



# Photocatalysis for Water Treatment

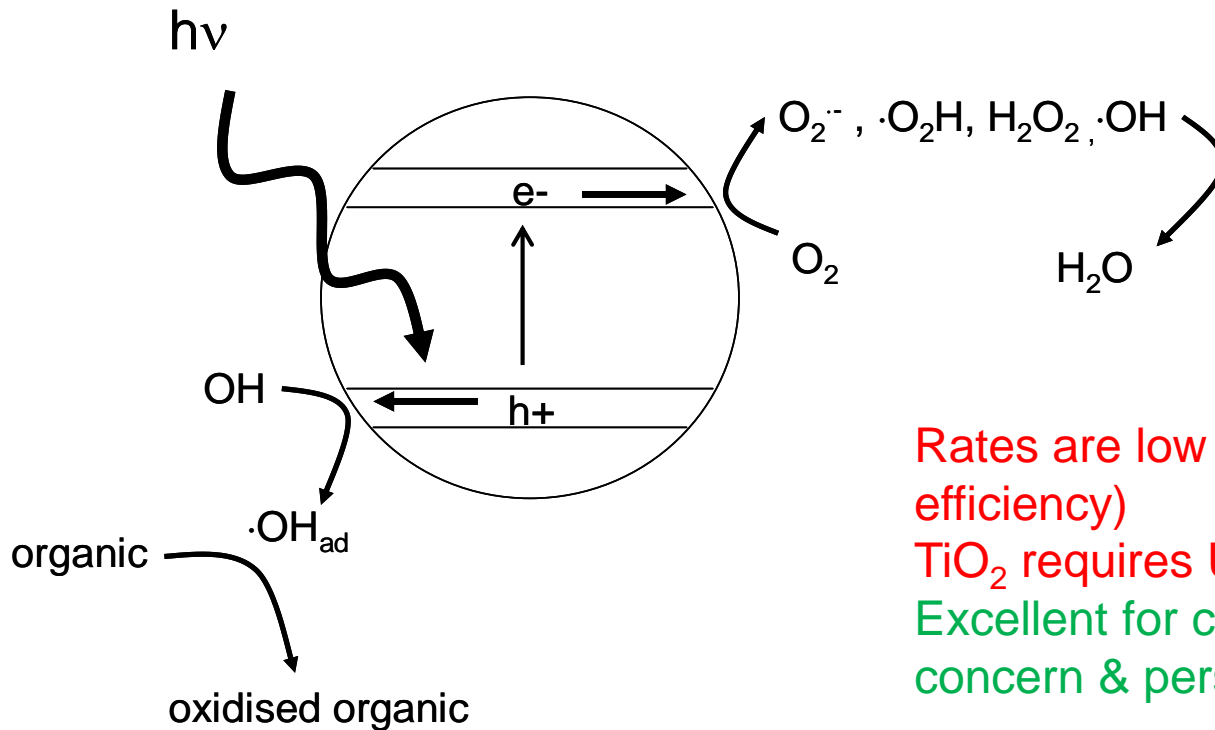
**J Anthony Byrne**

**Nanotechnology and Integrated BioEngineering Centre  
Engineering Research Institute**

**SUNSNUGUIDENANO Sustainable Nanotechnology Conference 2015**

**[ulster.ac.uk](http://ulster.ac.uk)**

# Basic mechanism of photocatalysis with $\text{TiO}_2$ in presence of $\text{O}_2$



Rates are low ( typically 1% quantum efficiency)  
 $\text{TiO}_2$  requires UV (only 5% of sunlight)  
Excellent for contaminants of emerging concern & persistent organic pollutants

- Nanomaterials give very high surface area for photocatalysis
- In some cases size quantisation effects may be observed
- Nano-engineering can give increased efficiencies
- $\text{TiO}_2$  most common photocatalyst due to stability and non-toxicity

# Titanium dioxide (TiO<sub>2</sub>)



... Rainbows are the same. Neither  
THE WRIGLEY COMPANY LTD., PLYMOUTH PL6 7PR.  
WRIGLEY IRELAND LTD., PO BOX 11578, DUBLIN 17.  
... CANDIES IN A CRISP SUGAR SHELL WITH FRUIT FLAVOURS.  
... INGREDIENTS: SUGAR, GLUCOSE SYRUP, PALM FAT, ACIDS CITRIC ACID,  
... ACID, DEXTRIN, MALTODEXTRIN, FLAVOURINGS, MODIFIED STARCH,  
... REGULATOR TRISODIUM CITRATE, COLOURS E120, E100, E171, E132,  
... E133, GLAZING AGENT CARNAUBA WAX, EMULSIFIER POLYGLYCEROL  
... OF FATTY ACIDS. PRODUCT MAY CONTAIN AN UNEVEN MIX OF  
... WRIGLEY GMBH, D-82004 UNTERHACHING.  
... GEEES IN KNUSPRIGER ZUCKERHÜLLE MIT FRUCHTGESCHMACK.

... rch, glucose  
... rap, shea fat,  
... nsifier (soya lecithin), stabiliser (gum arab  
... 133, E160a, E160e, E171), dextrin, glazing  
... coconut oil, salt, flavourings. (May contain: ha  
... hocolate contains milk solids 14% minimum.  
... before: see base



Photocatalysis has been shown to be effective for the degradation of a wide range of problematic pollutants in water including EDCs, pharmaceuticals, pesticides, dyes, etc.

effective for the inactivation of disinfection resistant microorganisms including viruses, bacteria (including spores), fungi (including spores), protozoan parasites (including oocysts).



Puralytics solar bag



# **Solar Photocatalytic Disinfection of Water**

Progress on

# Drinking Water

2014  
UPDATE

# and Sanitation

**The Millennium Project commissioned by the United Nations in 2002**

**Millennium Development Goal Target 10:**

“by 2015, reduce by half, the 1.1 billion people lacking access to safe drinking water and basic sanitation”.

