Metal-TiO<sub>2</sub> Nano-Photocatalysts for Detoxification of Toxic Pesticides, Dyes, Polyaromatics Pollutants and Bacteria under UV-Sunlight Irradiation





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# About Thapar University...



Established	: 1956
<b>Deemed University</b>	: 1985
Lush Green Campus	: 251 Acre
Departments	:07
Schools	:06
Centres	: 05
UGC-NAAC	: A grade
AICTE	: AAA+
ISO-9001	: Certified
Academic Programmes	: UG, PG & PhD



**Placement Highlights 2015-16** 



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MHRD. Gol)

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**Engineering Institute** of Super Excellence\* \*Competition Success Rewiew

amongst top Private Universities<sup>#</sup> "The Week

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- No. 1 in placement in the region (90-100%)
- NO RAGGING INSTITUTE
- Fully residential campus; 7000 students;
   6 Boys hostels + 4 Girls hostels

# Life a TU Campus













# Life @ TU Campus





#### Photocatalytic Degradation of Toxic Pesticides, PAHs, Dyes and Photokilling of pathogenic/agro bacteria using greener processes



#### Polycyclic Aromatic Hydrocarbons (PAHs)

- ✤ Produced due to incomplete combustion<sup>1</sup> of organic mass.
- ✤ Huge amount of straw stubble burning in Punjab

Present in :

•*Cooking oil* (0.15- 13.98µg/kg)

•*Air* (0.41-8.2ng/m<sup>3</sup>)

•*Soil* (0.79-15.9 ng/kg, burning of crop waste)

2A: Probabal human carcinogenic; 2B: Possible human carcinogenic

	S. No.	Name	Classification		
			(US EPA, 1997)	(IARC)	
	1.	Naphthalene	$\checkmark$	2B	
	2.	Phenanthrene			
	3.	Anthracene	$\checkmark$		
Ī	4.	Acenaphthylene	$\checkmark$		
	5.	Dibenz[a,h]anthracene	$\checkmark$	2A	
	6.	Benz[a]anthracene	$\checkmark$	2A	
	7.	Benzo[b]fluoranthene	$\checkmark$	2B	
	8.	Acenaphthene	$\checkmark$		
	9.	Chrysene	$\checkmark$		
	10.	Benz[a]pyrene	$\checkmark$	2A	
)	11.	Fluoranthene	$\checkmark$		
	12.	Indeno[1,2,3]pyrene	$\checkmark$	2B	
	13.	Fluorene	$\checkmark$		
	14.	Pyrene			
	15.	Benzo[k]fluoranthene		2B	
	16.	Benzo [ghi]perylene		10	

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- Influence of heteroatoms (N, Cl, O, P, S etc.,) present in pesticides, for imparting the stability, toxicity to the photoproduced intermediates need to be studied.
- Photodegradation of pesticides results in fragmentation of parent molecule into smaller intermediates that finally decomposes to CO<sub>2</sub> and inorganic ions. However, mechanism during degradation and the fate of heteroatoms present in the pesticides requires investigation..
- Visible light sensitive TiO2 photocatalysts of different shapes and sizes and effect of metal co-catalysts loading for effective mineralization of dyes, pesticides, toxic pyrene and killing of bacteria etc present in industrial effluents and agricultural land under UV/sun light exposure





Extensively used, Neurotoxic & carcinogenic  $t_{1/2} = 30-162$  days, Solubility = 550 mg/l, Causes: weakning of breathing muscles



Potential Health
 Affects :
 Headache, loss of
 vision and conscious,
 severe depressions,
 sleep walking, and
 death

OH







OH

CO2+H2O



#### ✓ Metal Co-catalysis effect for TiO<sub>2</sub> photocatalysis



≻Nature of metal effects the rate of reaction.

Each shape has its own characteristic property.

➢ Fermi level shift to more negative potential

> Number of  $TiO_2$ -metal junction and Interfacial contact area influence the reaction rate.

Quick charge transfer from photocatalyst to metal co-catalyst.

Preventing e<sup>-</sup>-h<sup>+</sup> pair recombination in varied extent.

#### •Quantum size particles result in higher surface activity

Au, Ag and Cu M-TiO2 photocatalysis under visible light light irradiation



**Figure 12.** Time course of photodegradation of (a) benzaldehyde and (b) nitrobenzaldehyde using various M–TiO<sub>2</sub> composites under direct sunlight irradiation.



**Figure 14.** Percentage of CO<sub>2</sub> evolution on photodegradation of benzaldehyde (BZ) and nitrobenzaldehyde (NBZ) by using various M-TiO<sub>2</sub> nanocomposites after 3 h of sunlight irradiation and (b) nitrobenzaldehyde degradation (%) after recycling with M-TiO<sub>2</sub> composites under visible light irradiation.





