Wastewater Reuse Applications and Contaminants of Emerging Concern

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Use of Advanced Oxidation Technologies to Destroy Contaminants of Emerging Concern in Water Treatment and Reuse Applications

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But credits go to :

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Concerns in Surface Water Treatment and Treatment of Wastewater for Reuse Applications

- Microorganisms
- Trace Organic Contaminants
  - Synthetic Organic Chemicals (SOCs)
  - Cyanotoxins
  - Pharmaceuticals and Personal Care Products (PPCPs)
  - Endocrine Disrupting Compounds (EDCs)
  - Pesticides
  - Antibiotics

Common characteristic of trace organic contaminants

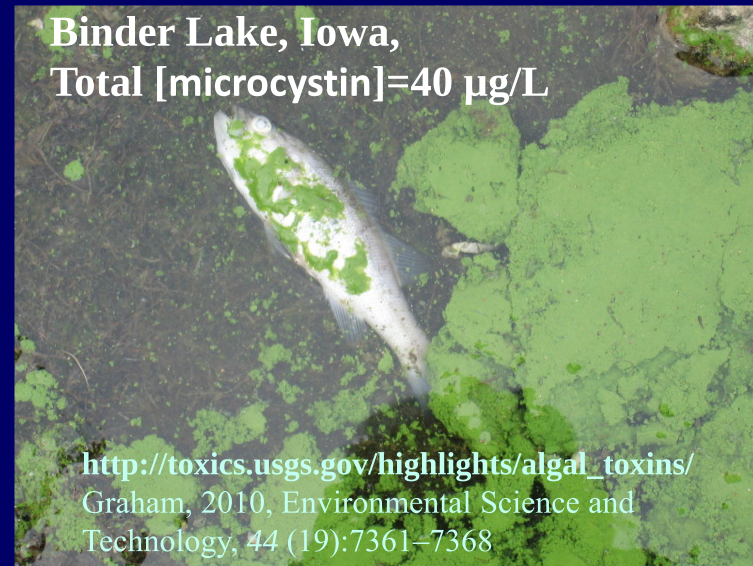
- Many are non-biodegradable
- Many are Hydrophilic
- Many are of relatively small molecular weight

Alturki, et al. 2010. *J. Membrane Science* 365 (1-2): 206-215.
Drewes, et al. 2003. *Water Research* 37 (15): 3612-3621.
Heberer, et al . 2002. *Water Sci. Technol*. 46(3): 81–88.

AOPs

HABs Contamination Events: North America

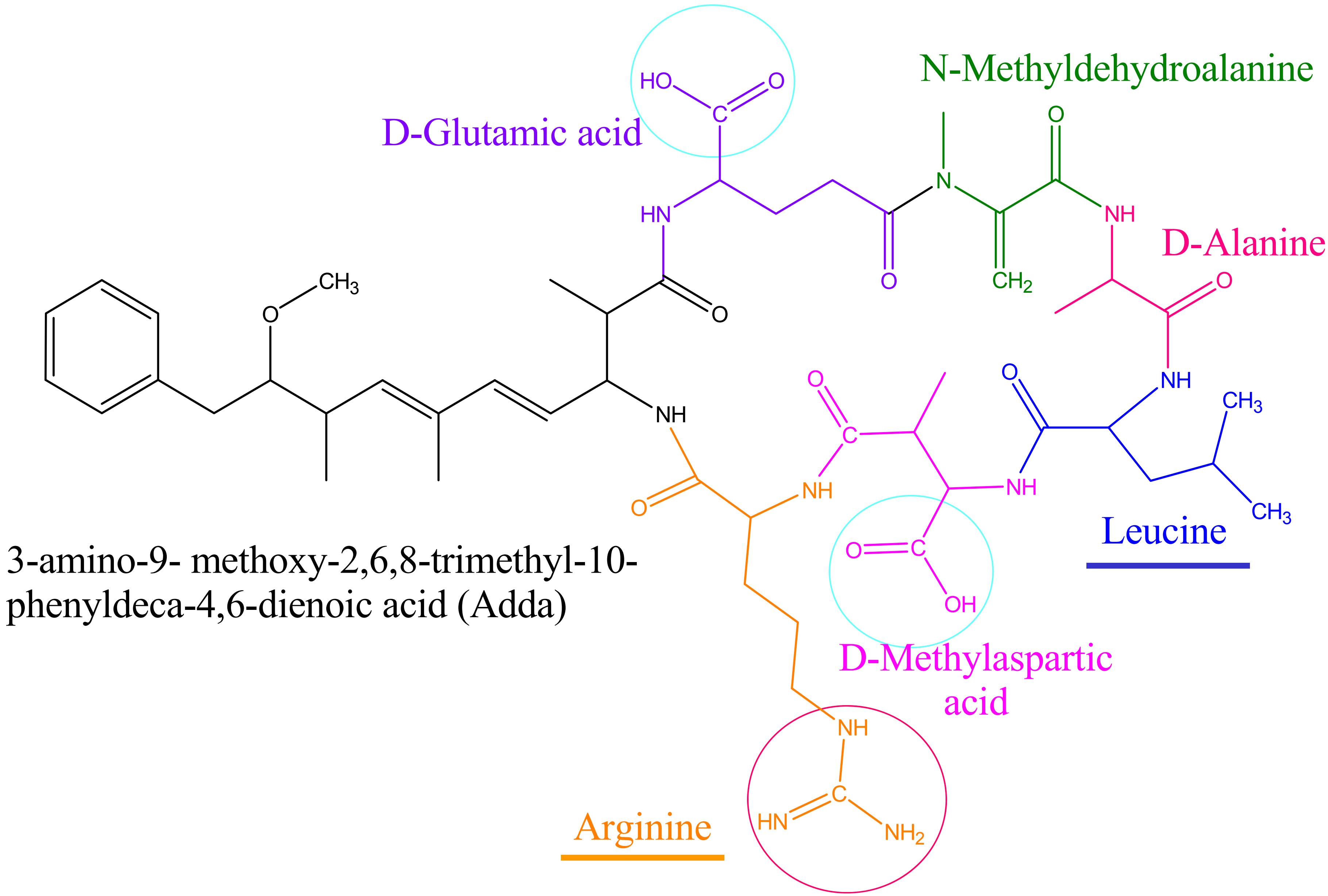
Pictures Courtesy: Gerry Pinto and Chris Williams (Jacksonville University Manatee Research, GreenWater Labs./ CyanoLab, Florida), Juli Dyble (NOAA), and John Lehman (Univ. Michigan).



HABs Contamination Events: Other Countries

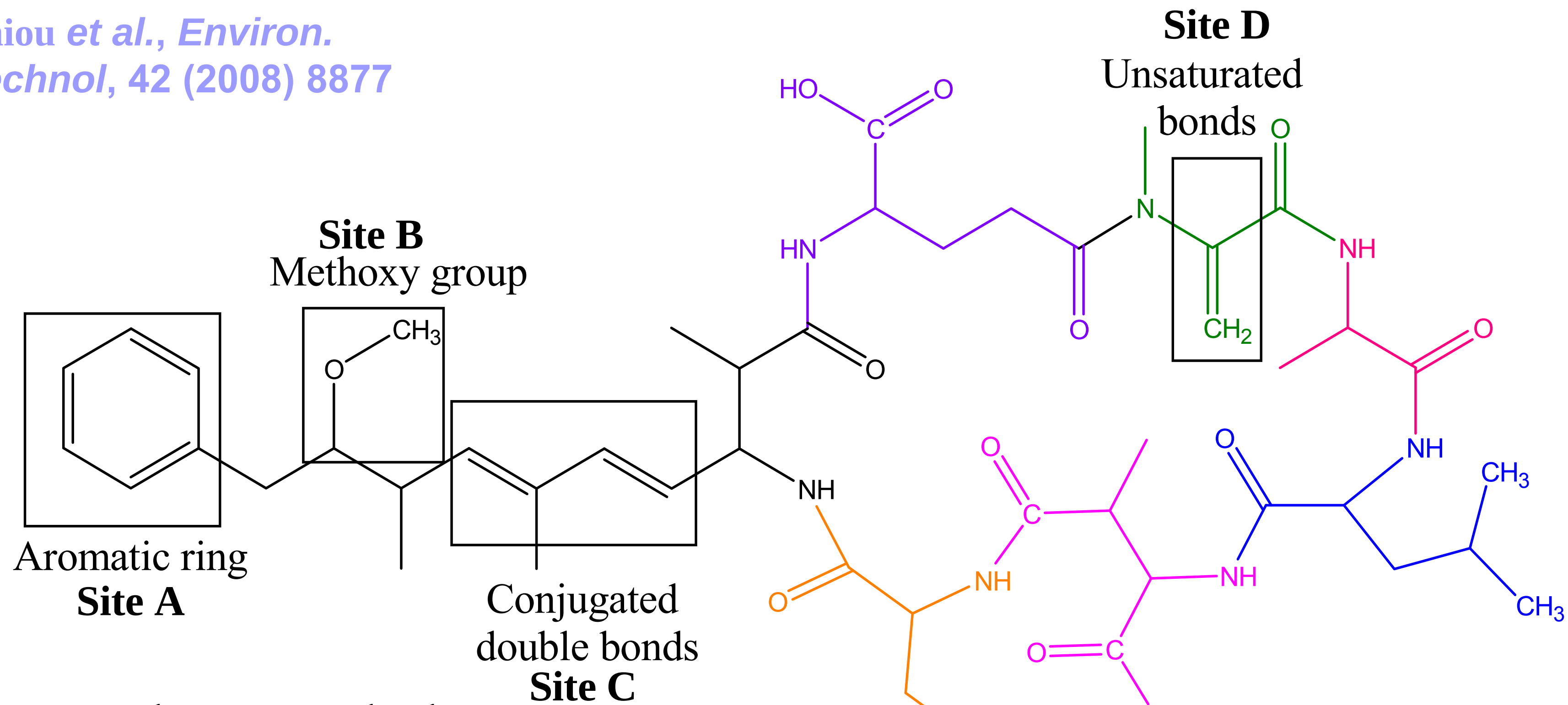
Blue green-algae bloom covering 377,000 sq km of the Baltic Sea (European Space Agency's Envisat satellite image). Lack of wind and prolonged high temperatures had triggered the largest bloom since 2005.