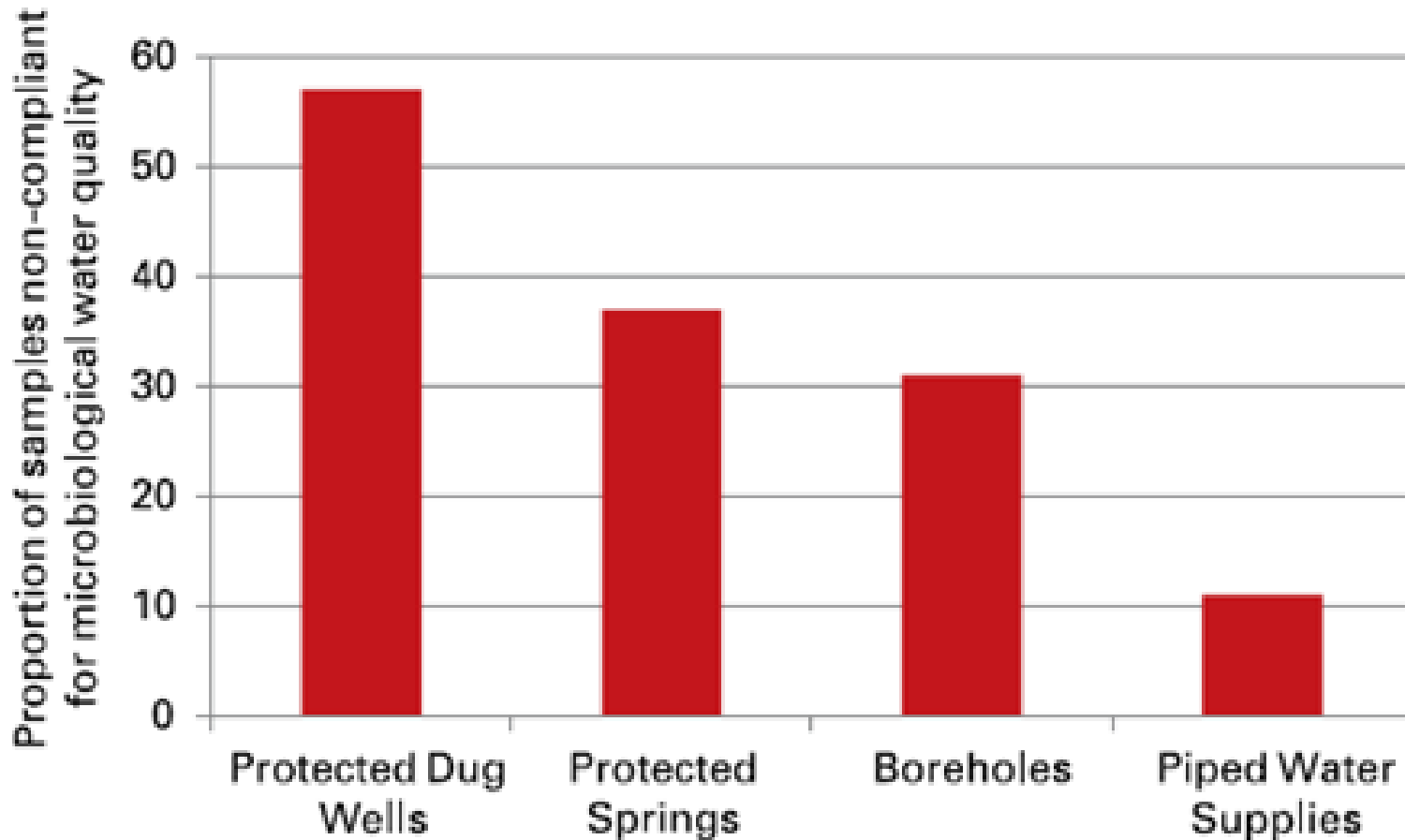
The MDG water target of 88% coverage was met in 2010

**748 million people still do not have access to an improved water source for drinking**

1.5 million children die each year due to unsafe water



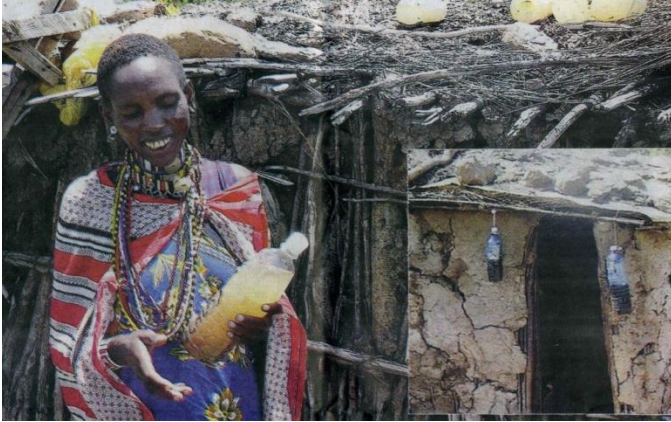
# Improved water source does not mean safe!



Non-compliance with microbiological water quality guideline values by improved drinking water source type. Proportion refers to percentage (from UNICEF and World Health Organization, Drinking Water Equity, safety and sustainability, JMP Thematic Report on Drinking Water 2011)



