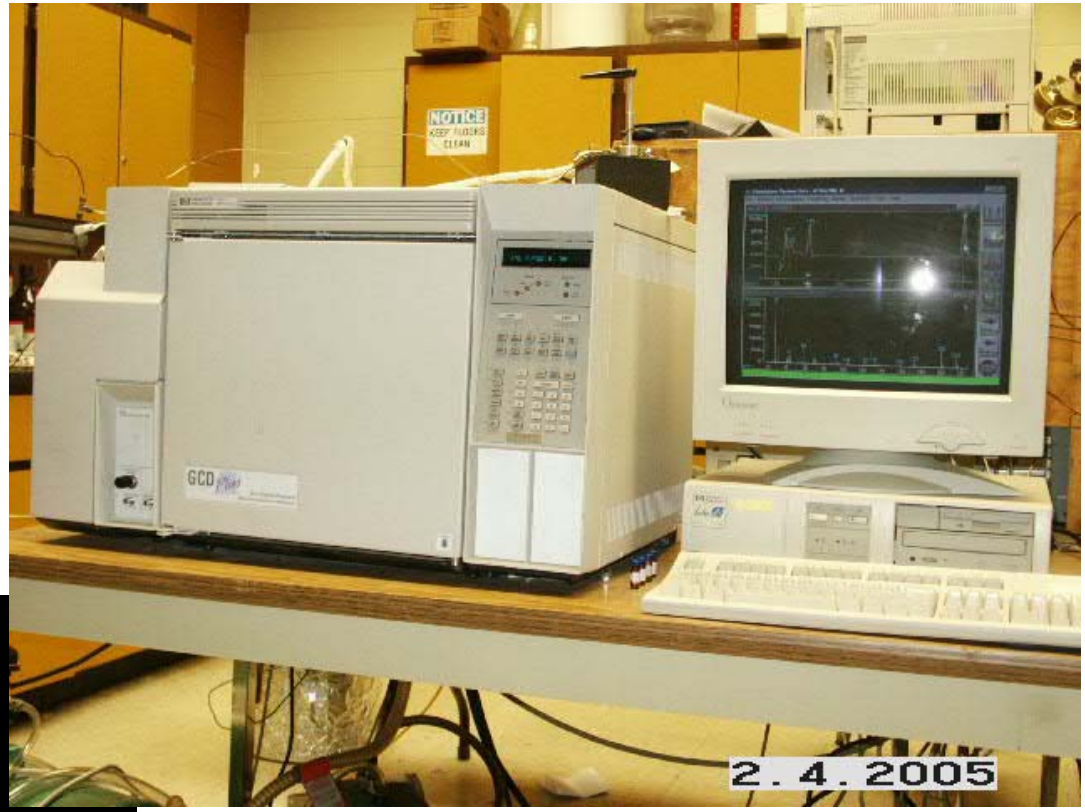
Field Demonstration

- **Demonstrate the developed technology with the approval of community and government agencies (City, TCEQ, TxDOT, EPA).**

