Building hope for a greener future: Celebrating progress in Advanced Oxidation Processes

Prof Alex T Kuvarega

CSET

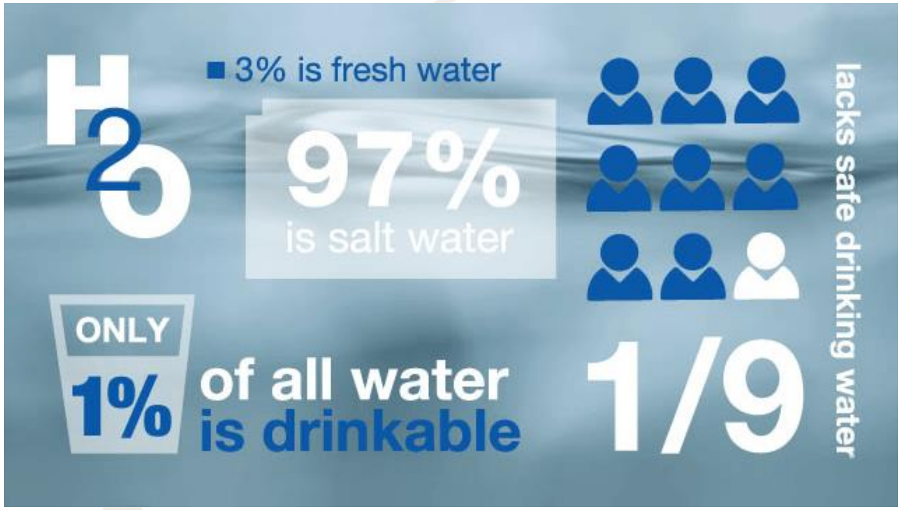
iNanoWS

Define tomorrow.

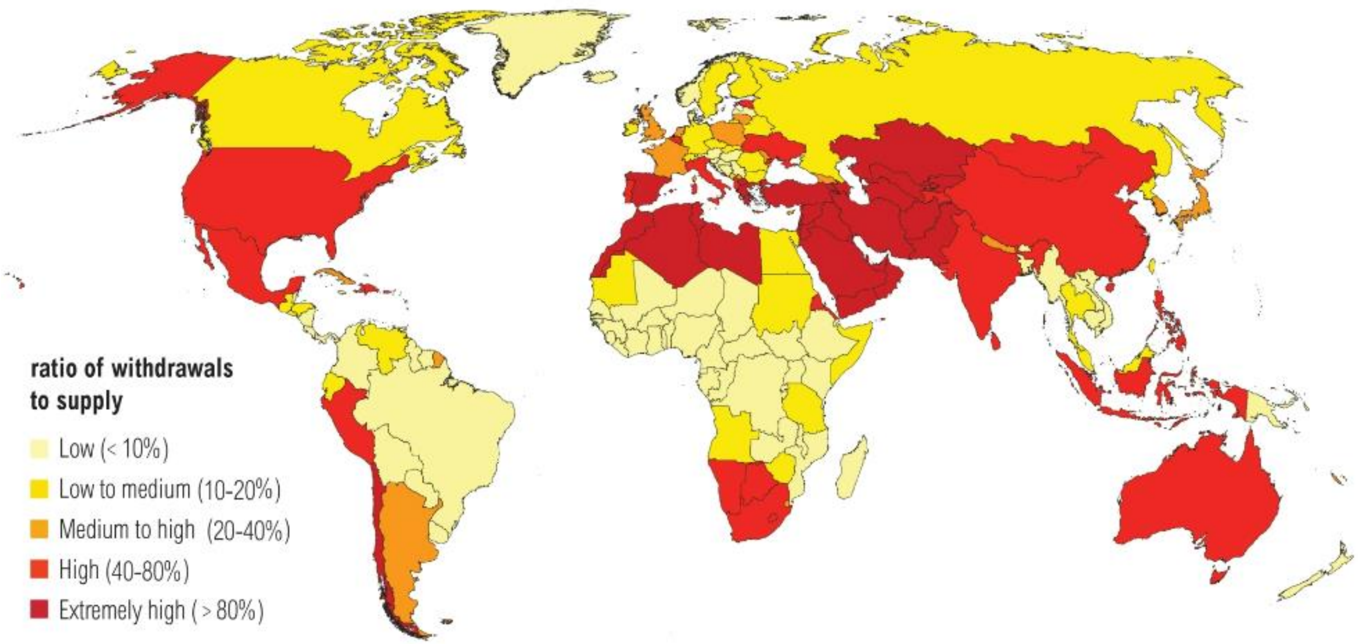
UNISA college of science, engineering and technology