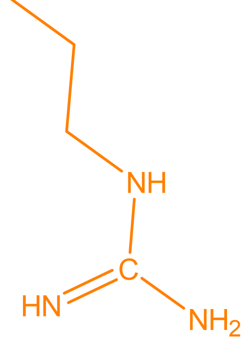
MICROCYSTIN -LR



UV/TiO_2: Observed MC-LR sites of hydroxyl radical attack[#]

[#] Antoniou *et al.*, *Environ. Sci. Technol*, 42 (2008) 8877





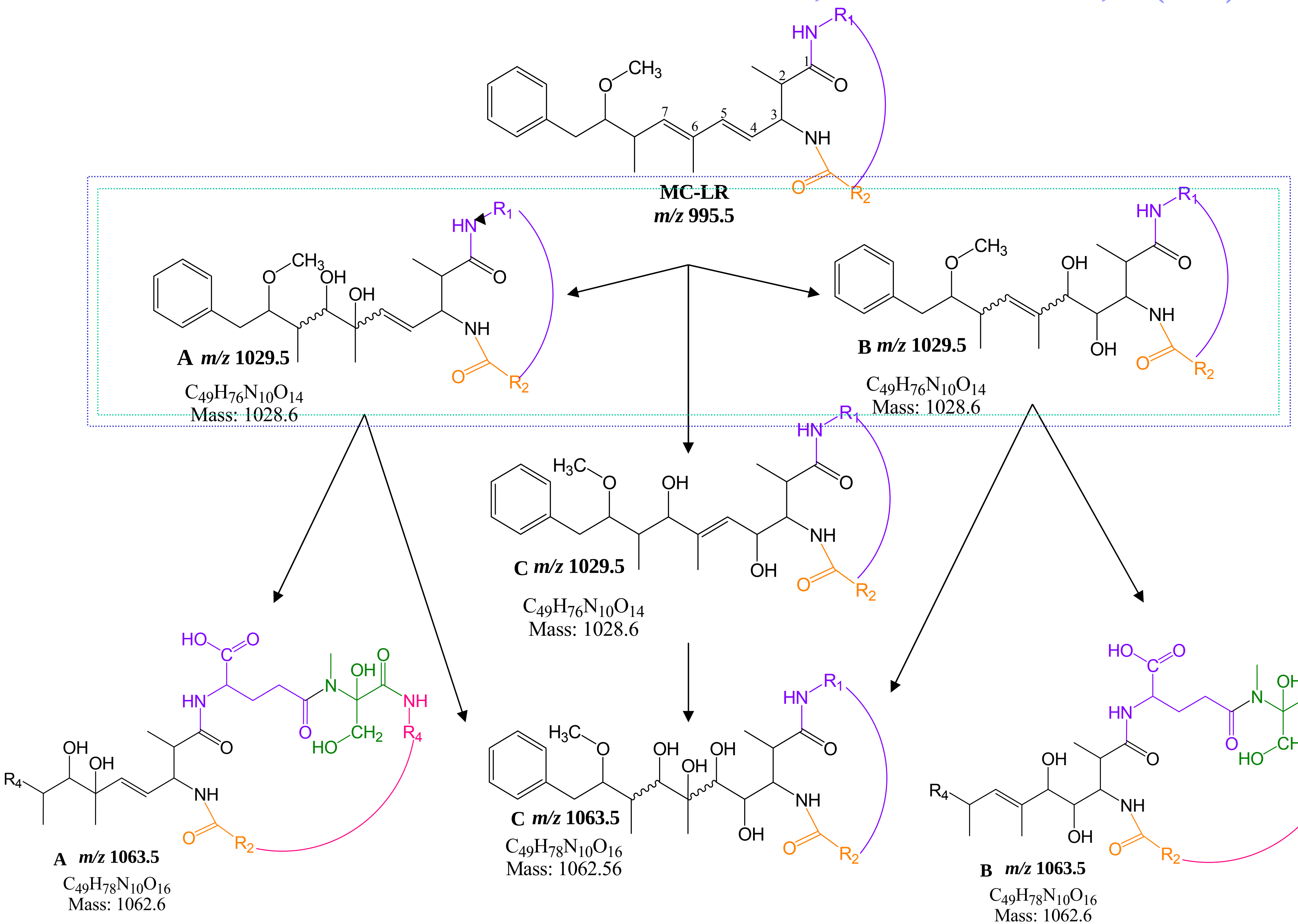
Our results revealed 21 intermediates (as *m/z*) with most of them being new findings.*

*Liu *et al.*, *Environ. Sci. Technol*, 37 (2003) 3214

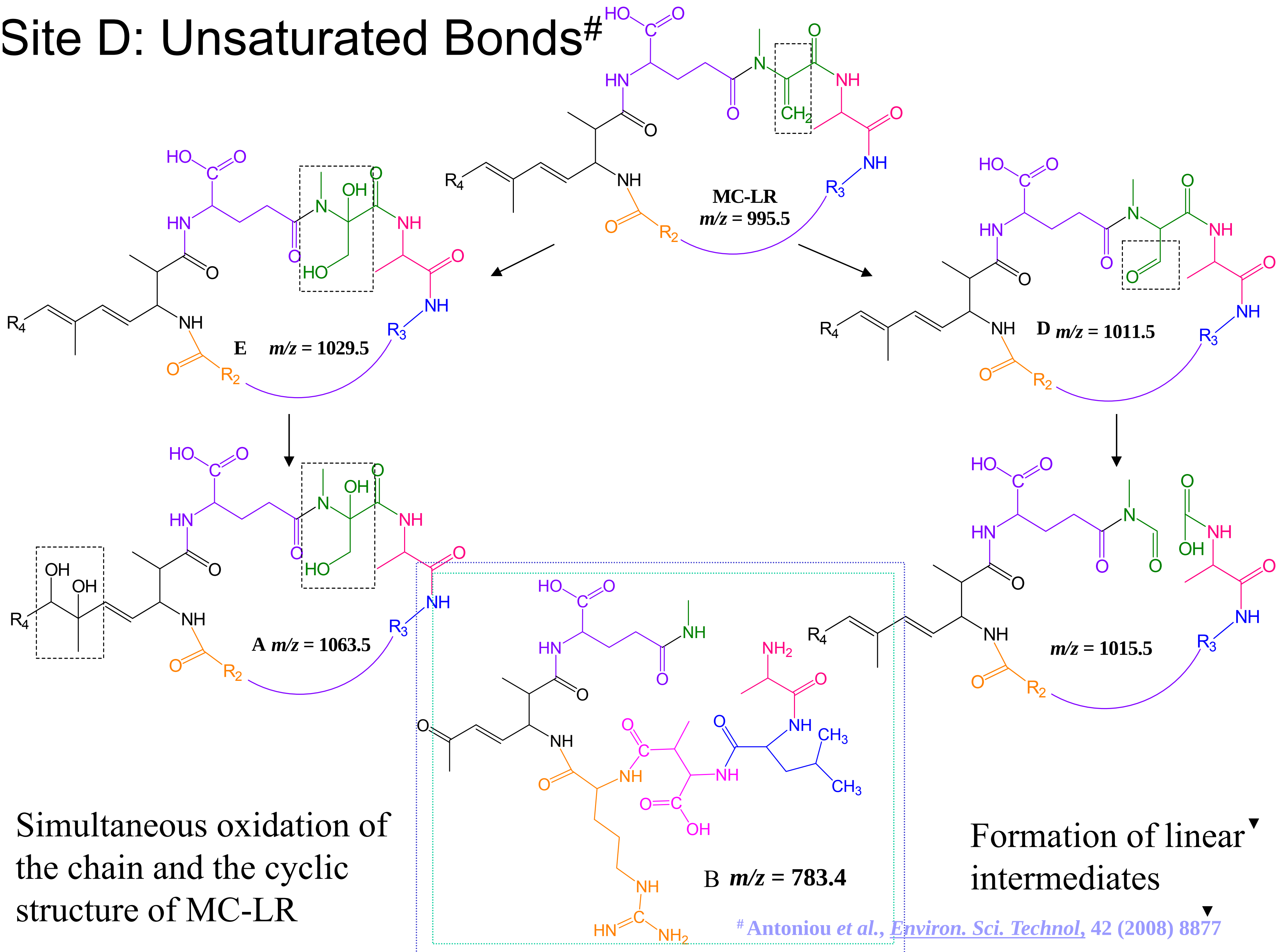
*Song *et al.*, *Environ. Sci. Technol*, 40 (2006) 3941