# Solar disinfection of water (SODIS)

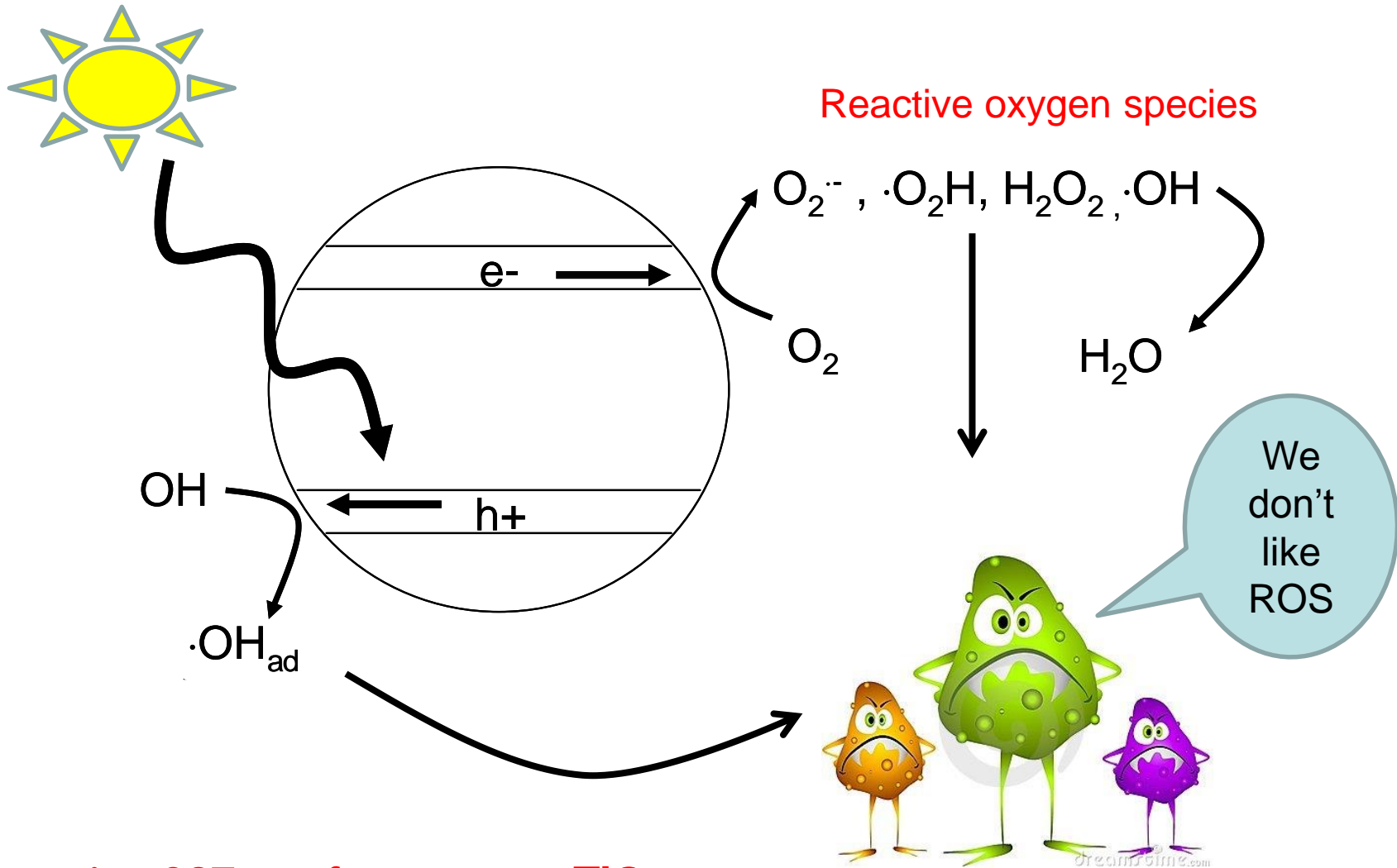


SODIS is used by more than 5 million people and in more than 30 countries around the globe





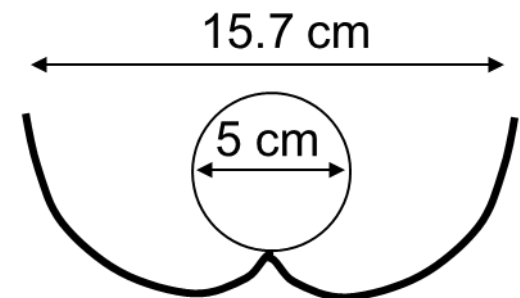
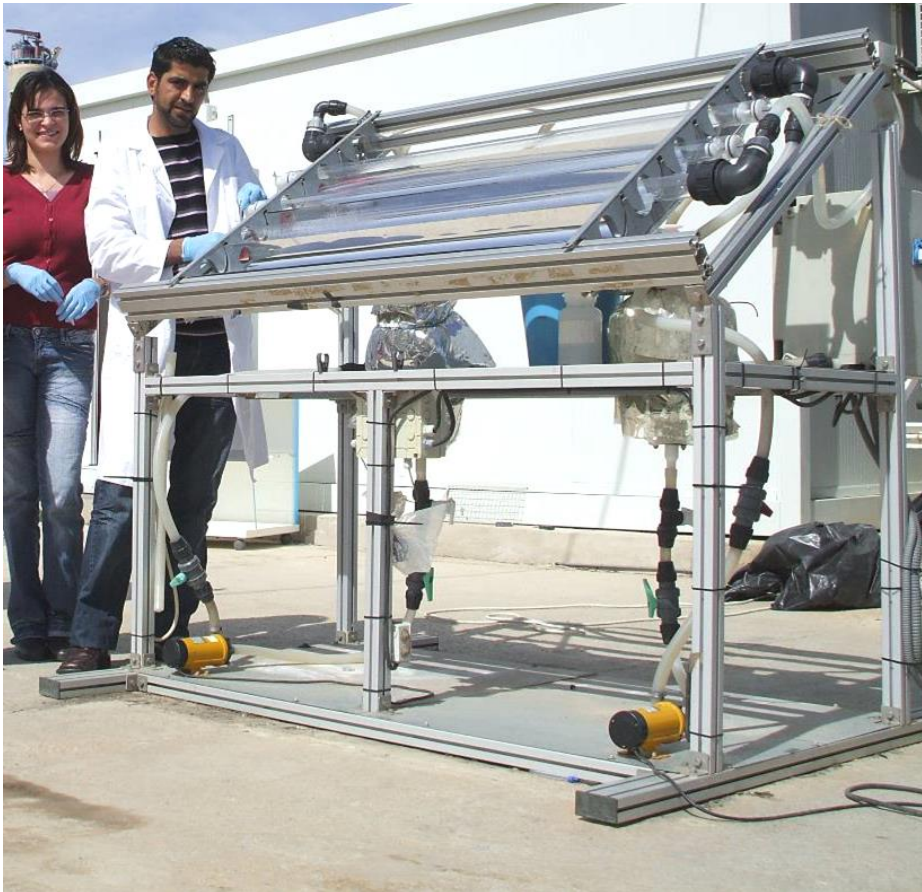
# Solar Photocatalytic Disinfection