Milestone Chart




Thermo Environmental Instruments Inc.
Model 10S


NOTICE
GCD
2.4.2005

Photocatalysis & Solar Processing Lab
Recent Papers/Grants

- X. Ye, D. Chen, K. Li, V. Shah, M. Kesmez, K. Vajifdar, “Photocatalytic Oxidation of Aldehydes/PCE Using Porous Anatase Titania and Visible-Light-Responsive Brookite” *Titania Chem. Eng. Comm.*, In Press.
- Ye, X., Chen, D.H., and Li, K. "Oxidation of PCE with a UV LED Photoreactor", *Chemical Engineering & Technology*, January 2005.
- “ Fiber-Optic Photoreactor Using Titania Modified with Ferroelectric Optical Crystals for VOC Destruction,” with K. Vajifdar, T. Han, B. Ardoin, D. Grooms, and K. Li, 13th International Congress on Catalysis, Paris, France, July 11-16, 2004
- “TiO_2 Photocatalytic Oxidation Of Nitric Oxide: Transient Behavior And Reaction Kinetics”Sid Devahasdin, Chiun-Jr Fan, Kuyen Li, and Daniel H. Chen, *Journal of Photochemistry and Photobiology A; Chemistry*, **156**/1-3 pp 161 – 170 (2003).
- "Photocatalytic Oxidation of Butyraldehyde over Titania in Air: Byproduct Identification and Reaction Pathways," with C. Huang, and K. Li, *Chem. Eng. Comm,*, **190**,*373-392, 2003*.
- "TiO_2 Photocatalytic Oxidation of Butyraldehyde and PCE in the Air through Concentric Reactors," with K. Li, S.Y.C. Liu, C. Huang, S. Esariyaumpai, *J. Adv. Oxid. Technol, 5(2), 227-232* (2002).
- Grants: USDA, EPA, Industry
- http://hal.lamar.edu/%7Eche_dept/photocatalysis/homepage.htm

Dr. Robert L. Yuan, P.E.

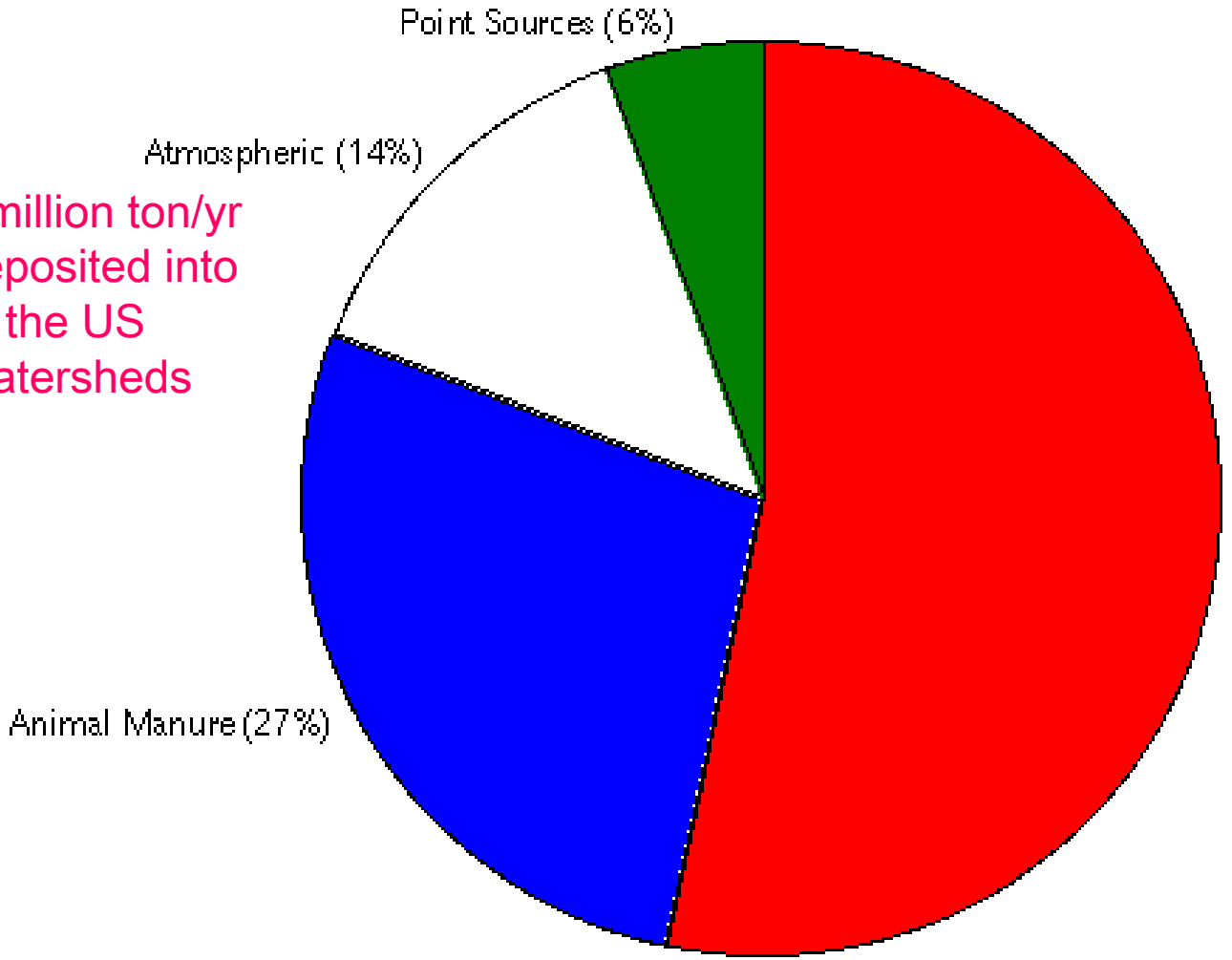
- **Area of Expertise**
  - **Fiber-Reinforced Polymer Composites in Civil Engineering Structural Application**
  - **Properties and Behavior of Plain Concrete Materials, Reinforced Concrete Structures, and Pre-stressed Concrete Structures**
  - **Experimental Mechanics and Computational Analysis**
- **Full-Scale Testing of Concrete Columns, Composite Columns, Composite Bridges, etc.**