Site C: Diene Bonds#

Antoniou *et al.*, *Environ. Sci. Technol*, 42 (2008) 8877



Site D: Unsaturated Bonds[#]



Simultaneous oxidation of the chain and the cyclic structure of MC-LR

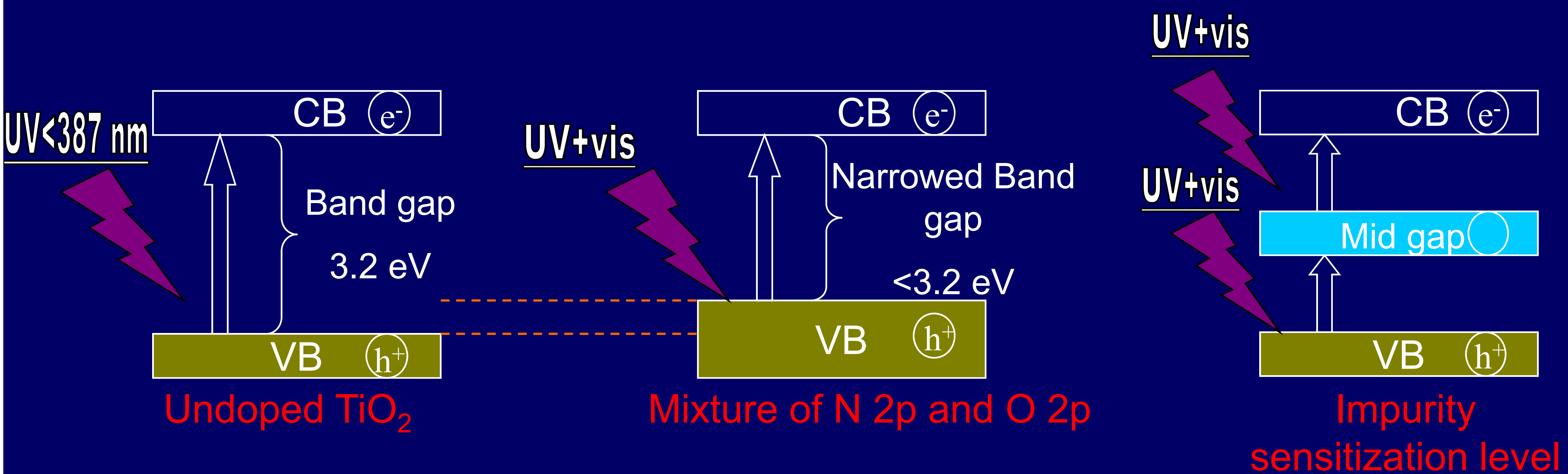
Formation of linear intermediates

[#] Antoniou *et al.*, *Environ. Sci. Technol*, 42 (2008) 8877

Visible Light Activation of TiO_2

- **Explore Solar Driven TiO_2-based Water Treatment Technologies**
  - Solar light: sustainable source of energy.

- **Band-Gap Narrowing of TiO_2 for Visible Light Activation**
  - Metal-doping (Pt, Ag) and non metal species like N, F, S, C.



Sato, *Chem. Phys. Lett* 123 (1986) 126; Burda *et al*., *Nano Lett*. 3 (2003) 1049; Bacsa *et al*., *J. Phys. Chem*. 109 (2005) 5994; Wu *et al*., *Appl. Phys. A* 81 (2005) 1411.

Asahi *et al*., *Science* 283 (2001) 269; Irie *et al*., *J. Phys. Chem. B* 107 (2003) 5483.

Sol-gel Synthesis route

FS:isopropanol:AA:EDA:TTIP

R:275:422:46:21

FLUOROSURFACTANT (Zonyl FS-300, FS) IN ISOPROPANOL

↓

ACETIC ACID pH~6.0

↓

ETHYLENEDIAMINE (EDA)

↓

TITANIUM PRECURSOR (TTIP)

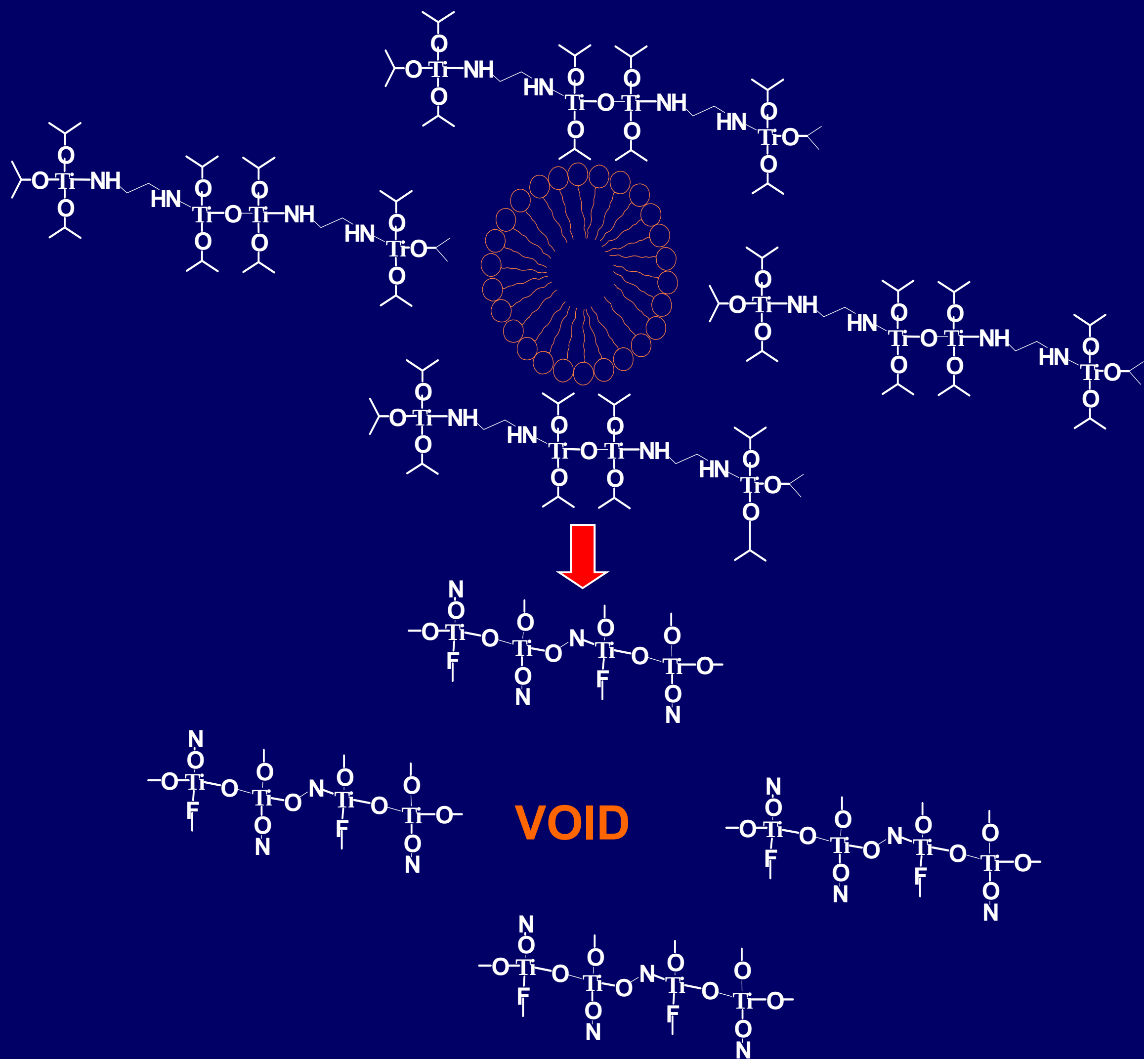
↓

ACETIC ACID (AA)

↓

HEAT TREATMENT (400°C/30min)

Mechanistic Aspects



The final structure consists of close-packed spherical micelles resulting in spherical pore arrangements after calcination.