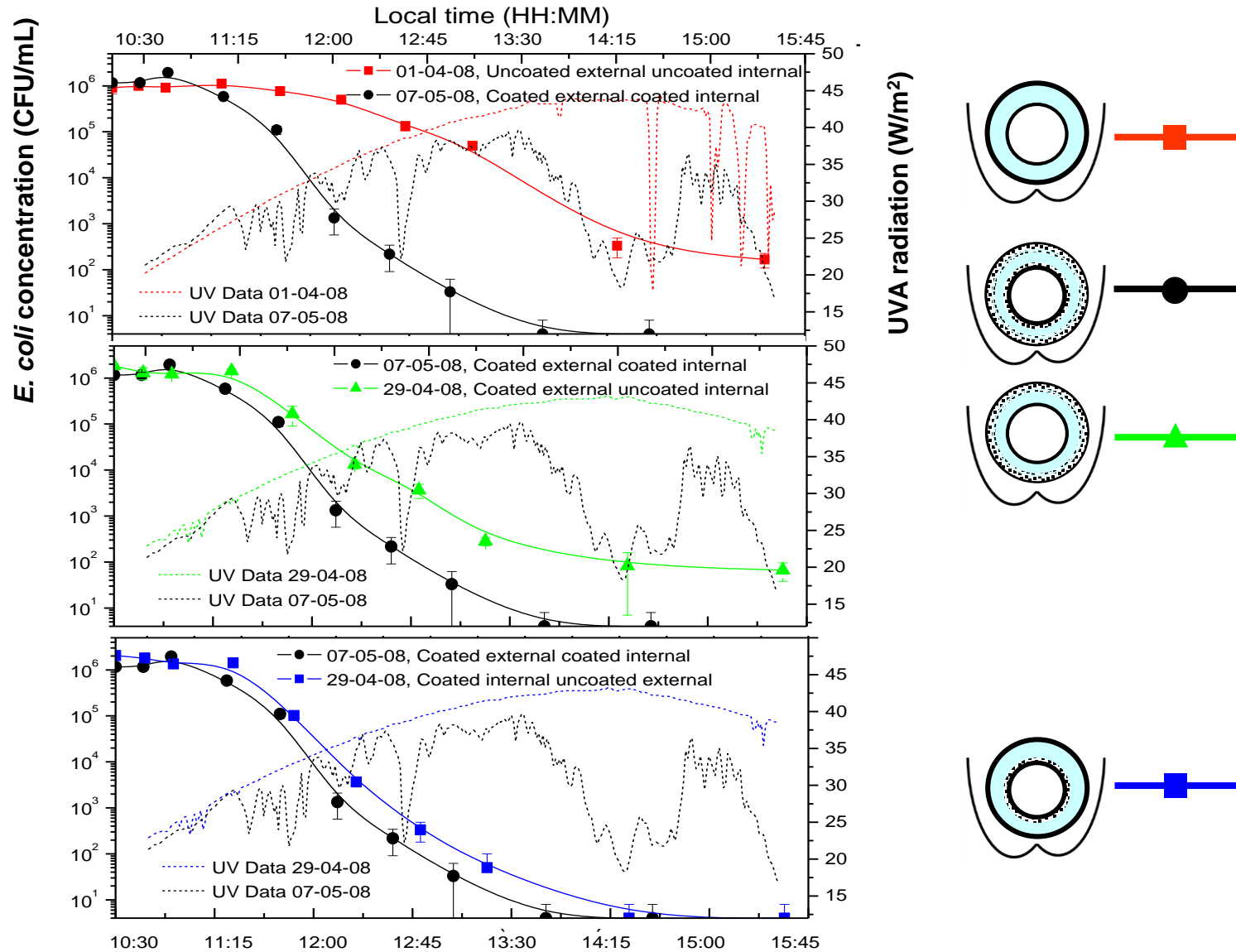
$\lambda < 387 \text{ nm}$  for anatase  $\text{TiO}_2$

## Continuous flow photocatalytic SODIS reactor with add on CPC.

TiO<sub>2</sub> (Evonik Aeroxide) coated borosilicate glass tubes (0.4 mg/cm<sup>2</sup>) were incorporated into the CPC-SODIS reactors used at PSA and used as a 7 L re-circulating batch system with *E. coli* K12 in saline (1x10<sup>6</sup> CFU/mL) as a model test organism.