150 YEARS

Water scarcity



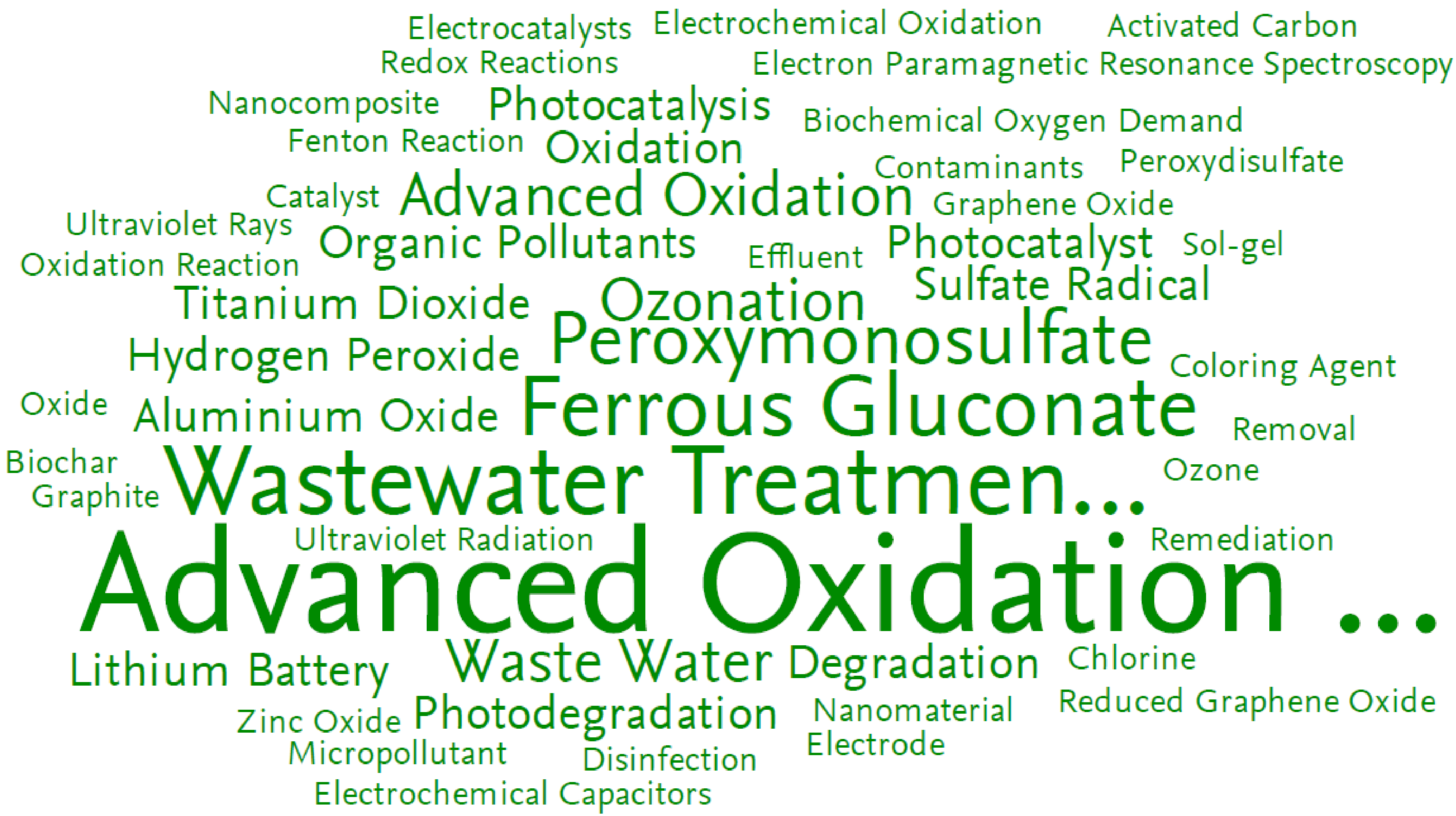
Financial Times January 23 2018



World Resources Institute

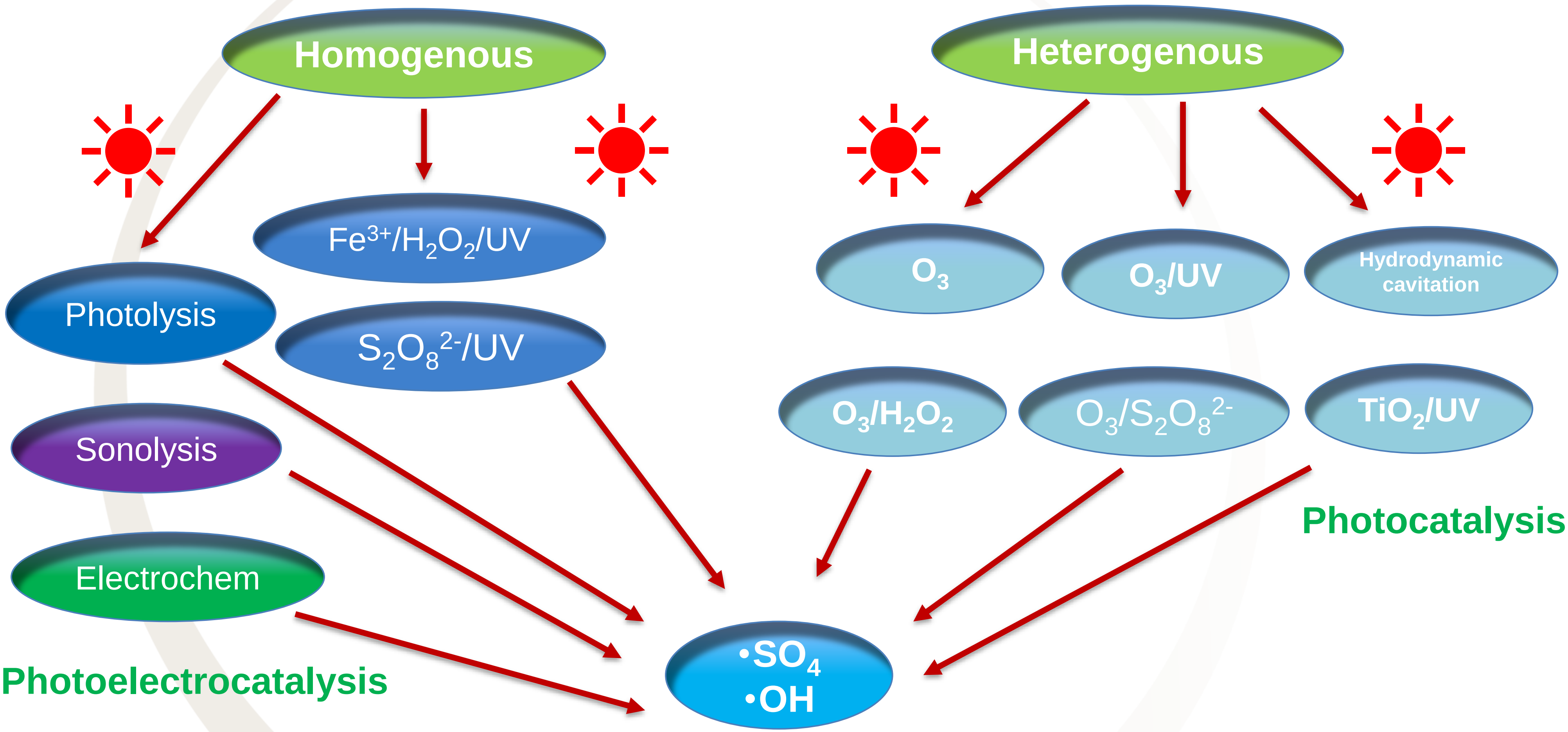
Technologies for water/wastewater treatment to contribute to improved access to clean and fresh water across the globe

Advanced Oxidation Processes_Terms



Top 50 key phrases in Advanced Oxidation Processes related research

Advanced Oxidation Processes - Classification

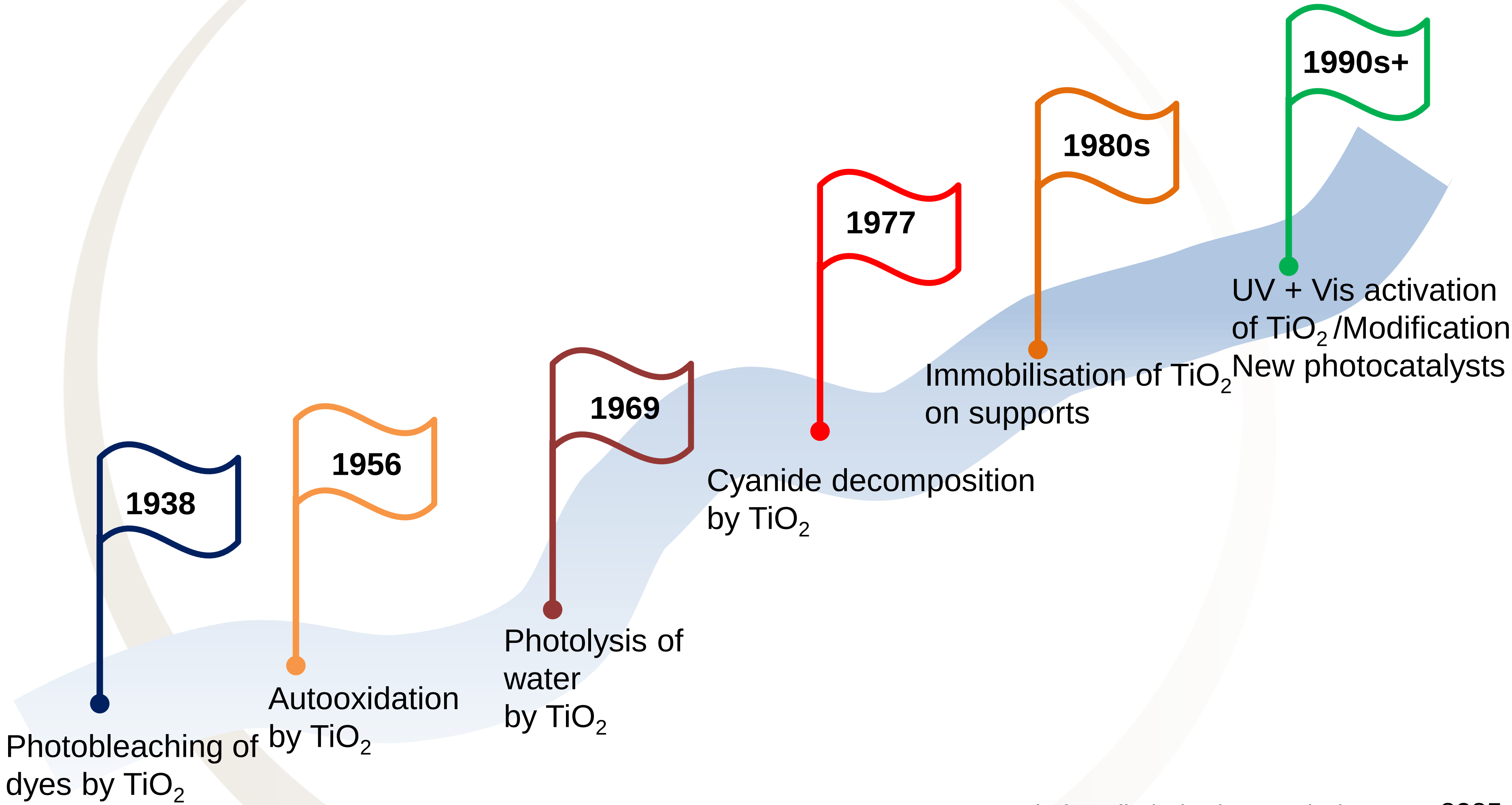


Reactive Oxygen Species (ROS)