Physicochemical Properties

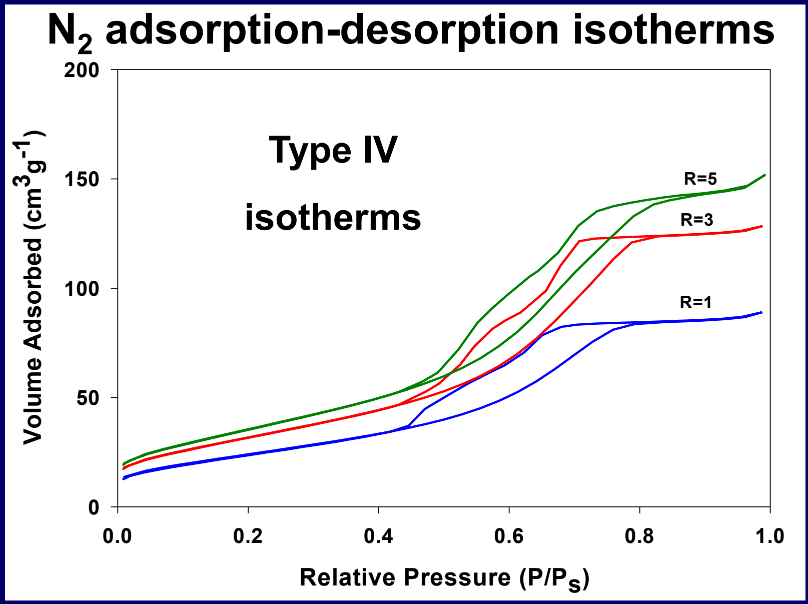
Material	S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})	Porosity (%)*	Crystal phase	Crystal size (nm)**	$D_{(101)}$***
P25 film	57	0.303	36	anatase (75%), rutile (25%)	28	3.52
R=1	91	0.1375	35	anatase	14	3.52
R=3	121	0.1984	44	anatase	12	3.51
R=5	136	0.2347	48	anatase	9	3.50

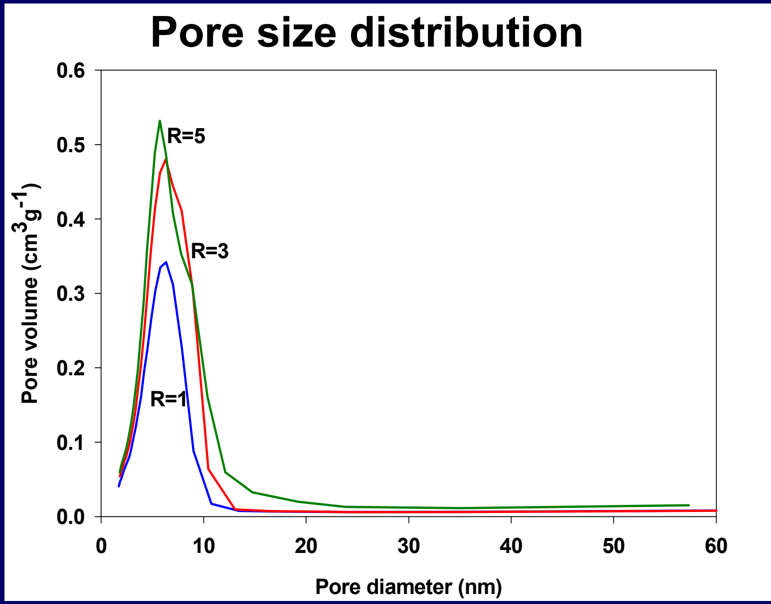
* Based on pore volume and 3.9 g/cm^3 of anatase density

** Based on XRD using Scherrer's equation

*** Based on Bragg's Law

- Structural properties significantly improved with the addition of fluorosurfactant compared to P25.





- Mesoporous materials with pore size controllability during synthesis.
- Narrow pore size distribution indicates good homogeneity of the pores even at a low surfactant ratio.

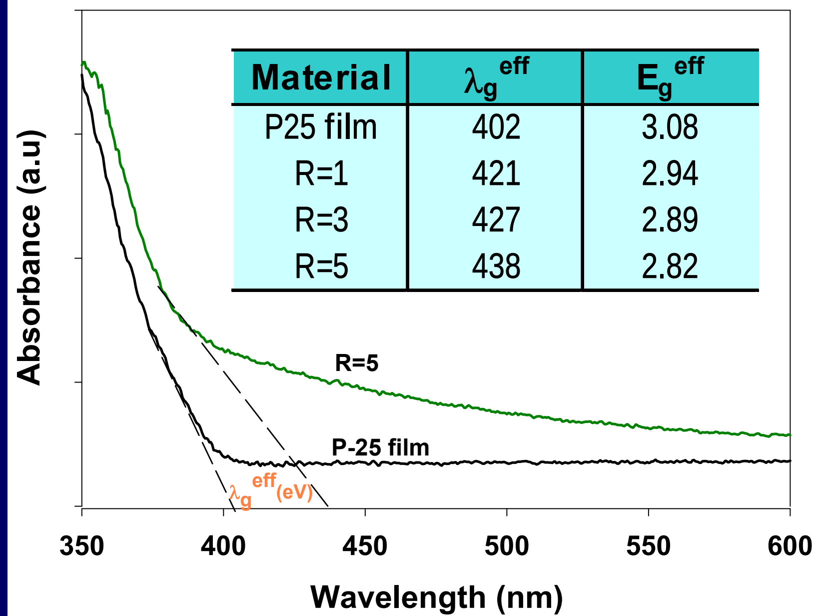
UV-vis spectra

- Effective optical band gap (E_g^{eff})

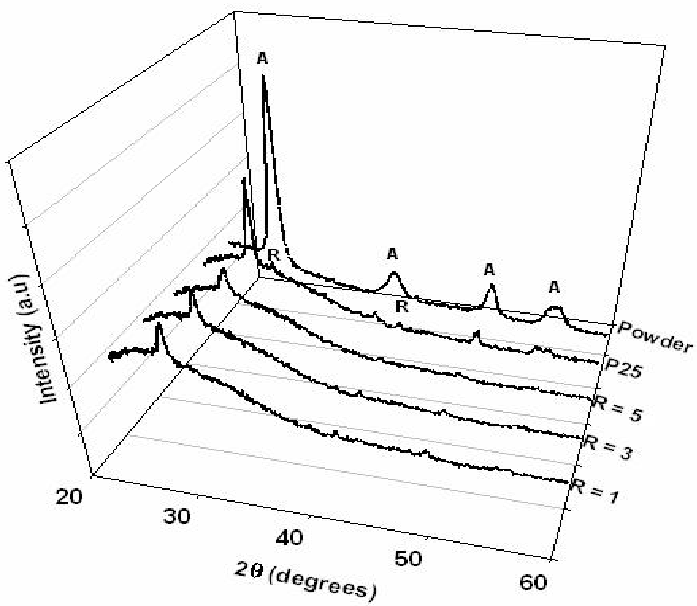
$$E_g^{eff} = 1239.6/\lambda_g^{eff}$$

Sun et al., Langmuir., 2005, 21, 11397-11403

- Band-gap ("effective") reduction for NF-TiO_2 films; shift in the absorbance spectra.
- Combination of nitrogen and fluorine impurity can induce the appearance of an absorption band in the visible region .



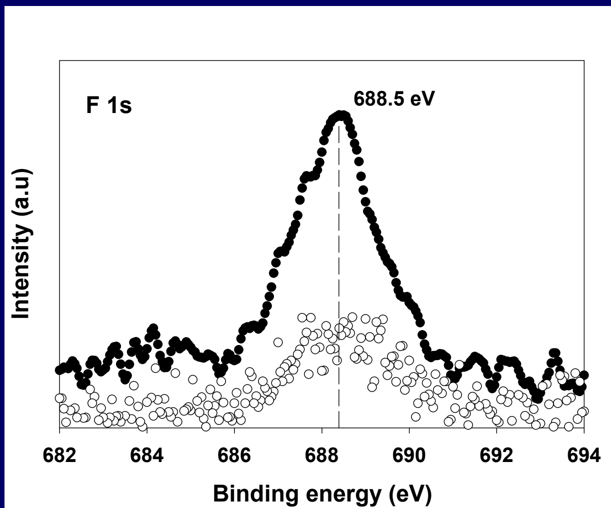
Material	λ_g^{eff}	E_g^{eff}
P25 film	402	3.08
R=1	421	2.94
R=3	427	2.89
R=5	438	2.82

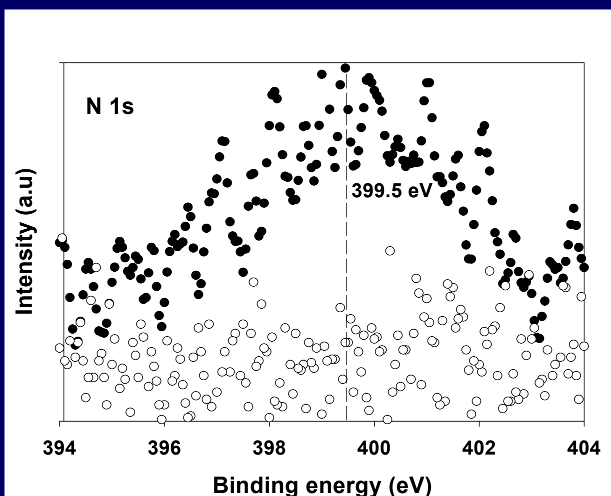


XRD

- Synthesized films are of anatase phase.
- No dopant-related crystalline products under the analyzed conditions.
- Nitrogen and fluorine atoms are found either in the interstitial or substitutional sites of the TiO_2 structure.