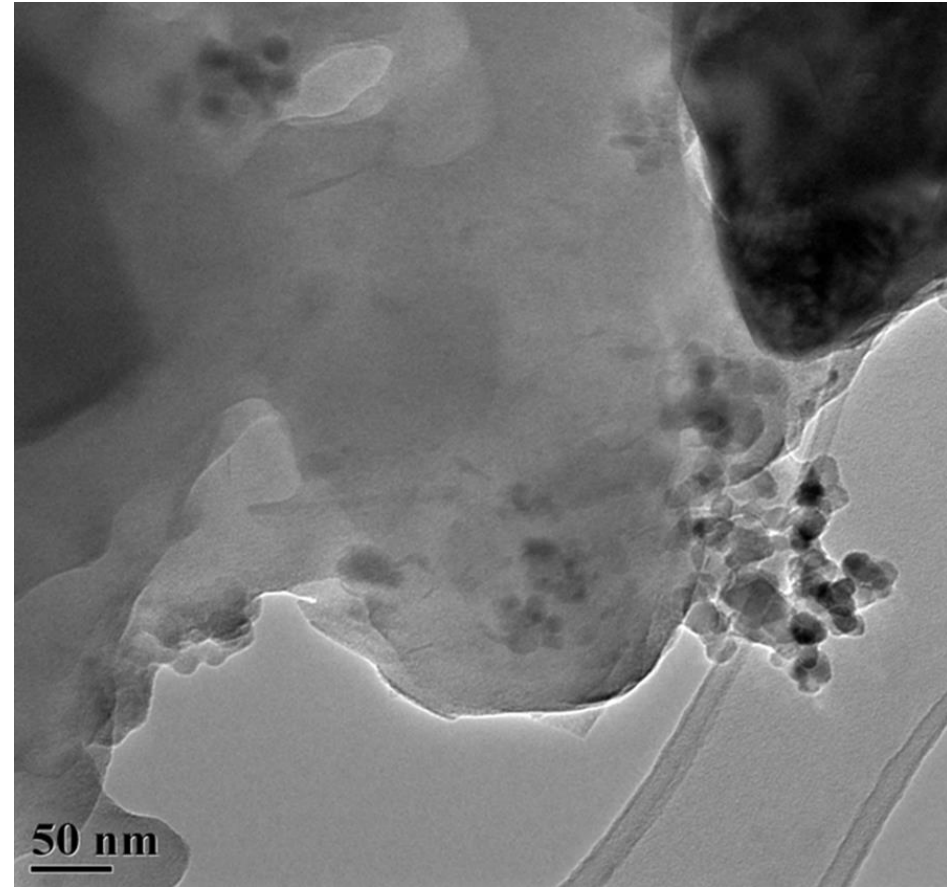
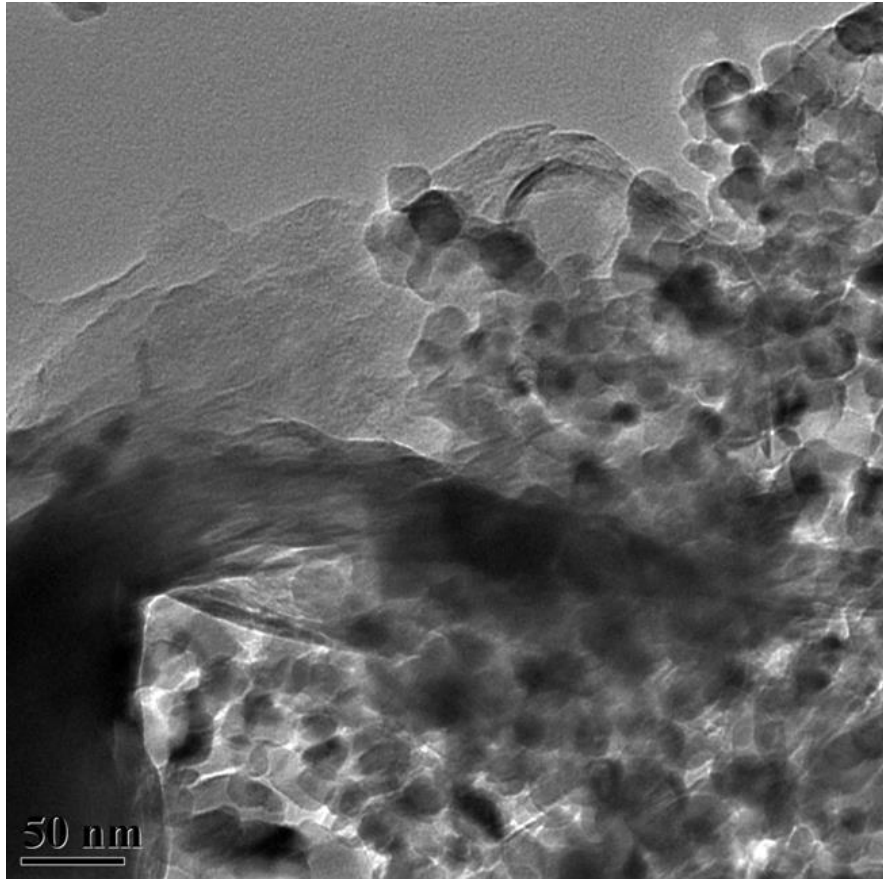