Woolen bun like microspheres  $(2\mu m)$  containing lengthy CdS nanowires for higher sun light absorption capacity and photoactivity









Fig. 7. (a) C/C<sub>o</sub> Plots versus irradiation time of (a) RhB and (b) MB (10 ml,  $5 \times 10^{-5}$  mol L<sup>-1</sup>) degradation (b) identified intermediates of RhB decomposition by GC-MS analysis and (c) time course of CO<sub>2</sub> evolution during RhB degradation with various CdS nanostructures (2 mg) under sunlight exposure.



# Metal (Au, Ag & Cu) –CdS composites for high photoactivity under sunlight exposure for degradation of salicylic acid



Rohit Singh and Bonamali Pal, "Enhanced photocatalytic activity of coinage metal-CdS nanorod composites under sunlight irradiation, accepted in Advance Materials Research (2012).

Movable CdO@CdS core-shell nanostructures in lengthy SiO<sub>2</sub> matrix







Sample	Cd (at%)	S (at%)	Si (at%)	O (at%)	Cu (at%)	Total
(a)Bare CdS- NR	36.63	40.57	-	5.07	17.73	100.00
(b) SiO <sub>2</sub> @CdS- NR	19.79	22.90	12.81	17.81	26.69	100.00
(c) SiO <sub>2</sub> @CdS- NR(PE) after 3 h	14.62	17.12	9.57	38.15	20.54	100.00
(d) SiO <sub>2</sub> @CdS- NR(PE) after 5 h	8.77	11.61	7.47	49.47	22.68	100.00

Photodegradation of Methyl orange (60  $\mu$ M)

Reusability test for MO (0.6 mM)



Superior photodecomposition of pyrene by metal ion-loaded TiO<sub>2</sub> catalyst under UV light irradiation

#### Malka Rani, Nidhi Gupta & Bonamali Pal



Scheme 1 Mechanism of pyrene decomposition at the metal ions-TiO<sub>2</sub> interface under UV light irradiation



Fig. 4 Effect of dissolved transition metal ions (100  $\mu$ mol) on the photocatalytic degradation of preadsorbed pyrene–TiO<sub>2</sub> under 2 h light irradiation

#### Environmental Science and Pollution Research

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## **Estimation for CO<sub>2</sub> formation**



Mineralization found after 240 min: (i) 73.0 % for Naphthalene (ii) 78.2% for Anthracene

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# Rapid photokilling of gram-negative *Escherichia coli* bacteria by platinum dispersed titania nanocomposite films

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#### HIGHLIGHTS

#### GRAPHICAL ABSTRACT

- Remarkable antimicrobial activity of photorradiated Pt-TiO<sub>2</sub> coated thin film.
- Pt impregnation-exhibits superior photoactivity than Pt photodeposition onto TiO<sub>2</sub>.
- Photokilling of E. coli cells occur within 10 min of UV (640 μW cm<sup>-2</sup>) irradiation.
- Size and nature of Pt deposition control the bactericidal effect of TiO<sub>2</sub> catalyst.
- Photodissolution of bacterial surface is occurred on prolong UV light exposure.







Fig. 3. (a) Bactericidal activity of bare TiO<sub>2</sub> and Pt–TiO<sub>2</sub> (PD & IR) films (5 mg catalysts) after 15 min light irradiation compared with control and UV exposure only, (b) gradual decrease (left to right plate) in bacterial colonies in sequence of Fig. 1a experimental results, (c) % cell survival after 5 and 10 min irradiation on Pt–TiO<sub>2</sub> (PD & IR) films, (d) disparity in colony counts after 5 min irradiation over Pt–TiO<sub>2</sub> (PD & IR) films as found in Fig. 1c experiment.



 $H_2O$ 

Shape-dependent bactericidal activity of TiO2 for the killing of Gram-negative bacteria Agrobacterium tumefaciens under UV torch irradiation













Fig. 6 TEM surface morphology of damaged A. tumefaciens cells (scale bar 200 nm) obtained after 30 min UV irradiation of P25-TiO2 and 3.6×10<sup>8</sup> CFU mL<sup>-1</sup> of bacterial suspension; a bacterial surface is etched at two different locations by attached TiO<sub>2</sub> particles, b bacterial surface is becoming thinner due to gradual dissolution of cell constituents, c an enlarged view of the etched cell surface by irradiated TiO<sub>2</sub>, d decomposed and ruptured bacterial lump





Fig. 7 FT-IR spectral bands of control cell culture, UV illuminated cells and UV irradiated P25–TiO<sub>2</sub> of *A. tumefaciens* suspension in the range of a 1,600-1,200 cm<sup>-1</sup> and b 2,400-2,300 cm<sup>-1</sup>