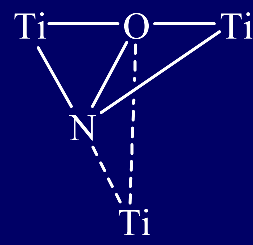
XPS Spectra





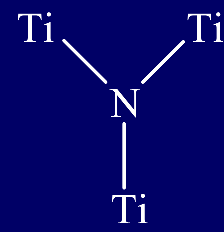
Material	F(%)	N(%)
R=5	1.9	1.5

Interstitial



Oxyanion

Substitutional



Nitride

Di Valentin et al., Chem. Phys. ***2007****, 339, 44-56*

Subs. N: 396.4eV

Inter. N: 398.3 and 400eV

Subs. F: 688.0 eV

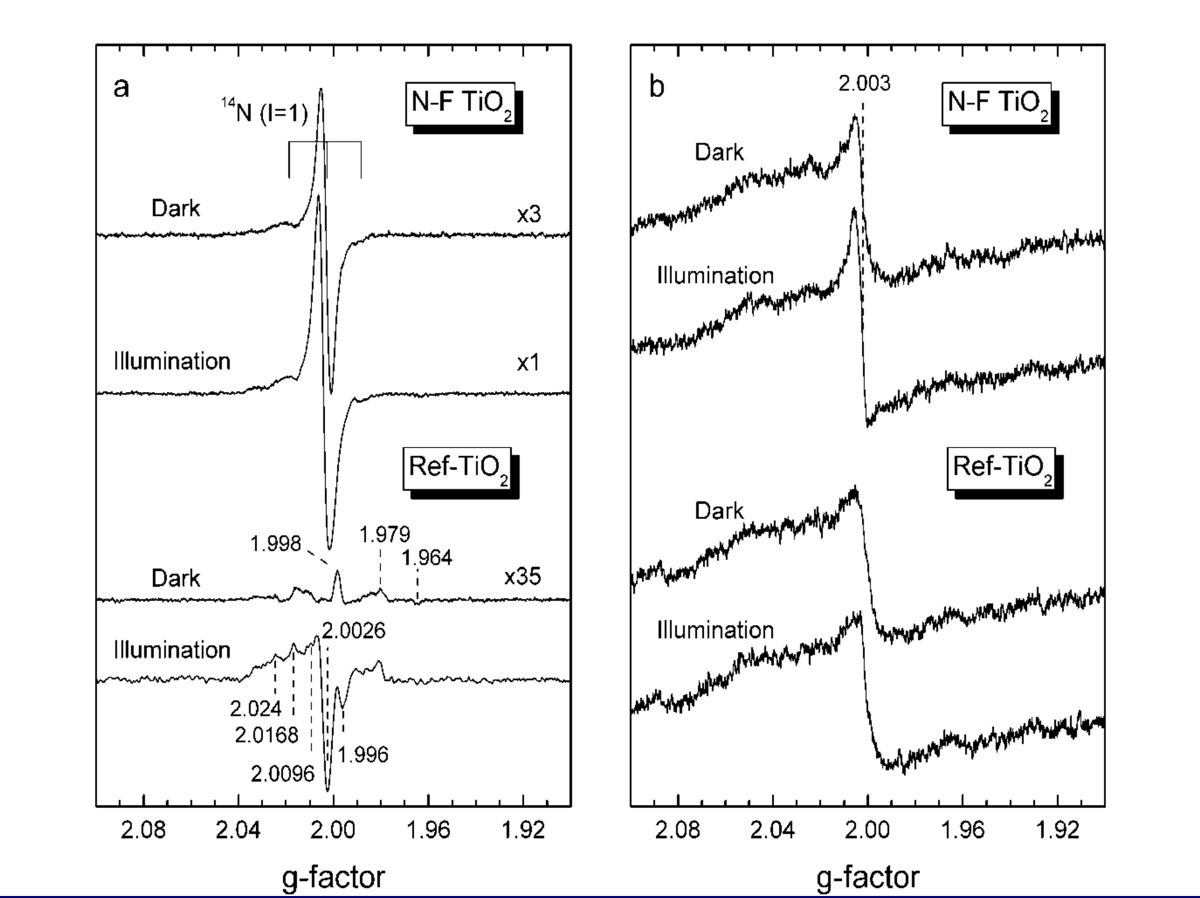
Li, et al. J. Solid State Chem. ***2005,*** *178, 3293-3302*

- Substitutional N-doping introduces energy states above the valence band while interstitial N-doping generate localized intergap states with π character; both induce visible light activity.
- Calcination at high temperatures favors the formation of interstitial N species.

  Kontos, et al. Phys. Stat. Sol (RRL). ***2008,*** *2, 83-85*

- Role of nitrogen and fluorine needs to be understood case by case. Preparation procedures leads to different observations in XPS data.

Electron Paramagnetic Resonance (EPR)



EPR analysis at a) 10 K and b) room temperature.

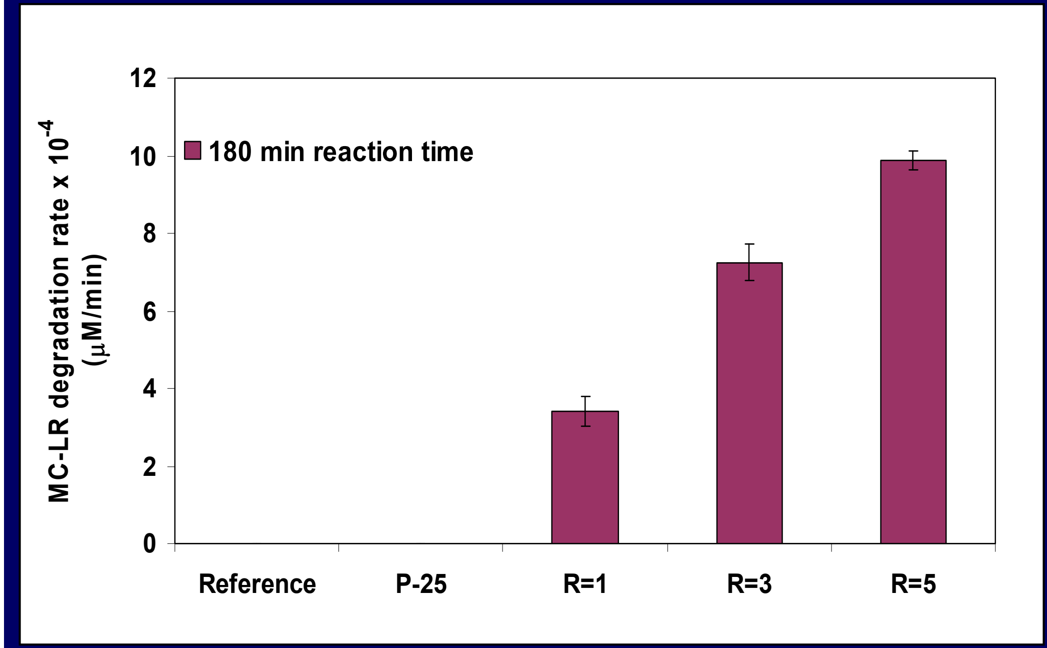
- At room temperature, peak at g=2.0030, g~2.019 and g~1.988 related to N spin species; enhanced under light illumination.

- Reference TiO_2 showed weak peaks EPR lines indicative of residual surface oxygen radicals only and not affected upon illumination.

- Similar behavior at 10 K.

- Dominance of the intense paramagnetic N species over Ti^{3+} ions; F doping promotes N incorporation in TiO_2 lattice.

Photocatalytic Evaluation of NF-TiO_2 Films



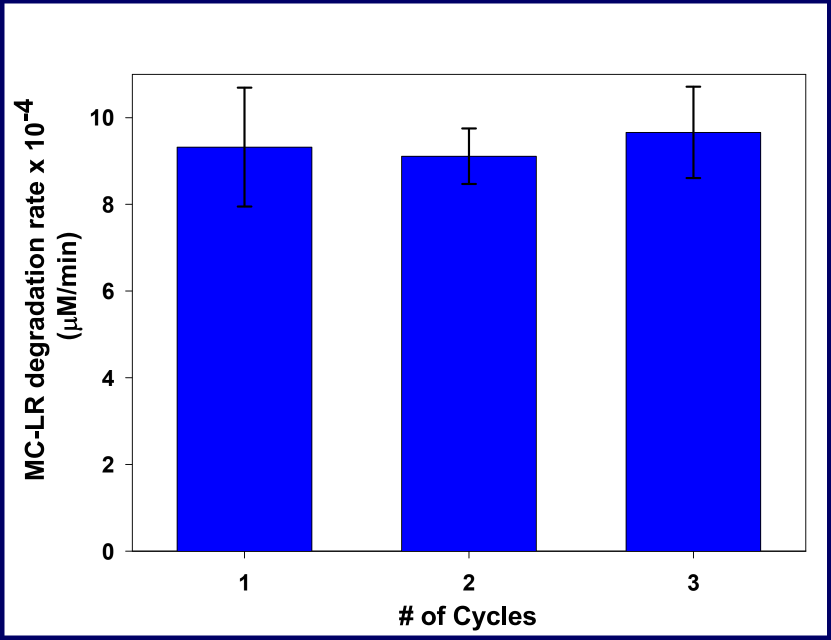
- MC-LR degradation rate of reference TiO_2 and NF-TiO_2 films at pH 3.0 under visible light (λ>420 nm) irradiation for 180 min.

Initial MC-LR concentration: 500 μg/L. Visible light intensity of 7.81 x 10^{-5} W cm^{-2}.

- Similar degradation rates were obtained when reusing the catalyst after 3 cycles under visible light.

- High mechanical stability of the films.