Oxidation potential of ROS

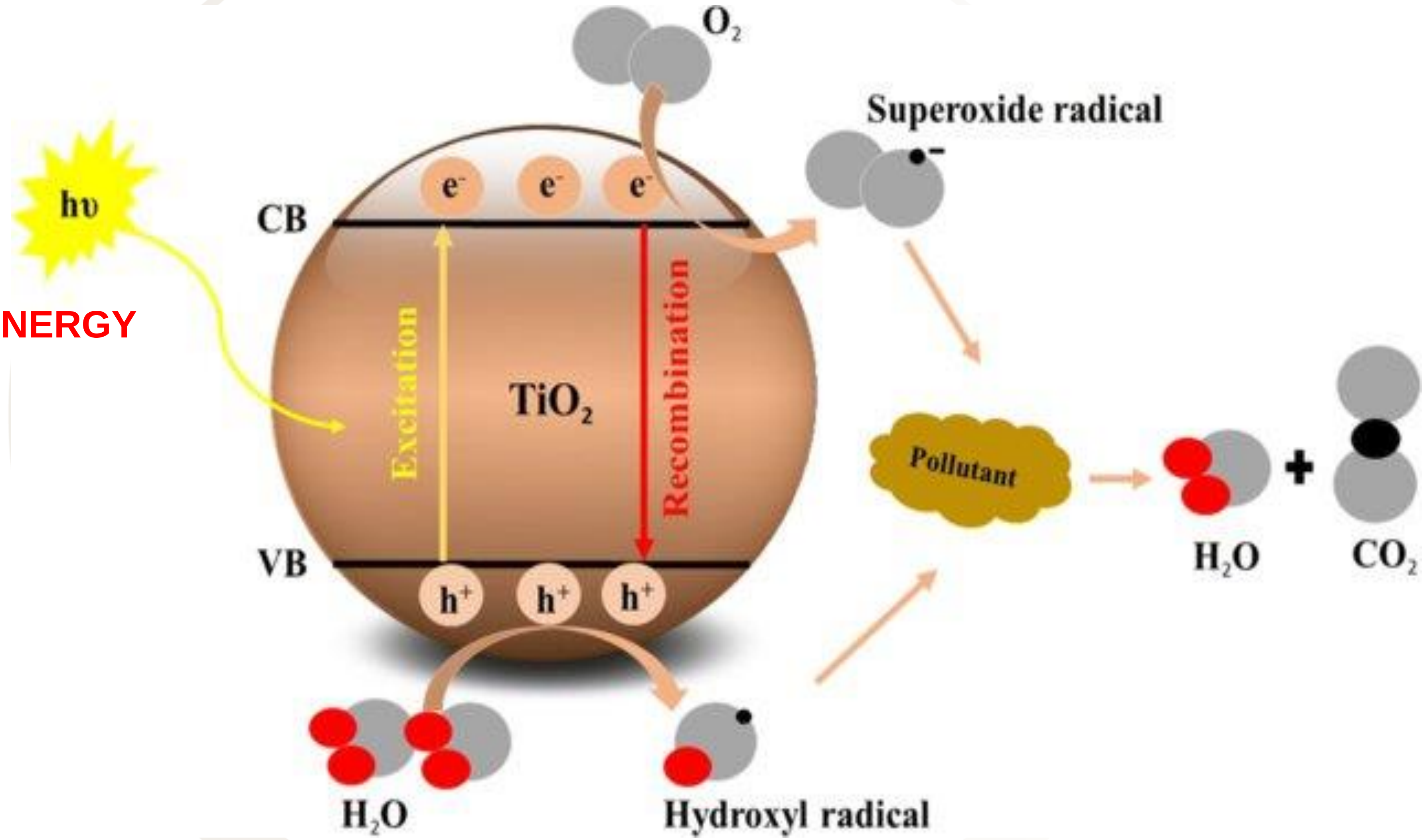
Oxidant	Oxidation Potential (V)
Fluorine [F_2]	3.0
Hydroxyl radical [$HO^{\bullet}$]	2.8
Sulfate radical [$SO_4^{\bullet -}$]	2.5–3.1
Ozone [O_3]	2.1
Persulfate [$S_2O_8^{2-}$]	2.1
Peroxymonosulfate [HSO_5^-]	1.8
Hydrogen peroxide [H_2O_2]	1.8
Permanganate [MnO_4^-]	1.7
Chlorine dioxide [ClO_2]	1.5

Photocatalysis - The roadmap



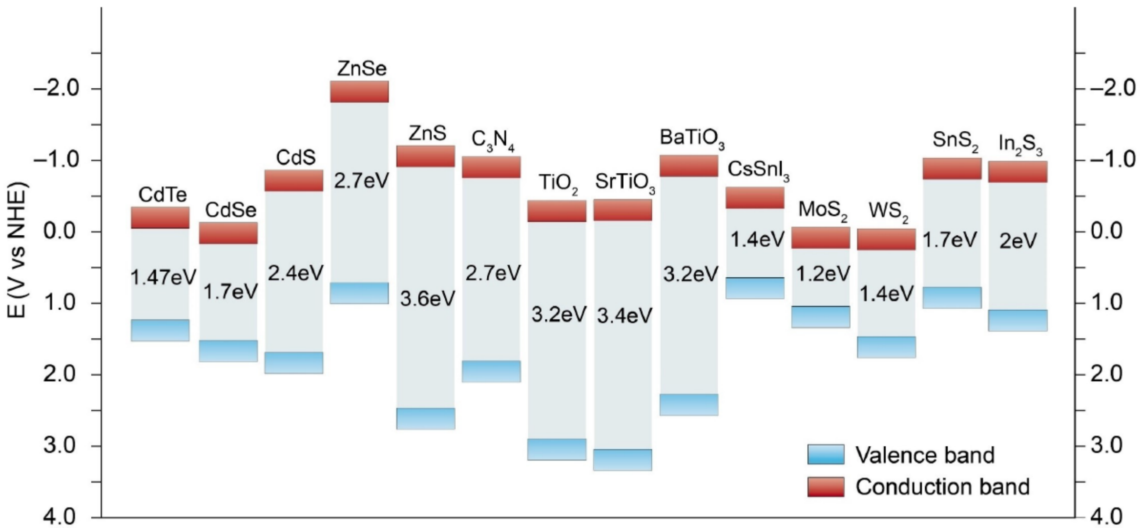
Japanese Journal of Applied Physics, 44, (12), 8269 - 8285

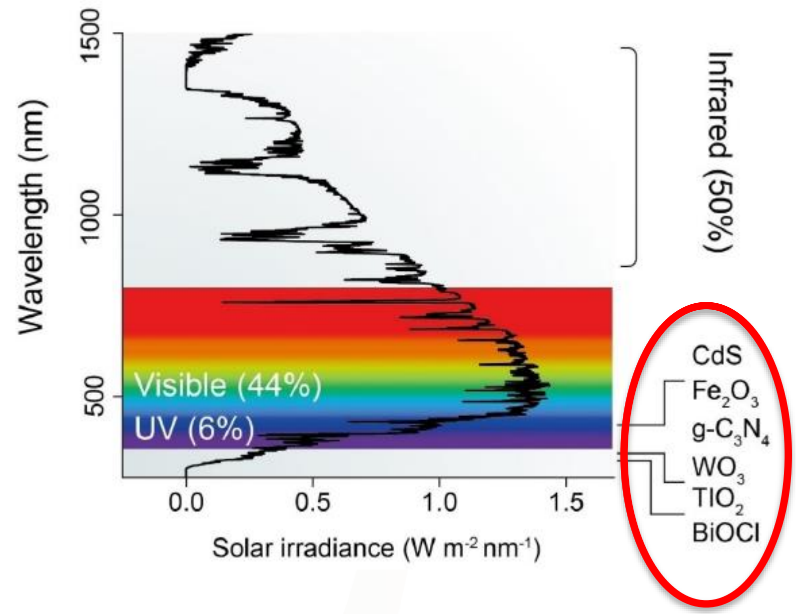
Basic principles – semiconductor photocatalysis



Environmental Science and Pollution Research, 2021, 28(33):1-29

Spectral region and band positions of some semiconductors





Activated by high energy UV photons

Chem Asian J. 2021, 16, 2596–2609

Light Sources –Artificial vs Natural

Can be UV, UV-Visible, Visible, IR or natural

- Hg/Ar Lamps
- Deuterium Lamps
- W-filament
- Xe Lamps
- Xe/Hg Lamps
- Florescence

- Solar Simulators
- LEDs
- Natural solar light

UV-lamps (High energy)