# Continuous flow photocatalytic SODIS reactor with add on CPC.



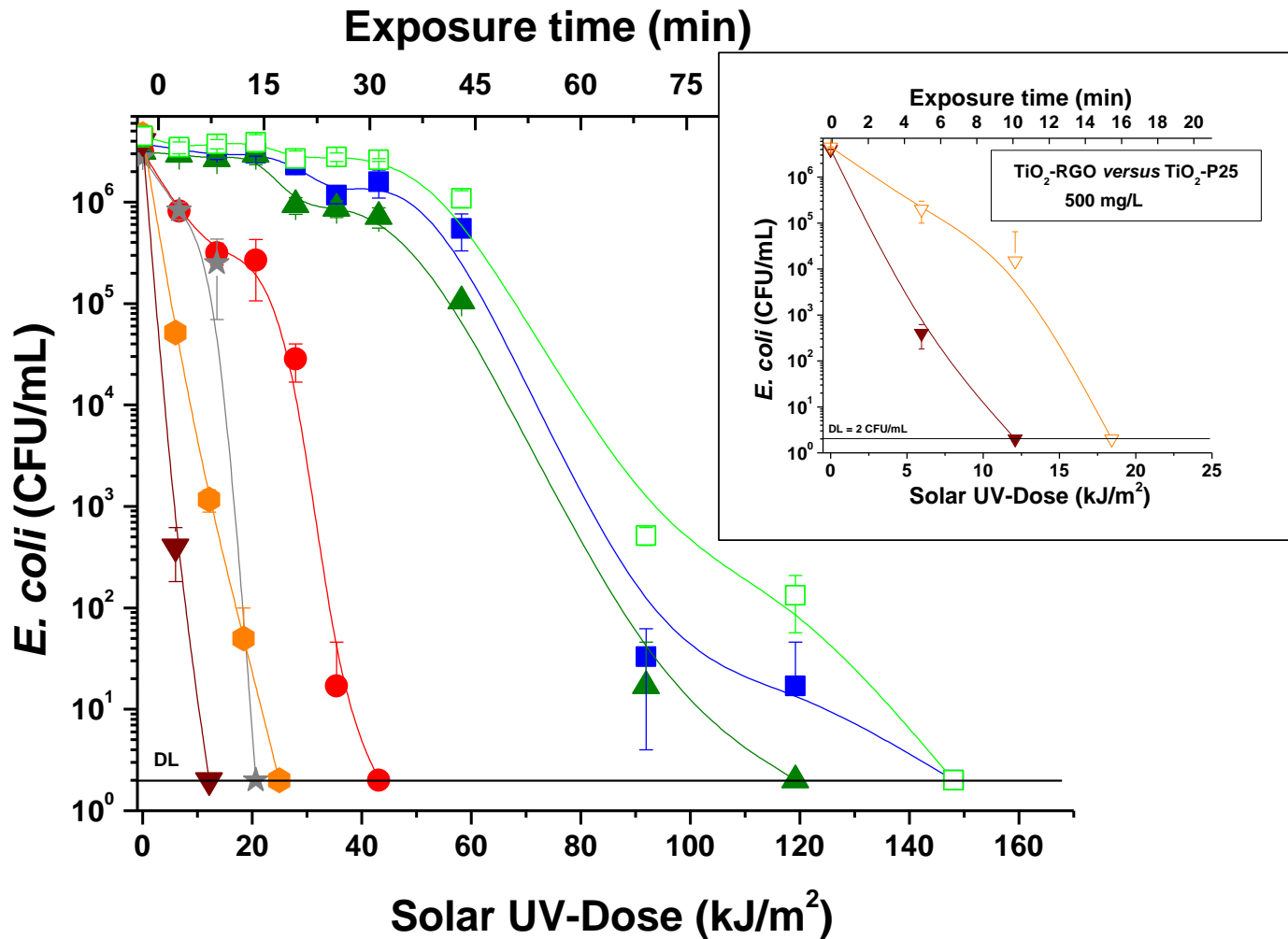


# Titania-graphene composites

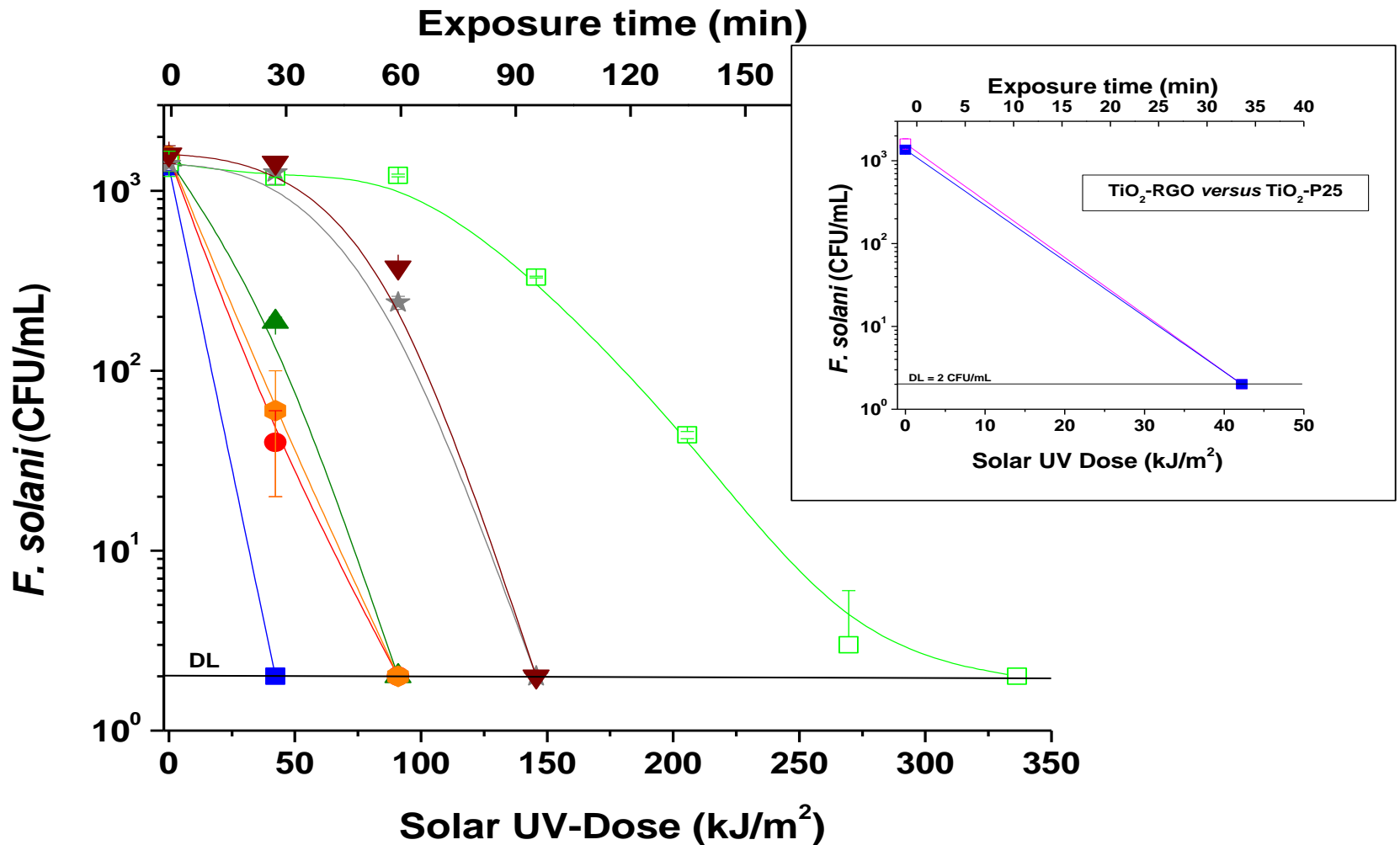


TEM of TiO<sub>2</sub>-RGO following photocatalytic reduction

Fernández-Ibáñez et al (2014) Chem Eng J, DOI: 10.1016/j.cej.2014.06.089.



*E. coli* inactivation at several TiO<sub>2</sub>-RGO concentrations: (□) 0 mg/L; (■) 10 mg/L; (▲) 20 mg/L; (●) 50 mg/L; (◆) 100 mg/L; (☆) 300 mg/L; (▼) 500 mg/L. DL (detection limit) = 2 CFU/mL. Inset shows the TiO<sub>2</sub>-RGO (▼) versus P25 (▽) efficiency on the *E. coli* inactivation at 500 mg/L of catalyst concentration. DL (detection limit) = 2 CFU/mL.