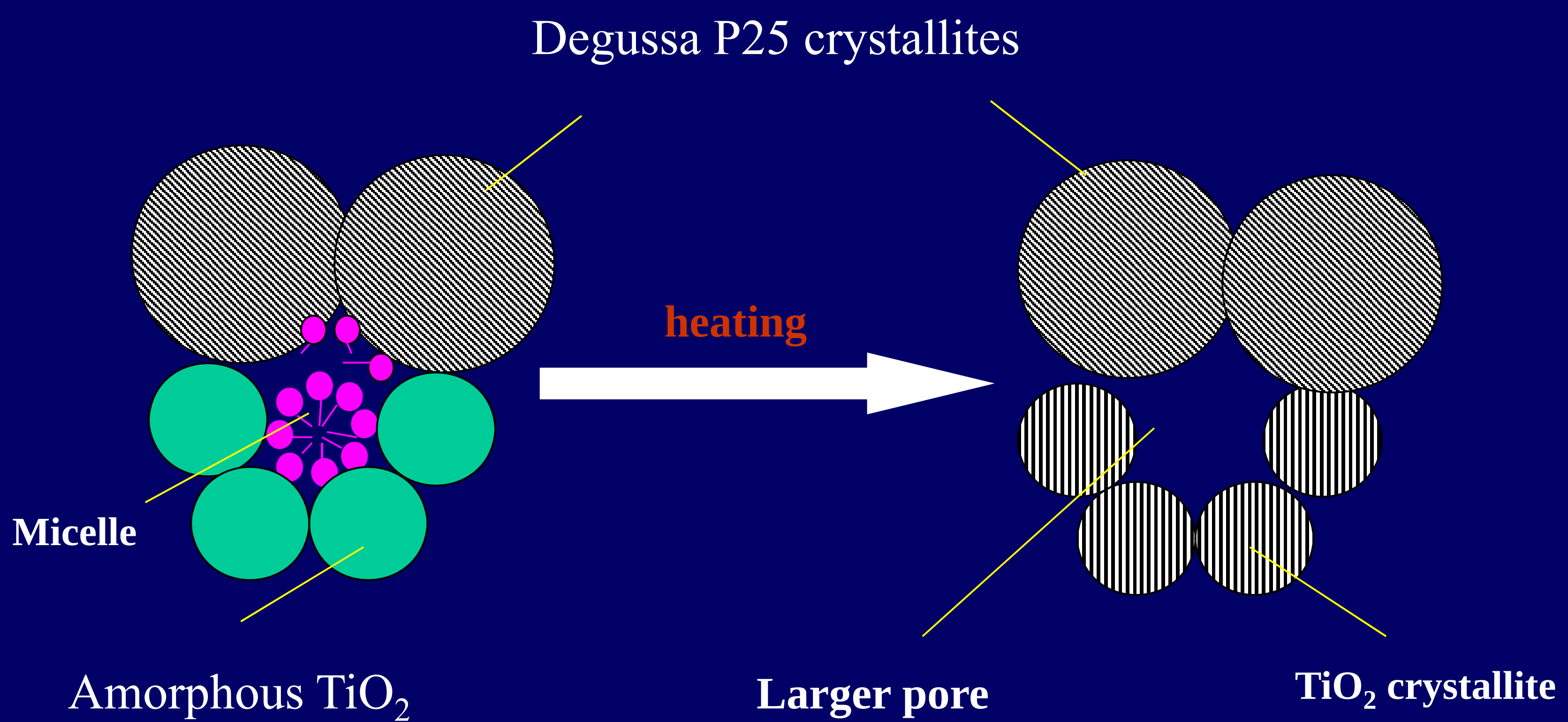
- Loss of catalyst was negligible during washing and reusing. Nitrogen and fluorine dopants are incorporated into the TiO_2 lattice.



Composite Mesoporous NF-TiO_2-P25 Films

Synthesis Approach:

Surfactants as templates and low loading Degussa P25 powders (i.e., 5, 15 g/L in the sol) as fillers*



* **Balasubramanian, et. al., *J. Mat.* Sci., 38 (2003) 823.**

Chen and Dionysiou, *Appl. Catal. B: Environ.*, 62 (2006) 255.

Chen and Dionysiou. *Appl. Catal. A: General.*, 317 (2007) 129.

Balasubramanian, et.al, *Appl. Catal. B: Environ.*, 47 (2004) 73.

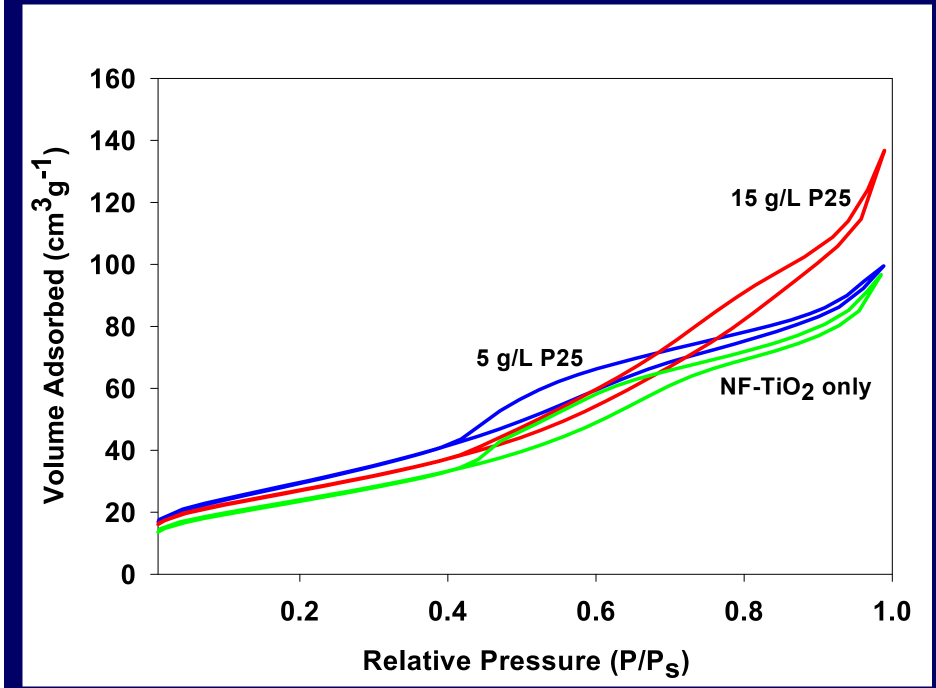
Chen and Dionysiou, *J. Mol. Catal. A: Chem.*, 244 (2006) 73.

Chen and Dionysiou, *Appl. Catal. B: Environ.*, (2008).

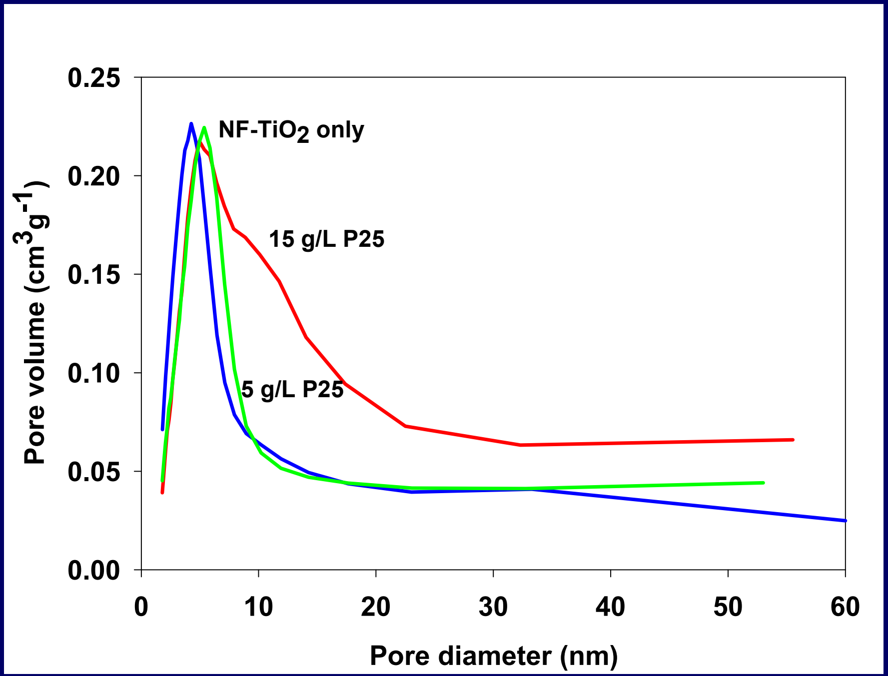
Physicochemical Properties of NF-TiO_2-P25 Films

Material	S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})	Porosity (%)	Crystal phase	Film thickness per layer (nm)
NF-TiO_2 only	89.77	0.149	36.75	anatase	648.7
5 g/L P25	111.47	0.153	37.37	anatase, rutile	777.9
15 g/L P25	100.38	0.211	45.14	anatase, rutile	981.6

- Structural properties significantly improved with the addition of TiO_2-P25 nanoparticles.