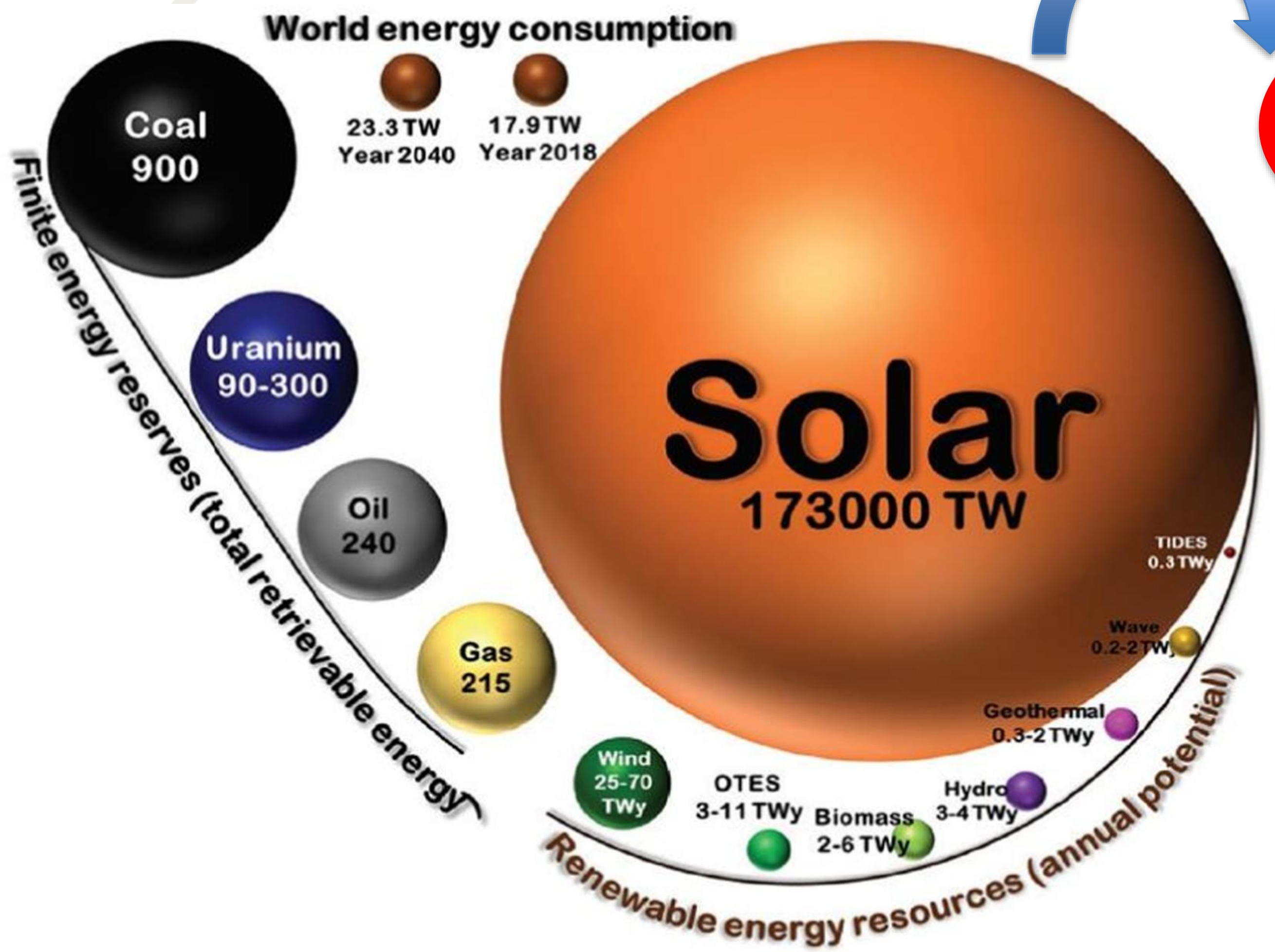
Expensive

UV handling – health hazard

Visible lamps (Low energy)

Cheaper/renewable

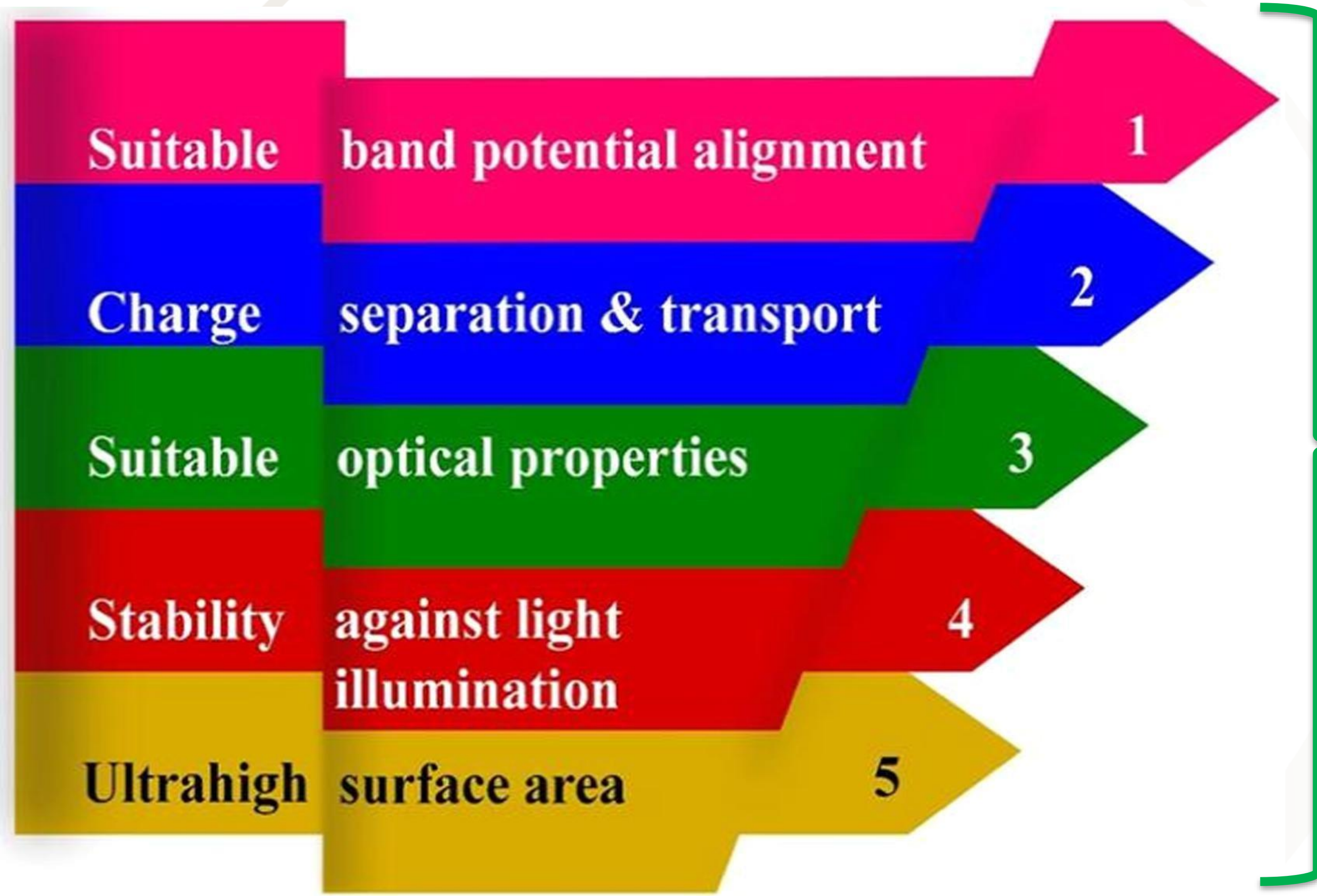
World Energy Consumption Vs Solar Energy