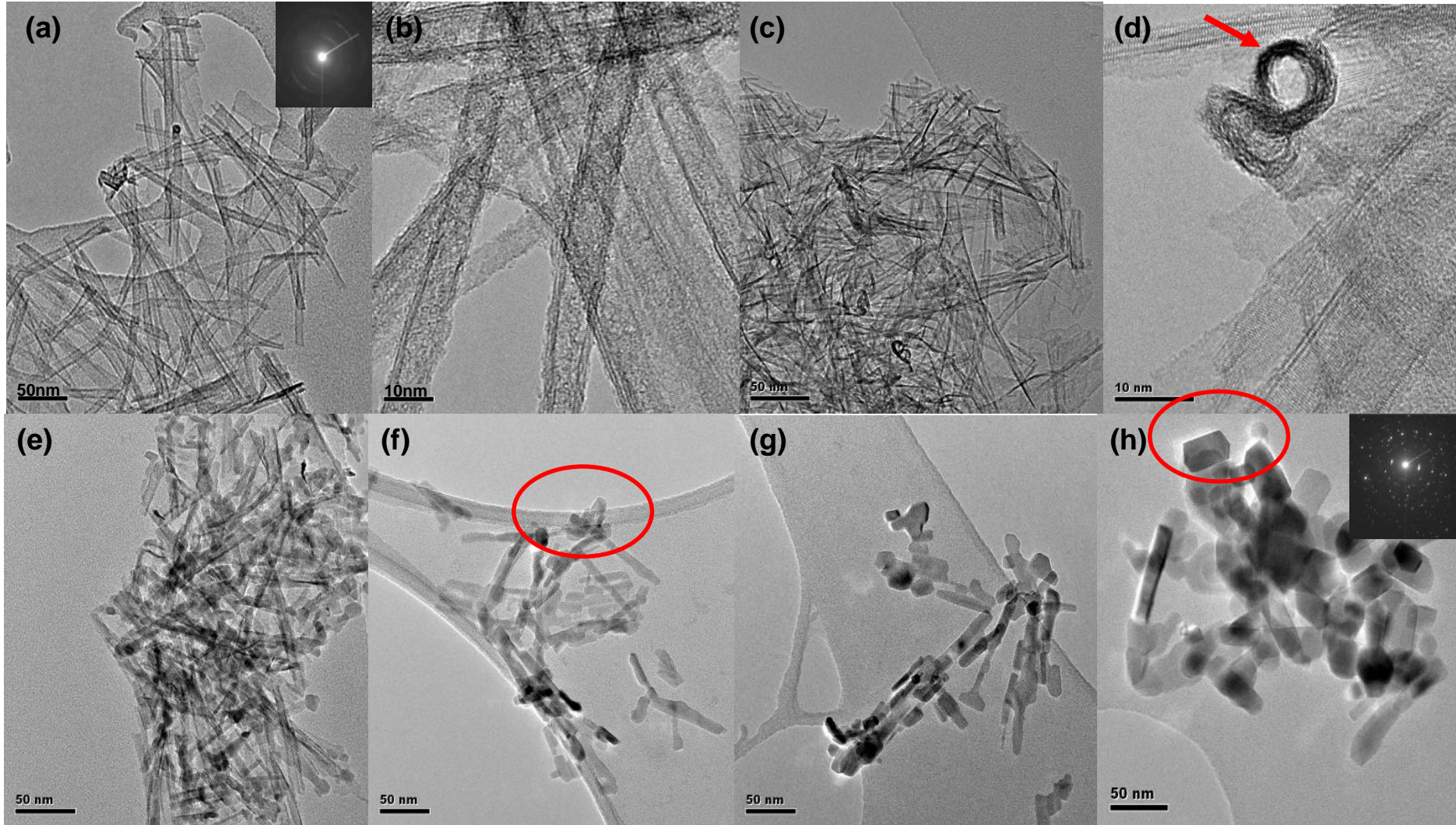


*F. solani* spore inactivation at several TiO<sub>2</sub>-RGO concentrations: (□) 0 mg/L; (■) 10 mg/L; (▲) 35 mg/L; (●) 50 mg/L; (◆) 100 mg/L; (★) 300 mg/L; (▼) 500 mg/L. DL (detection limit) = 2 CFU/mL. Figure insert shows the efficiency of TiO<sub>2</sub>-RGO (■) with 10 mg/L versus TiO<sub>2</sub>-P25 (□) with 35 mg/L on the *F. solani* spores inactivation. DL (detection limit) = 2 CFU/mL.



# **Titania Nanotubes**

# Comparison of titania nanostructures formed by hydrothermal treatment



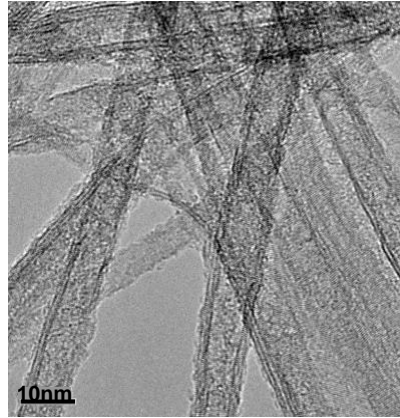
HRTEM images of (a)-(b) as-prepared and samples annealed at (c)-(d) 300°C (e) 400°C (f) 500°C (g) 600°C (h) 700°C

# HRTEM

Crystallinity,  
BET (m<sup>2</sup>/g)