Fig. 8 Leakage of  $K^+$  ion from *A. tumefaciens* under different conditions; a control, i.e., P25–TiO<sub>2</sub> treated with bacterial suspension placed in the dark; b UV irradiation for 5 min without catalyst; and c P25– TiO<sub>2</sub> and bacterial suspension irradiated with UV for 5 min







Control

Culture + UV



P25-TiO<sub>2</sub> Au 1 wt %

P25-TiO<sub>2</sub>Ag 1 wt %



## TEM images of lenghty Titanate Nnotubes



Photomineralization and mechanistic study of Imidacloprid insecticide by Ag deposited sodium titanate nanotubes

Photocatalytic activity



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✓ Formation of ions confirms mineralization
 ✓ 0.5-Ag-TNT showed maximum mineralization = 34 %

Time course study for intermediate formation/degradation during photooxidation of imidacloprid and mass balancing



# High temperature synthesis of anatase TiO<sub>2</sub> and its improved photocatalytic activity for degradation of Methyl Parathion



Gradual Improvement in crystallinity with rise of calcination temperature.

#### Initiation of anatase-to-rutile transformation at > 800 °C

Calcination Temp. (°C)	*Anatase Crystallite Size (nm)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )
200	16	79
300	20	68
400	23	61
500	28	57
600	31	49
700	34	40
800	38	35
900	40	31

\*Calculated using Scherrer Equation d =  $0.9\lambda/(\beta \cos \theta)$ , d= crystallite size,  $\lambda = 1.5 \text{ Å}, \beta$  =full width at half maxima

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# **HR-TEM Images**



TiO<sub>2</sub> Nanorods (C-2)

Length =81-134 nm,

Width = 8-13 nm







Fig. (a-e)HR-TEM Images for 1 wt% Au- TiO2 nanorods calcined at 800 °C and (f) corresponding lattice fringe width

49

## **Photocatalytic activity**



Restricted, since 1999 as per EPA

Potential Health Affects : Headache, loss of vision and conscious, severe depressions, sleep walking, and death



#### **Estimation for CO<sub>2</sub> formation**

#### **Intermediate's Identification**



Conclusions: Stability of Anatase phase > 800 °C. Increment in photocatalytic activity with rise of calcination temperature for C-2 to C-9 catalyst. Higher activity than P25-TiO<sub>2</sub>. No detrimental influence of decrease in S<sub>BET</sub> and increase in anatase crystallite size THAPAR UNIVER



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Preparation and characterization of TiO<sub>2</sub> nanowires for improved photocatalytic under sun light irradiation





## Photocatalytic activity





**Conclusion: Higher relaxation** time of photoexcited charger carriers resulted into higher catalytic for bare **TNW** and Au-TNW in comparison to **P25-TiO<sub>2</sub>**.

**Conclusion:** Mechanistic study for mineralization of imidacloprid was proposed; Presence of intermediates (I-2, I-4and I-6) after 180 min of reaction explains the lack of stoichiometric mass balance.





### Natural pathway for Imidacloprid degradation



## Photocatalytic activity



Photodegradation of aqueous suspension of imidacloprid (25 ppm) and (a) P25-TiO2, (b) titania nanorod, (c) sodium titanate nanotube particles and  $CO_2$  produced by (d) titania nanorod and (e) sodium titanate nanotube.



HPLC chromatograph for (a) authentic imidacloprid and (b) its photooxidation by TNT after 120 min of UV-light irradiation.

**Conclusion:** Change in shape of titania nanoparticles alters electro-kinetic properties. *Higher Surface area of nanotubes resulted into its higher photoactivity.* 58

### **Summary and Conclusions**

Photocatalytic degradation of pesticides and polycyclic aromatic hydrocarbons by metal doped titania nanoparticles could be effective under sun light amd more greener route

In summary, present work demonstrated thatdifferent sizes, shapes of titania/titanate nanoparticles and studied the complete decomposition of pesticides (imidacloprid, sulfosulfuron, propiconazole and methylparathion) and PAHs (naphthalene and anthracene)

Crystalline sodium titanate nanorods exhibiting comparable photoredox activities to that of P25 for photoreduction of m-DNB and photooxidation of sulfosulfuron. TNW displayed much higher PCA than P25 for decomposition of propiconazole under UV- and sun-light,

**Ag-photodeposited TNT is an efficient catalyst for** the decomposition of IMI to CO2 and inorganic ions. The formation of number of identified intermediates reveal the complexity of photocatalytic process, suggesting the existence of various oxidation routes and non-specific attack of hydroxyl radicals that result in multi-step and interconnected pathways for decomposition of IMI.