Thank You

Asphaltic Pavements

- **The asphaltic pavements are important to consider**
  - **TiO_2 powder can be easily put on new paved asphaltic surfaces just as active carbon used as a P-25 titania support for enhanced NOx/VOC adsorption.**
  - **Lime stone as part of the aggregate can also be mixed with asphalt to provide neutralization capability.**
- **In the initial efforts, we would like to focus on cement surfaces. Asphaltic surfaces will be included in a sister proposal to other agencies.**

Impact of Nitrate



3.2 million ton/yr redeposited into the US watersheds

Agriculture accounts for over 80% of Nitrate-nitrogen input into the environment

Source: USGS; Nonpoint and point sources of nitrogen in major watersheds in the U.S. (Pucket, 1994) (http://www.ewg.org/reports/Nitrate/Figure1.html)

Impact of Nitrate

- **Assuming the best (worst?) scenario:**
  - **For HGA, 2500 km^2 coated area, the photocatalytic coating is estimated to remove 20,000ton/yr of nitrogen from air.**
- **That represents a 28% reduction of NOx in air**
  - **But only represents 2% of the nitrate-nitrogen to the Gulf of Mexico (total 10^6 ton/yr nitrate nitrogen in Mississippi River Basin)**
- **Our preliminary estimate is the nitrate contribution will not be significant.**
- **Total nitrate increase may be less than estimated because some NOx emitted into the air will be eventually oxidized and redeposited to water.**

NO Photocatalytic Decomposition

Dissociation of NO:

O^{2-} (cus) + $h^+ \rightarrow O^-$ (cus)

NO(ads) + $e^- \rightarrow NO^-$ (ads)

NO^- (ads) + O^- (cus) $\rightarrow$ N (ads) + O (ads) + O^{2-} (cus)

N(ads) + N(ads) $\rightarrow$ N2 (ads) $\rightarrow$ N2 (gas)

O (ads) + O(ads) $\rightarrow$ O2 (ads) $\rightarrow$ O2 (gas)

2 NO $\rightarrow$ N_2 + O_2

cus: coordinatively unsaturated

ads: adsorbed

N.W. Cant, J.R. Cole, J. Catal. 134 (1992) 317.