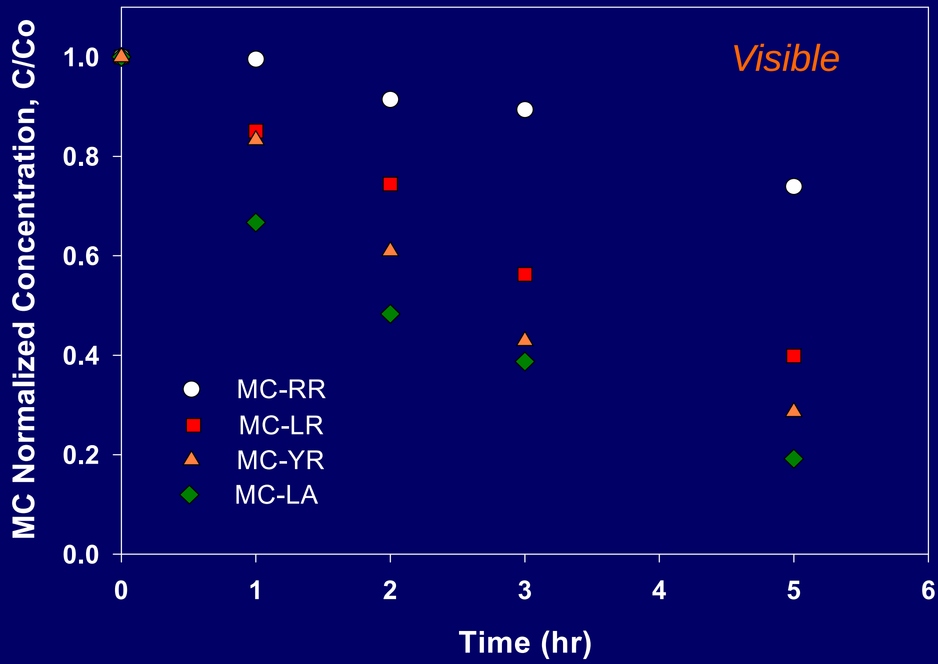


- Mesoporous materials with pore size controllability during synthesis.



- Narrow pore size distribution with a broad large pore with 15 g/L P25. Formation of P25-associated larger pores.

MCs Removal with NF-TiO_2



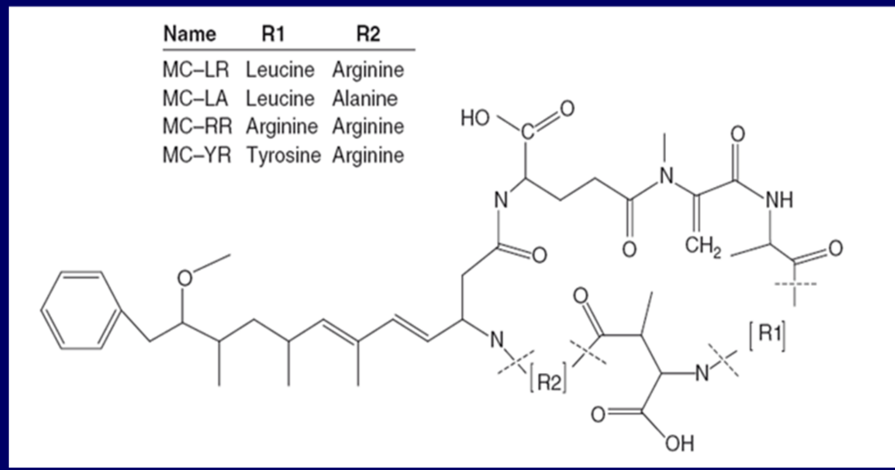
	Dark adsorption (%)			
Sample	MC-LR	MC-RR	MC-LA	MC-YR
NF-TiO_2	16.3	8.8	26.5	40.9

- The degradation process is a function of the surface interaction between each MC and the photocatalyst (Net charge of the toxin and hydrophobicity).

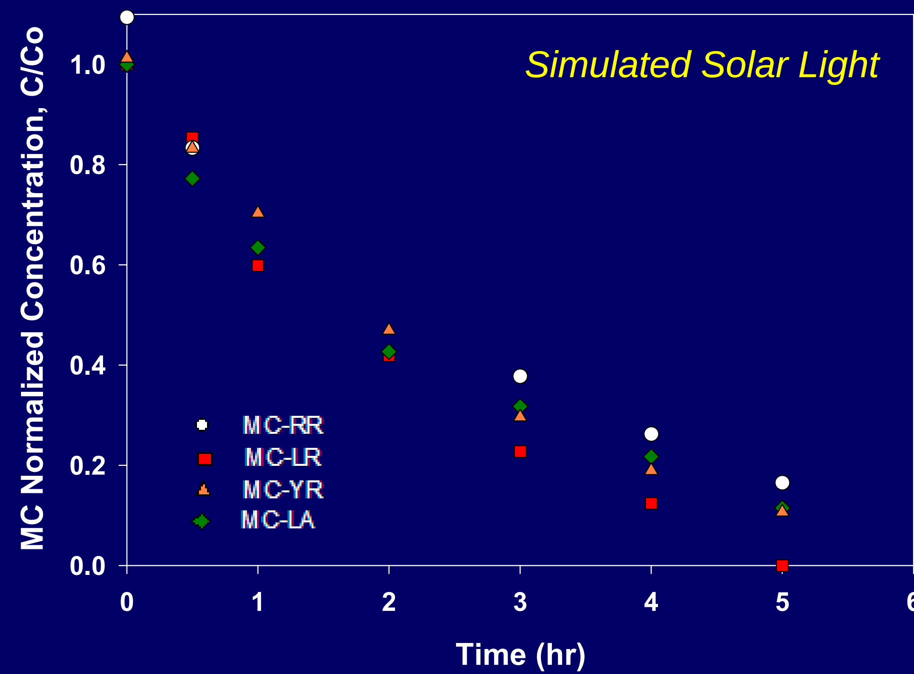
	MC-RR	MC-YR	MC-LR	MC-LA
Net charge, pH 3.0	+	—	—	—
Molecular weight	1038	1044	995	910

➡ *Increased hydrophobicity*

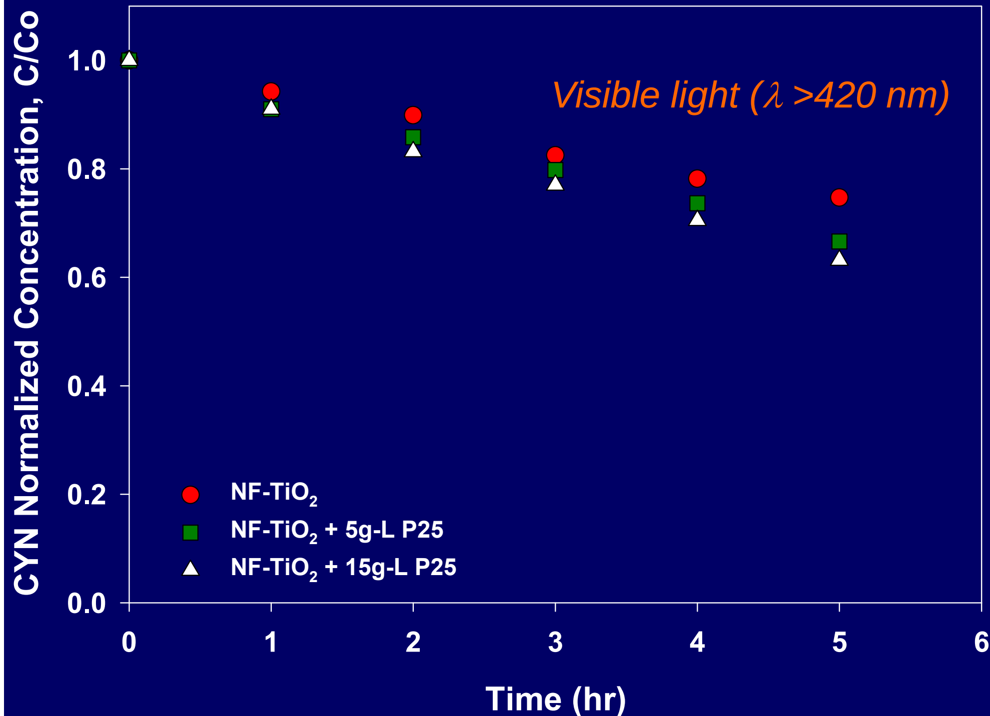
General structure of a microcystin (MC)