TiO2 crystal phase played a vital role for superior photoactivity for MP degradation, the detrimental influences of decreased surface area, increased particle size and crystallite size are not observed for the C-2 to C-9 catalysts that were thermally treated at high temperatures. THAPAR UNIVERSITY, PATIALA 59

## **Publications of this current presentation:**

Applied Surface Science, <u>280</u> (2013) 366–372, RSC Advances, 4 (2014) 51342 - 51348. RSC Advance, 4 (2014) 24704-24709. Journal of Nanosci. Nanotech. 14 (2014) 1-9. Journal of Agricultural and Food chemistry 62 (52), 12497-12503 Environmental Science and Pollution Research 20 (9), 6521-6530 Environmental Monitoring and Assessment, 185 (2013) 6459-6463 Environmental Monitoring and Assessment, 185 (2013) 6291–6294 Journal of Industrial and Engineering Chemistry, 31, 223-230, 2015. Environmental Science and Pollution Research, 19 (2012) 2305–2312. Materials Chemistry and Physics, 136 (2012) 21-28. New Journal of Chemistry, 39 (2015) 5966-5976. Journal of Molecular Catalysis A: Chemical 396 (2015) 15–22. Journal of Molecular Catalysis A: Chemical, 391 (2014) 158–167. Chemical Engineering Journal, 246 (2014) 260-267. Environmental Science and Pollution Research, 20 (2013) 3956–3964.

#### Total SCI publications: 87, Citations: 1413, h-index= 16 Project: DST/CSIR/UGC (~ 1.7 Crores) 8 Ph.D. Guided, 7 Persuing Recent Publications:

- R. Kaur and B. Pal, J. Mol. Catal. A. Chem., 395 (2014) 7-15.
- N. Gupta and B. Pal, Chem. Eng. J., 246, 2014, 260-267.
- J. Kaur and B. Pal, Catal. Comm., <u>53</u>, 2014, 25–28.
- J. Kaur and B. Pal, Chem. Commun., 2015, 51, 8500-8503.
- R. Kaur and B. Pal, New J. Chem., 39 (2015) 5966-5976
- A. Monga and B. Pal, RSC Advance, 2015, 5, 39954-39963.
- R. Singh and B. Pal, ChemPlusChem., 5, 851-858, 2015.
- A. Monga and B. Pal, New J. Chem., 39 (2015) 304-313.
- B. Pal and B. Pal., Chem. Eng. J., <u>263</u>, 2015, 200–208.
- *R. Kaur and B. Pal, Appl. Catal. A Gen.*, <u>491</u>, 2015, 28–36.
- I. S. Grover, S. Singh and B. Pal, *RSC Advance*, 2014, **4**, 24704-24709.
- I. S. Grover, S. Singh, B. Pal, J. Agri. and Food Chem. 2014, 62, 12497-12503.
- S. Sareen, V. Mutereza, S. Singh and B. Pal, *RSC Advances*, 2015, 5 (1), 184-190.
- S. Sareen, V. Mutreja, S. Singh and B. Pal, J. Colloid and Inter. Sci., 461 (2016) 203–210.

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## **School of Chemistry & Biochemistry**

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- School consistently features in top 3 departments/School of TU in academic research score (on the basis of publication + research funding + Ph.D. thesis guidance)
- In faculty strength, SCBC in bottom 3 of TU



## **Research Achievements of the School of Chemistry & Biochemistry**

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- > Average impact factor per publication: 2.5
- ➢ No. of on-going Major Research Projects: 15
- Grant-in Aid (on-going Projects): ~ ₹ 30 million ( Euro 4,64,000)
- ≻ No. of completed Major Research Projects: 24
- ➢ Grant-in Aid (completed Projects): ~ ₹ 400 million (Euro 5,90,914)
- ≻ No. of Ph.D on-going: 50
- ≻ No. of Ph.D completed: 35

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  Chemical Sensors, Biosensors
  Biocatalysis & Biotransformation
  Biofuels & Catalysis
  Synthetic Organic Chemistry
  Biophysical and Bioinorganic Chemistry
  Medicinal Chemistry
  Supramolecular chemistry
- •Advanced Nanomaterials
- •Metal Hydrides, Organometallic Chemistry







# Thanks

## **Organizing Committee -----Pollution Control 2016**

School of Chemistry and Biochemistry, Thapar University

## Ph.D.Student:

<u>Nidhi, Rohit, Inder, Rupinder, Bhupinder, Anila,</u> <u>Jaspreet, Shweta, Reyees, Tanushree, Projapot,</u> <u>Upraaj, Manpreet, Sakshi, Ritika, Smriti</u>

> Project: DST-Nanomission, UGC and CSIR (Total 1.70 Crores)