NO/NO_2 Photocatalytic Reduction

Reduction of NO/NO2:

NO_2 + CO $\rightarrow$ NO + CO_2

NO_2 + HC $\rightarrow$ NO + CO_2 + H_2O

2 NO + 2CO $\rightarrow$ N_2 + 2 CO_2

Photocatalytic Oxidation of VOC/CO

Oxidation of VOC/CO:

$TiO2 \rightarrow TiO2\ (h^+ + e^-)$ under UV/Vis light irradiation

$h^+ + OH^- \rightarrow OH\bullet,$

$e^- + O_2 \rightarrow O_2^-$

$O_2^- + H^+ \rightarrow HO_2\bullet$

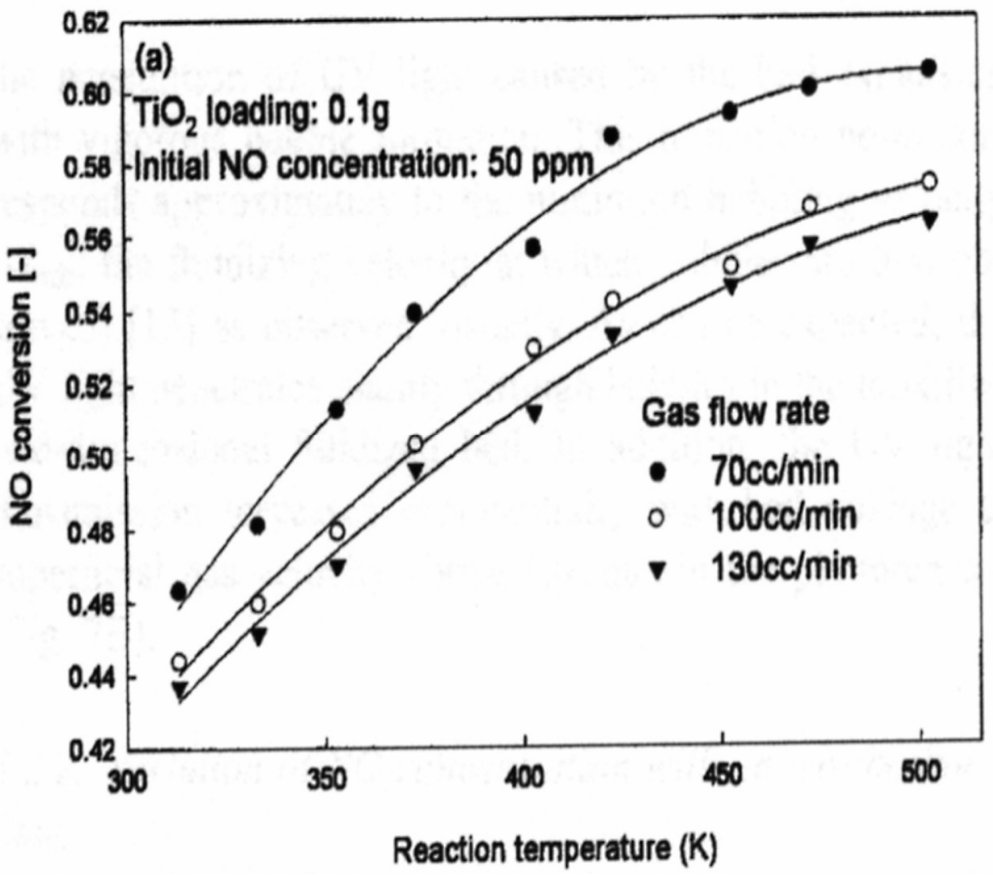
$O_2 + 2CO \rightarrow 2\ CO_2$

$O_2 + HC \rightarrow CO_2 + H_2O$

Where HC is a hydrocarbon.