LEDs

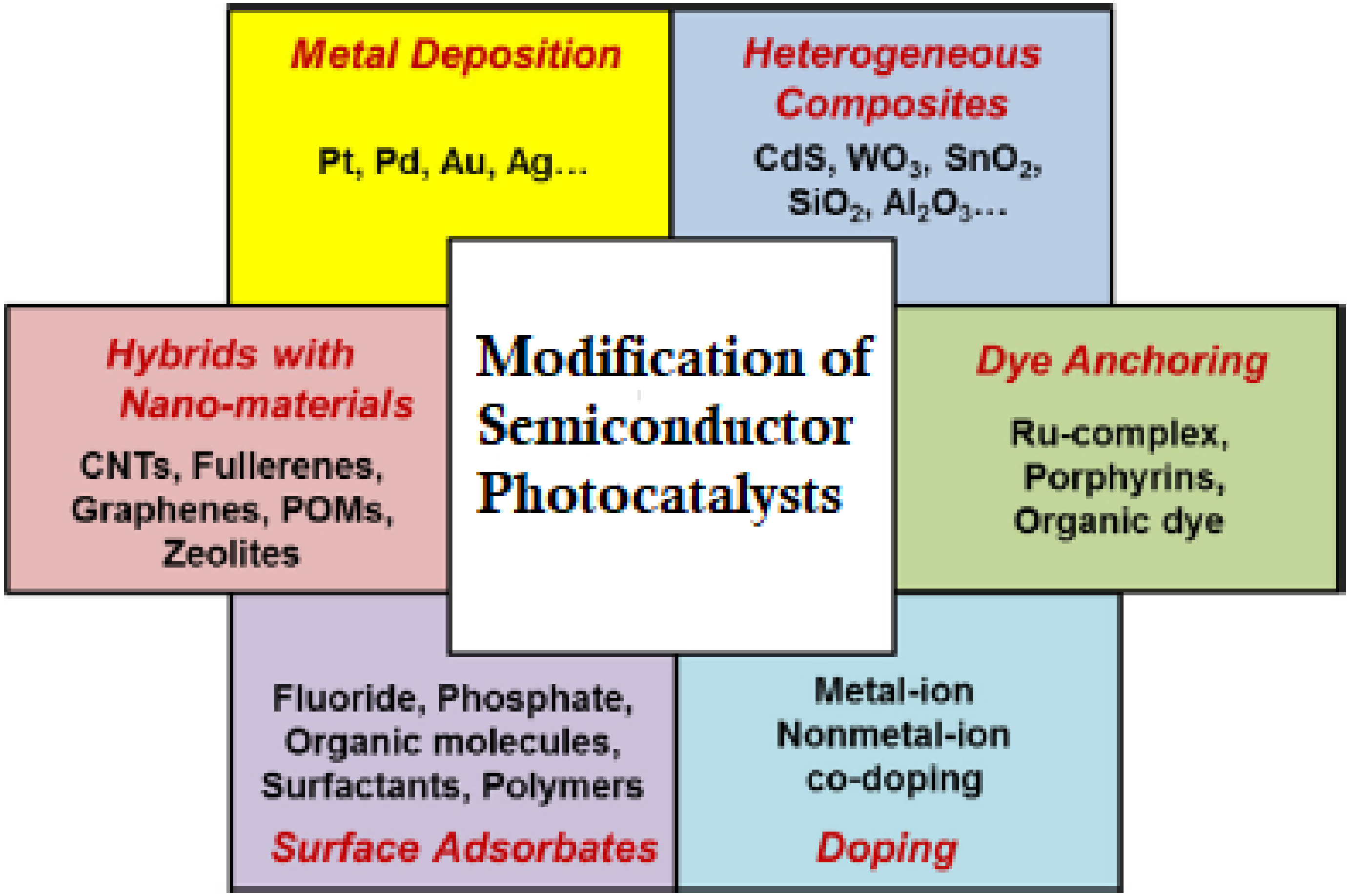
Fuel 2021, 303, 121302

Desirable properties of photocatalysts



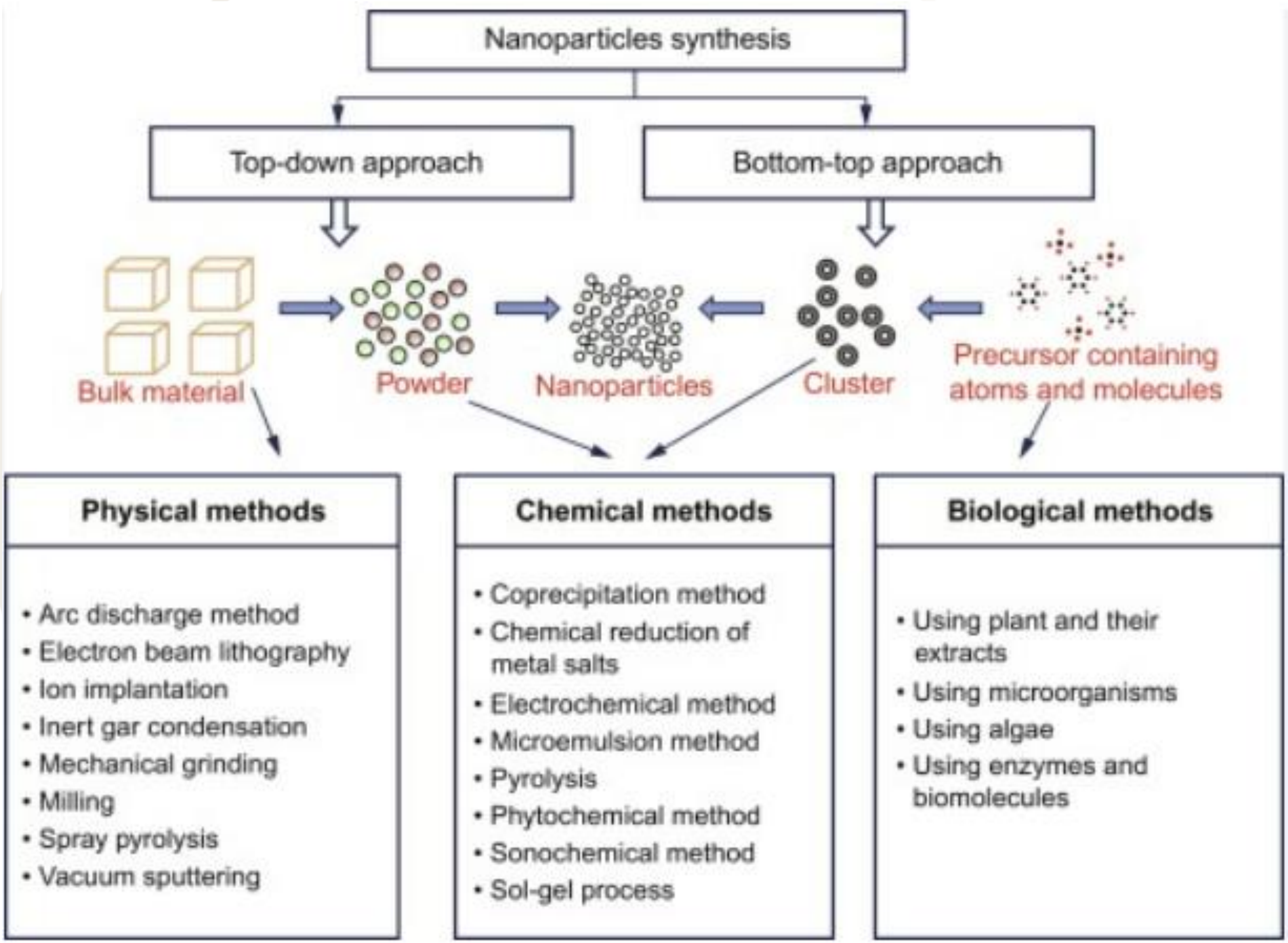
Motivation for modification or tuning of semiconductor photocatalysts

Modification of semiconductors



Journal of Photochemistry and Photobiology C: Photochemistry Reviews *15 (2013) 1– 20*