Optimum  
photoactivity  
for

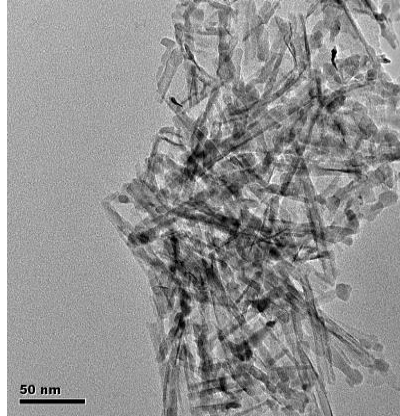
As-prepared



Amorphous,  
~401

100% tubes

400°C

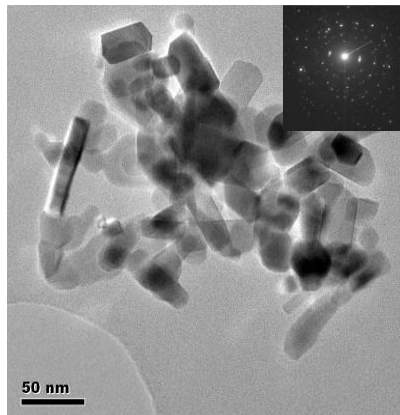


Anatase,  
~265

30% tubes

formic acid

700°C



Anatase,  
~48

100% hexagonal crystals

Phenol

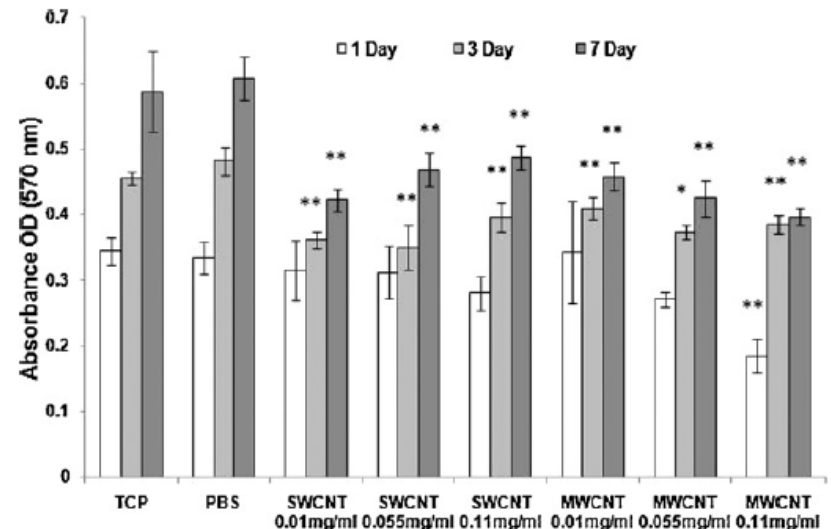
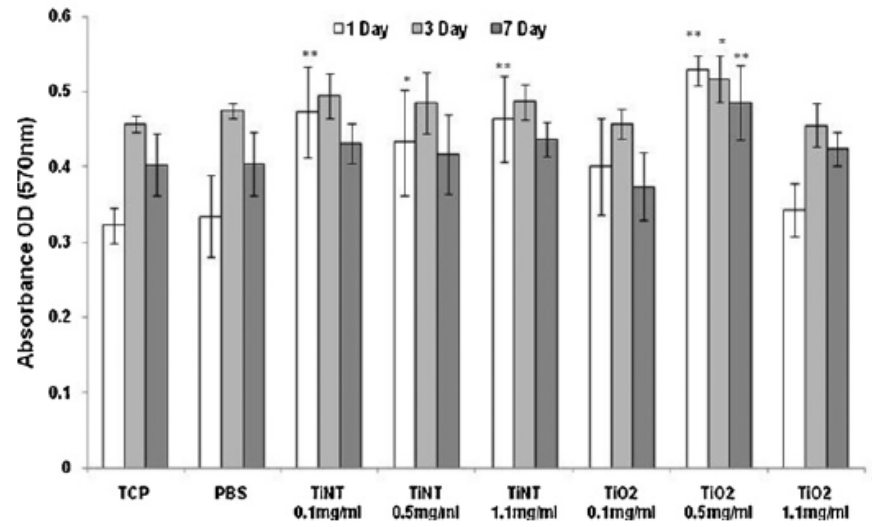
Observed  
best material  
depends on  
the model  
pollutant  
tested



# Toxicity study of titania nanostructures as compared to MWCNTs

Cell viability was determined using A549 human lung adenocarcinoma cell line obtained from ATCC after 1, 3 and 7 days in culture using the standard colorimetric MTT assay. A commercial MTT assay kit (Sigma–Aldrich, UK) was used, employing a modification of the Mosmann method

No significant cytotoxic effects were observed with titania but significant cytotoxic effects were observed with the MCNTs.

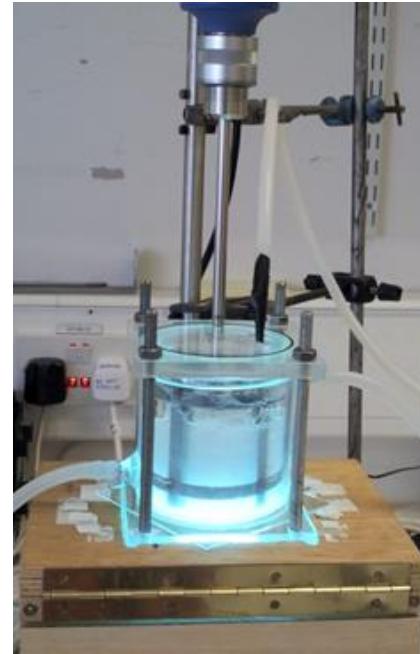


# Suspension vs Immobilised Photocatalyst

In laboratory scale experiments many researchers employ a basic photoreactor system utilising the photocatalyst as a powder suspension (slurry) in water.

The main issue with suspension reactors is catalyst recovery following treatment.

P25 is widely used. It has a small primary particle size ( $\sim 25$  nm) and is hydrophilic in nature forming well dispersed suspensions in water. The particles do tend to agglomerate to some extent giving a particle size between  $0.2 - 0.45$   $\mu\text{m}$ .



Post treatment catalyst recovery would add to the overall capital and running costs of any system. Nevertheless, some workers have developed pilot scale and even full scale water treatment systems employing  $\text{TiO}_2$  in suspensions.



Photocatalytic treatment plant at Plataforma Solar de Almeria, CIEMAT-PSA  
<http://www.psa.es/webesp/instalaciones/aguas.php>



# Challenges

There are few, if any, full scale photocatalytic water or wastewater treatment systems operating.

Effective reactor engineering is required to demonstrate photocatalysis can be applied at full scale and to demonstrate the cost-benefits

Novel visible light active materials are needed to improve the solar photocatalytic efficiency

Photocatalysis, like other AOPs is a degradative (not simply removal) therefore control engineering of the process is difficult

New photocatalytic materials must be assessed for toxicity and toxicology before deployment.

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