Extreme Weather Conditions

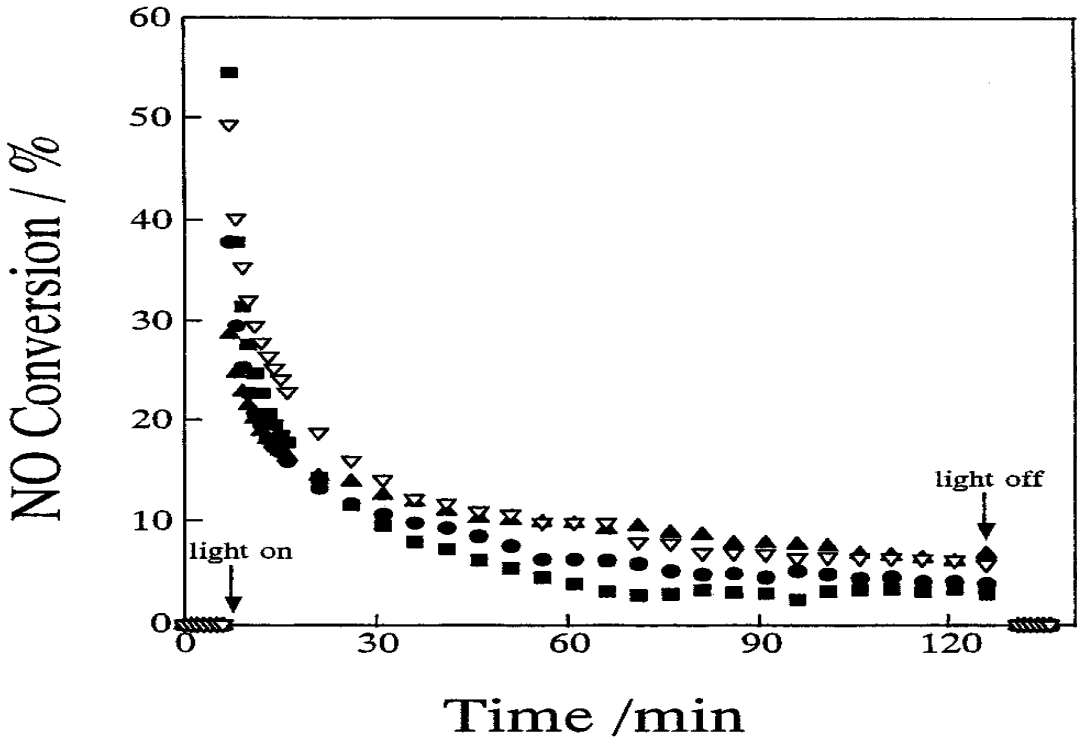
- Temperatures/Humidities are known to go to extremes in Texas
  - Temperature & Humidity impacts will be studied.
- Lim et al. found that NO conversion increases from 48% to 60% from 37°C to 227°C at an initial NO concentration of 50ppm.
- Studies show humidity has a positive effect on NO oxidation up to RH 50% then declines between 50%-80%.



Lim et al. found that NO conversion increases from 48% to 60% from 310K (37C) to 500K (227C) at an initial NO conc. of 50ppm*.

Issue: NOx Decomposition

- **Photocatalysts that decompose NOx to N_2 and O_2 are available** .(N. W. Cant, J.R. Cole, J. Catal. 134 (1992) 317).
- **We will include this part in the 3rd year tasks if funded.**



Reaction time profiles of the photocatalytic decomposition of NO at room temperature on the TiO_2 photocatalyst pretreated with O_2 at 573 K. Pretreatment: under a flow of O_2 (20 cm^3/min) and Ar (20 cm^3/min) at 573 K, heated in an Ar flow (20 cm^3/min) at 295 K (d), 373 K(j), 473K(m), and 573K(,), respectively. Gas component: 10 ppm NO in He, 100 cm^3/min. Catalyst: JRC-TIO-4, 150 mg. J . of Catalysis, **198**, 1-8 (2001)

CMAQ Modeling

- CMAQ employed nitrate formation and dry/wet deposition models (e.g., acid, and mercury) (http://www.cmascenter.org/2003_workshop/session3/morris_abstract.pdf)
- We agree that
  - it is beneficial to use the CMAQ model in sensitivity mode to demonstrate the effectiveness/impact of this approach.
  - it is beneficial to incorporate the NOx deposition model on heterogeneous surfaces into the future CMAQ package).
- However, experiments need to be conducted first in order to generate good data of NOx deposition flux