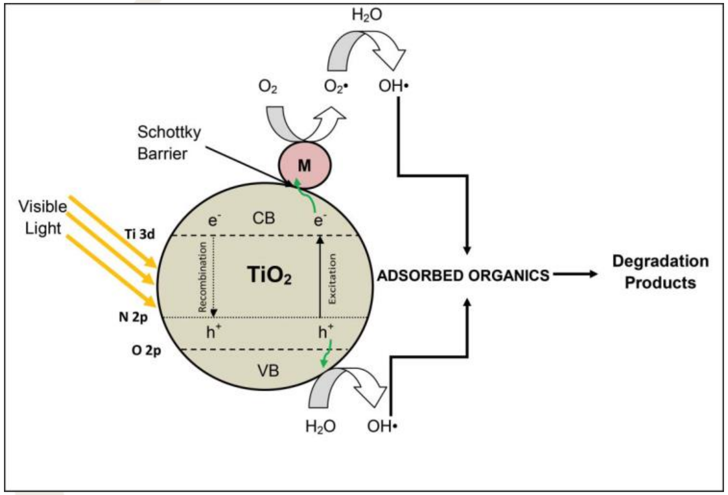
Synthesis methods

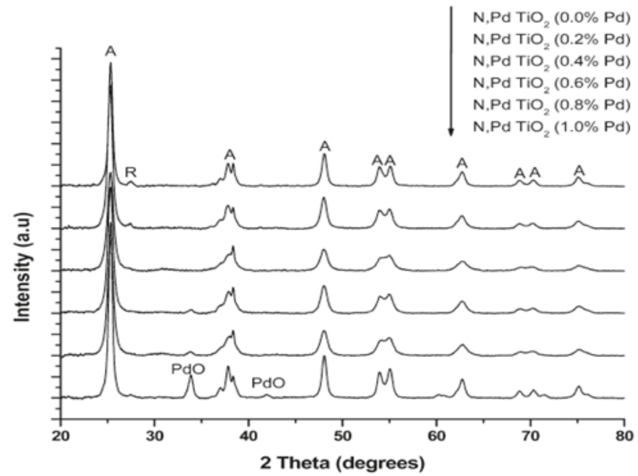


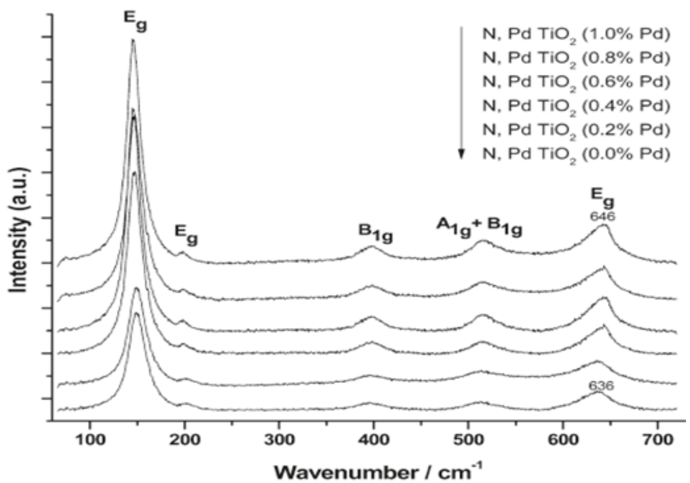
J Genet Eng Biotechnol 18, 67 (2020).

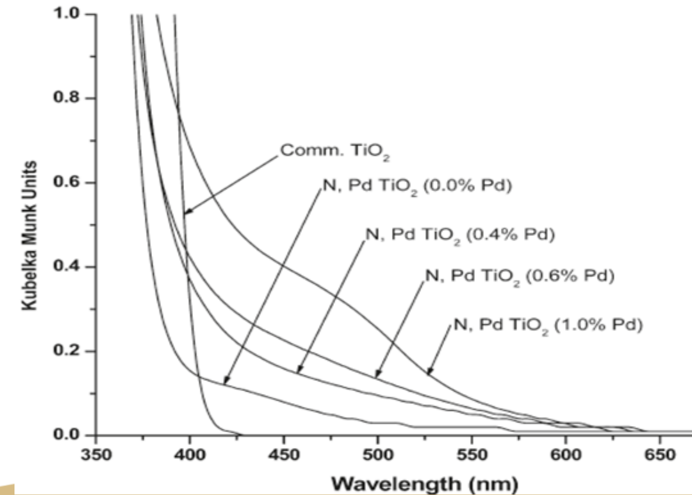
Metal deposition, doping and co-doping

Slowing down e-/h+ recombination rate through addition of non metal and metal dopants (Fe, Cu, Pd, Os, Ir etc)



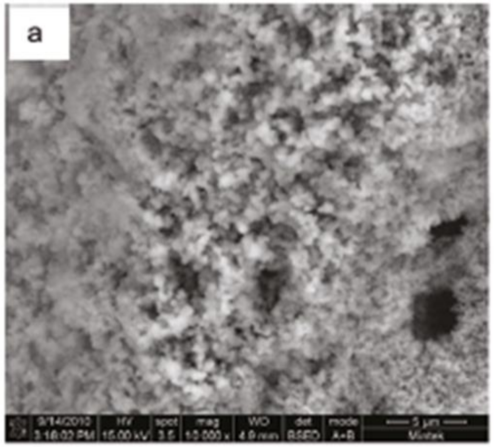


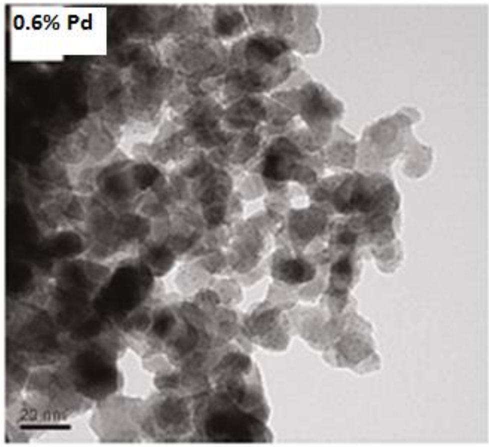


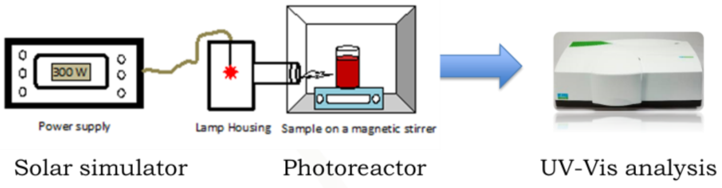


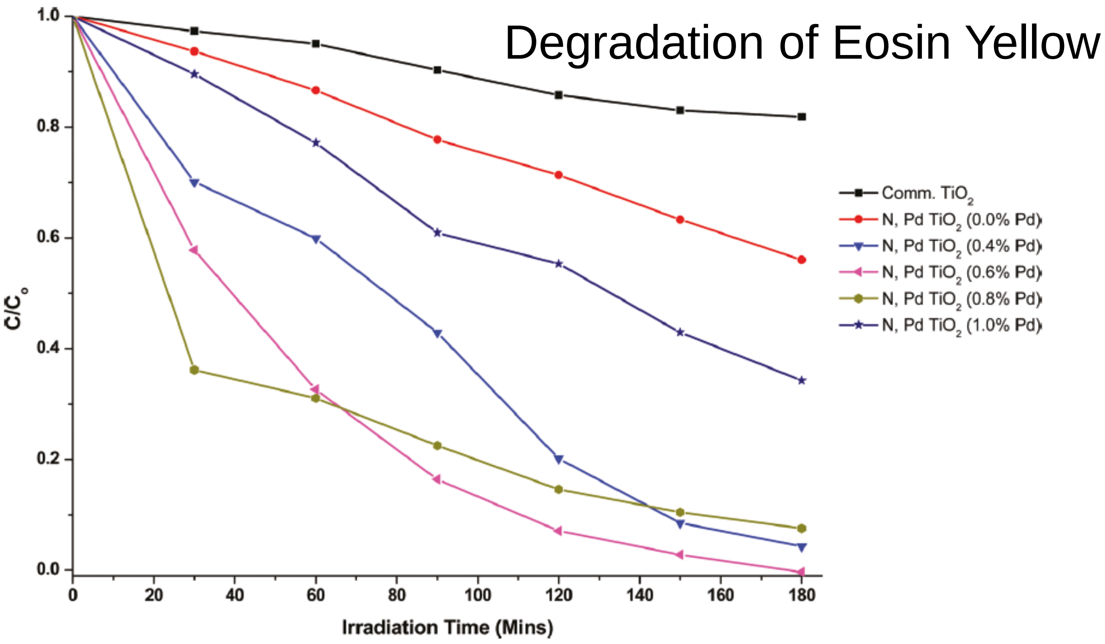
J. Phys. Chem. C 2011, 115, 45, 22110–22120

N,Pd co-doped TiO_2 for dye degradation









sample	indirect band gap (eV)
commercial TiO_2 (Degussa P25)	2.95
N/Pd-codoped TiO_2 (0.0% Pd)	2.16
N/Pd-codoped TiO_2 (0.4% Pd)	1.87
N/Pd-codoped TiO_2 (0.6% Pd)	1.85
N/Pd-codoped TiO_2 (0.8% Pd)	1.99
N/Pd-codoped TiO_2 (1.0% Pd)	2.06