- *Initial MCs molar concentration: 0.5 μM, pH 3.0.*



CYN Removal

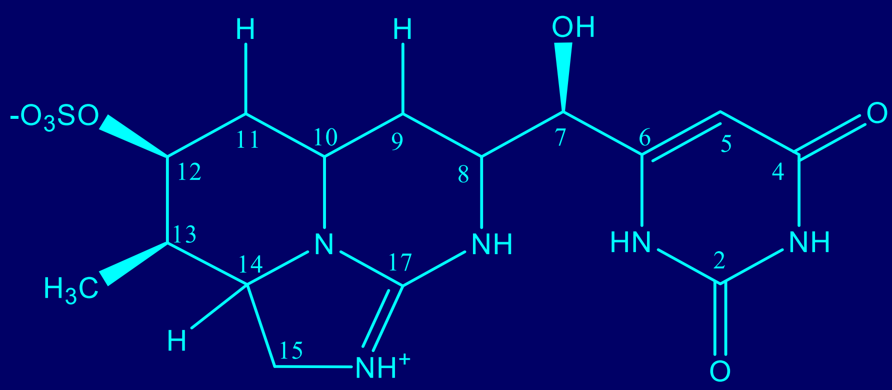


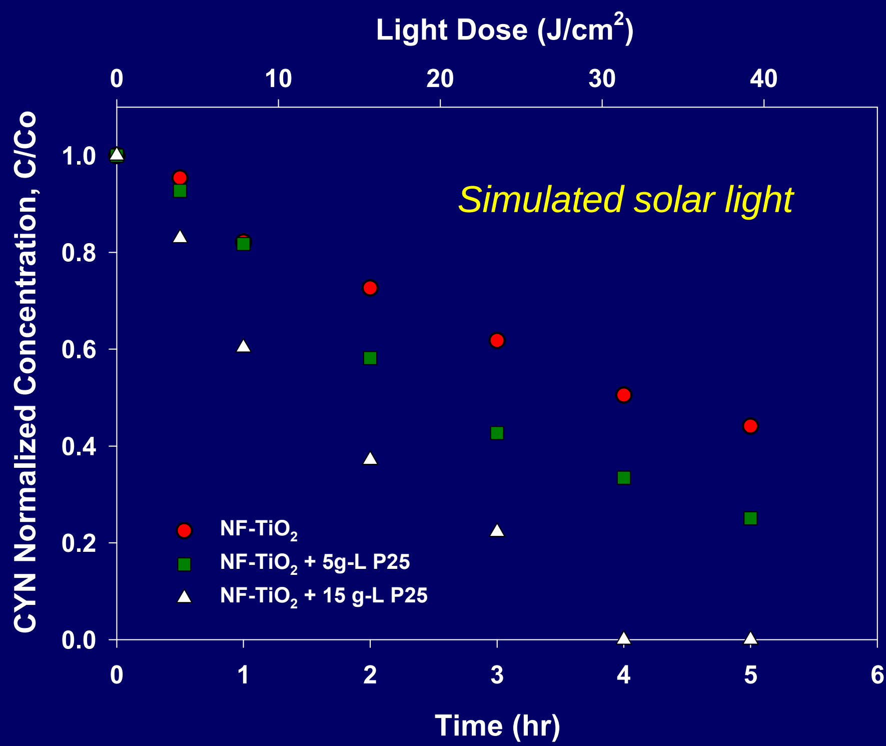
- No significant adsorption of CYN in any synthesized film. Very hydrophobic and overall positively charged under acidic conditions.

- Enhanced photocatalytic degradation of CYN with higher P25 loading under solar light.

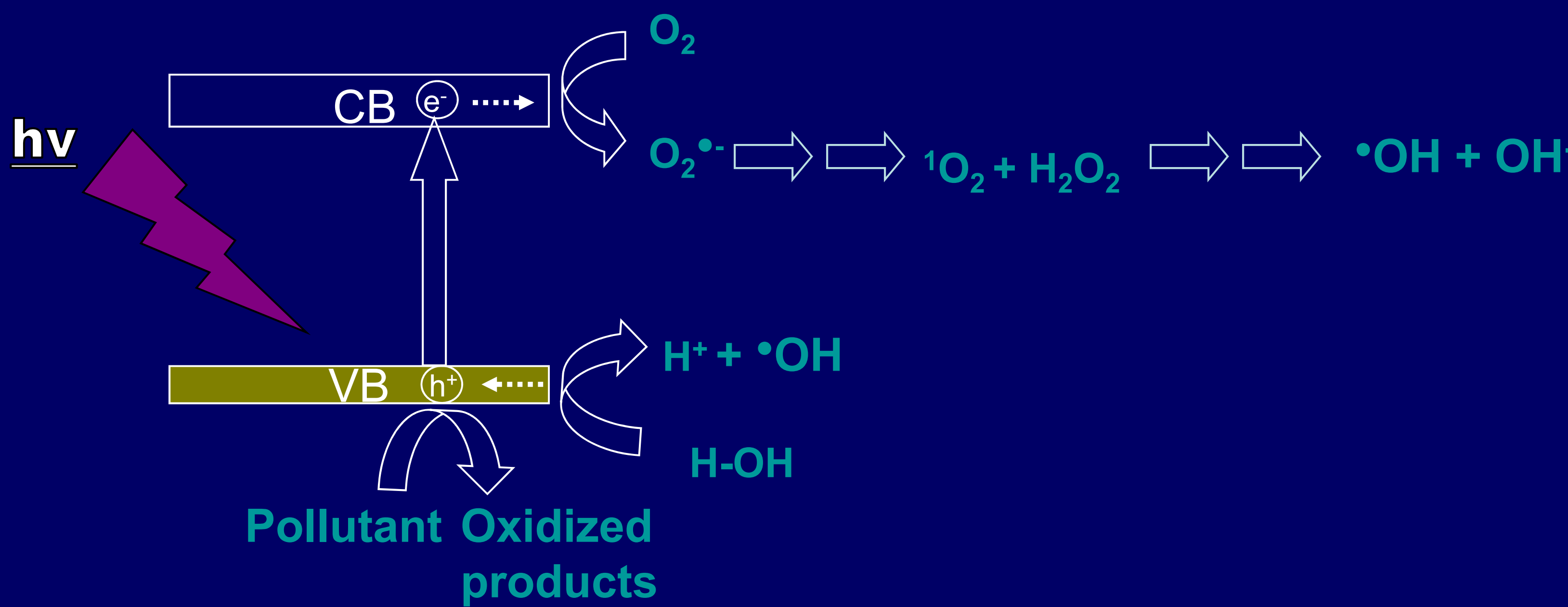
- ***Initial CYN molar concentration: 0.5 μM, pH 3.0***

Chemical structure of cylindrospermopsin (CYN)





Formation of Radical Oxygen Species (ROS) in TiO_2 photocatalysis

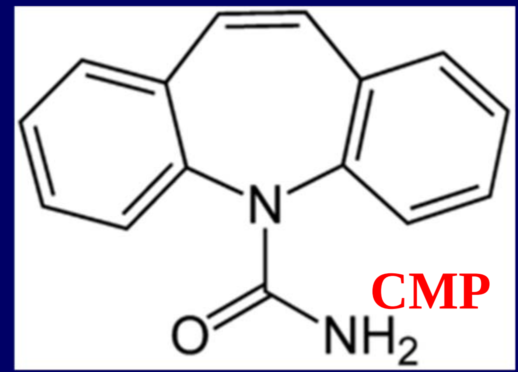


- Formation of ROS with non-metal doped TiO_2 under visible light. Possible involvement of different mechanism in which OH radicals may not be the primary oxidizing species.
  - Nature of the oxidation mechanism is ambiguous.
  - Hole generated in VB may not oxidize surface hydroxyls to form $^{\bullet}OH$.

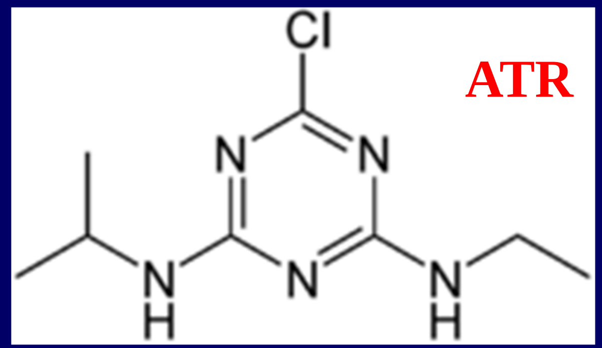
Selected Organic Contaminants

(**4 µmol L^{-1}** each in mixture):

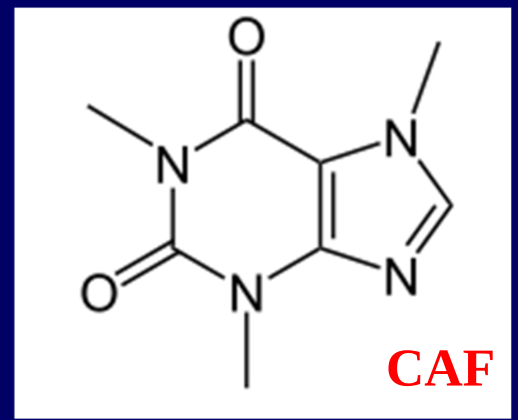
- **Carbamazepine (CMP)**
  - **Pharmaceutical**
  - **Persist and accumulate in organic components**
- **Atrazine (ATR)**
  - **Herbicide**
  - **Persistent groundwater contaminant**
  - **Banned in the European Union**
  - **Endocrine disrupting effects**
- **Caffeine (CAF)**
  - **Frequently detected in the environment**
  - **Potential effects on fish**



CMP



ATR



CAF

Stamatelatou et al., *Water Science Technology Water Supply* **3** (2003): 131–137. Kolpin et al. *Environ. Sci. Technol.* 36(2002) :1202-1211. Ackerman et al., *International Journal of Occupational and Environmental Health* **13** (2007): 437–445.

Some Notes ….

- Development of new AOPs or improvements of existing AOPs are on going efforts with many challenges.

- New advances in the field of nanotechnology and reaction engineering show promising results and encouragement for the removal of CEC but detailed mechanistic aspects need to be understood.

- Effective coupling of processes can yield targeted removal efficiencies of CEC but optimization schemes are necessary for a specific source water.

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QUESTIONS?


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