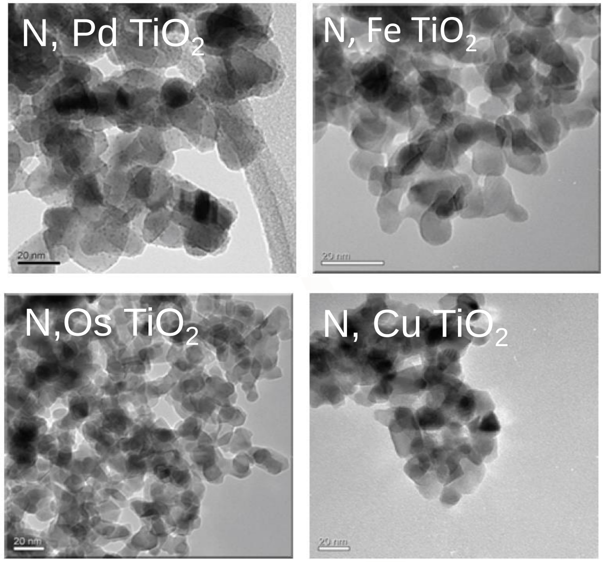
sample	% degradation after 180 minutes
commercial TiO_2 (Degussa P25)	18.2
N/Pd-codoped TiO_2 (0.0% Pd)	44.0
N/Pd-codoped TiO_2 (0.4% Pd)	95.7
N/Pd-codoped TiO_2 (0.6% Pd)	100.0
N/Pd-codoped TiO_2 (0.8% Pd)	92.5
N/Pd-codoped TiO_2 (1.0% Pd)	65.8

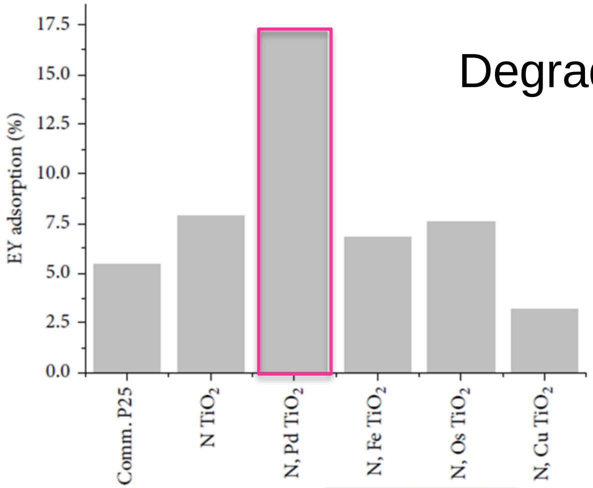
J. Phys. Chem. C 2011, 115, 45, 22110–22120

Comparative study of N,M co-doped TiO_2

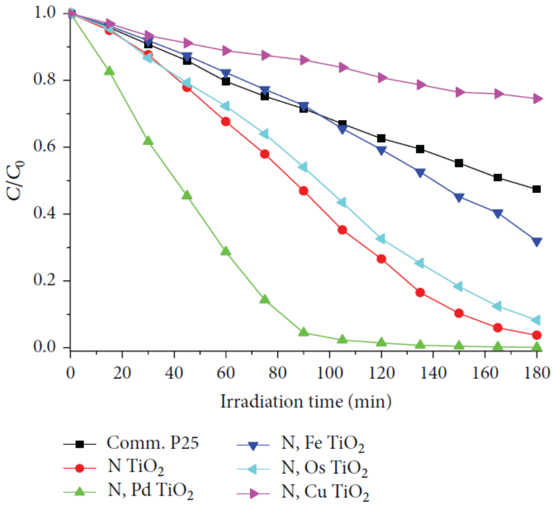
Sample	Particle size (nm)	Anatase phase (%)
Commercial TiO_2 (P25)	26.7	79.2
N, Pd codoped TiO_2	15.8	97.3
N, Fe codoped TiO_2	26.2	85.8
N, Os codoped TiO_2	14.0	87.9
N, Cu codoped TiO_2	24.9	72.1

Sample	Optical band gap (eV)
Comm. TiO_2 (P25)	3.1
N TiO_2	2.7
N, Pd TiO_2	2.1
N, Fe TiO_2	2.6
N, Os TiO_2	2.0
N, Cu TiO_2	2.8

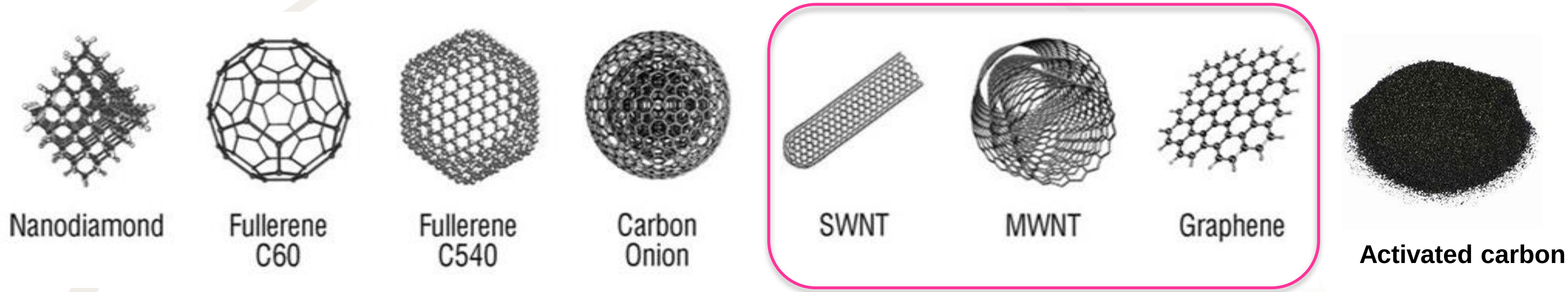




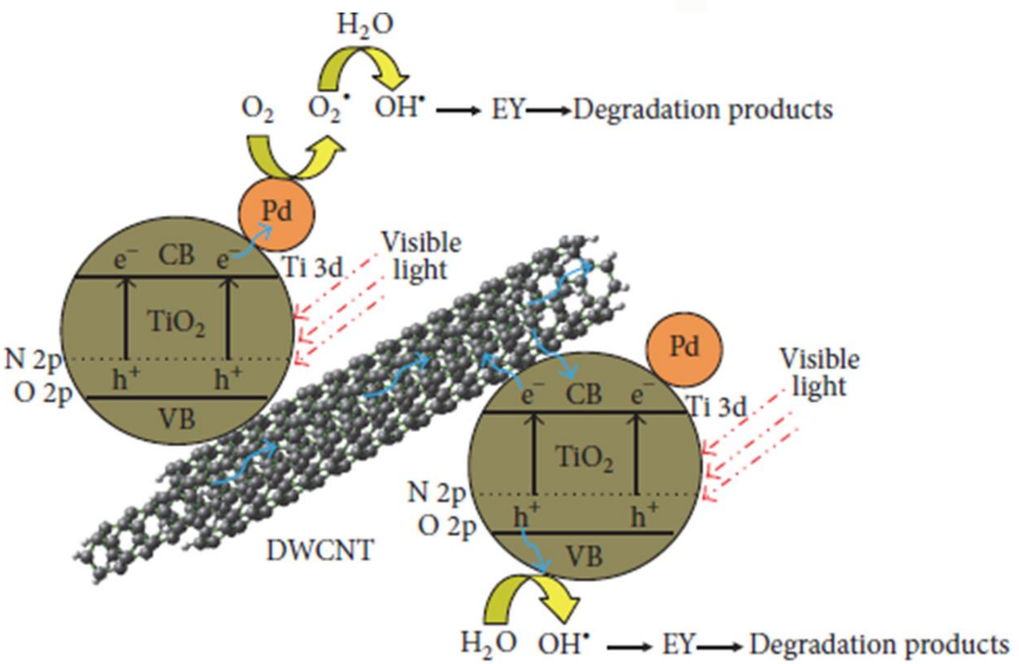
Degradation of Eosin Yellow



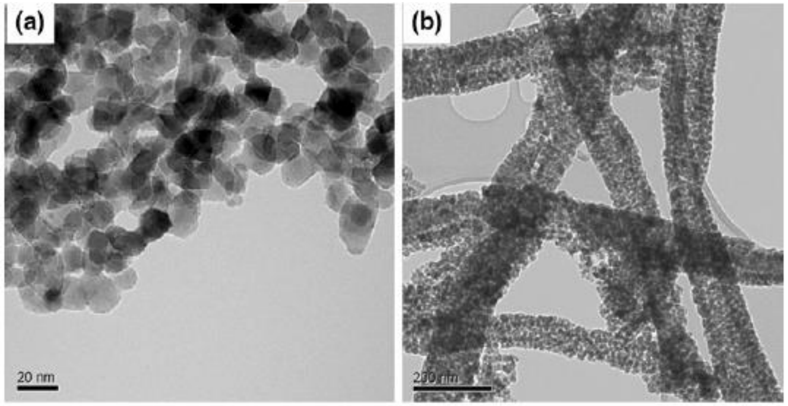
Composites with carbon materials



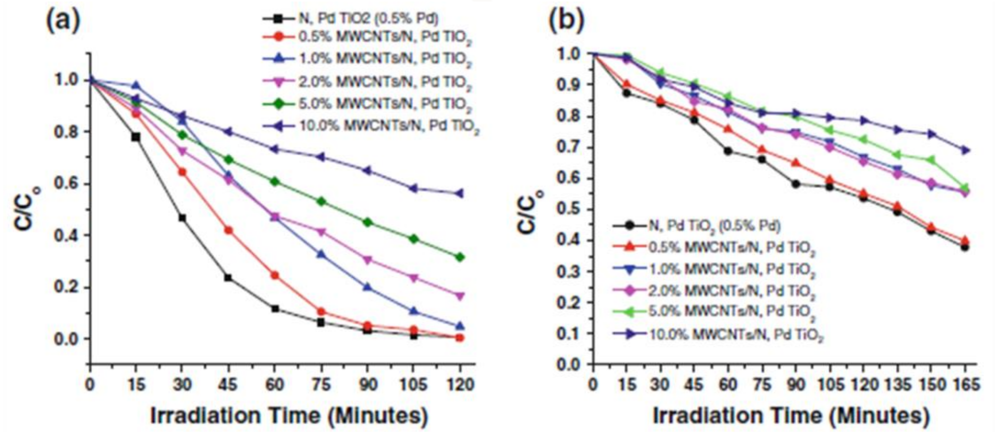
- Can be made from cheap waste materials
- Consist of **sp³** and **sp²** hybridised **carbon** network
- Remarkable **mechanical, electrical, biological, optical** and **thermal** properties
- Used as **adsorbents**, templates, actuators, composite reinforcements, **catalyst supports**, filters or chemical sensors



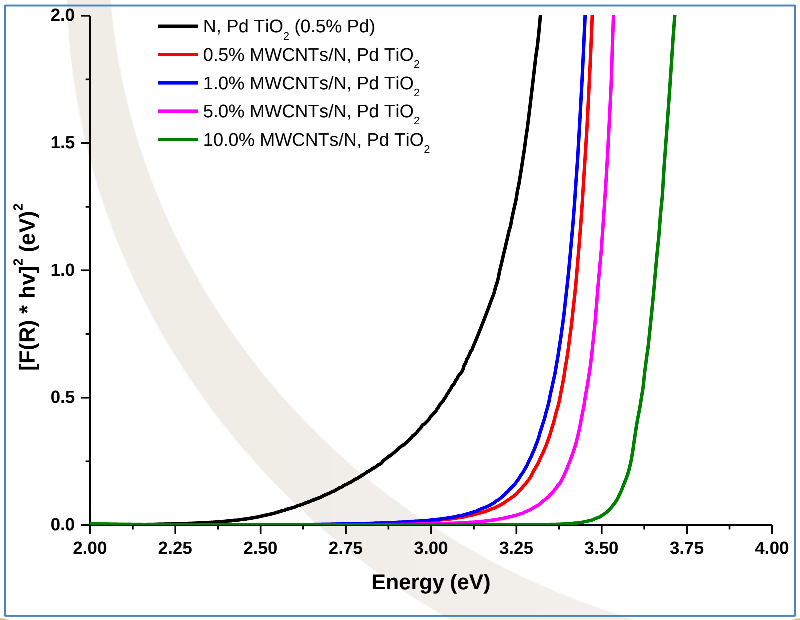
TiO_2/MWCNT composites



N,Pd co-doped TiO_2 (0.5% Pd) 0.5% MWCNT/N,Pd co-doped TiO_2

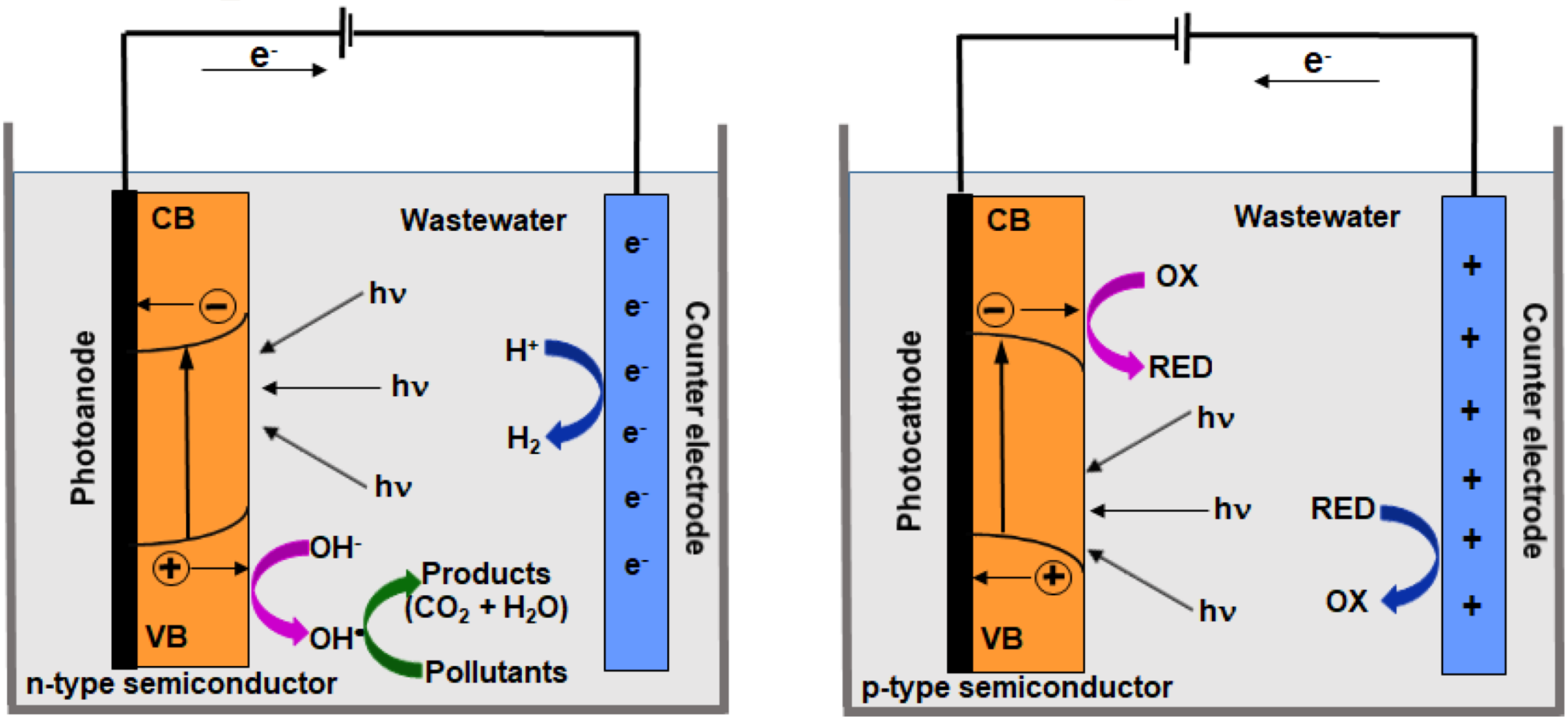


(a) Simulated solar light irradiation (b) Visible light irradiation(λ > 450 nm)



Sample	Degradation after 120 min (%)
N, Pd co-doped TiO_2 (0.5% Pd)	99.30
0.5% MWCNT/N, Pd co-doped TiO_2	99.55
1.0% MWCNT/N, Pd co-doped TiO_2	95.21
2.0% MWCNT/N, Pd co-doped TiO_2	83.18
5.0 % MWCNT/N, Pd co-doped TiO_2	68.36
10.0 % MWCNT/N, Pd co-doped TiO_2	43.84

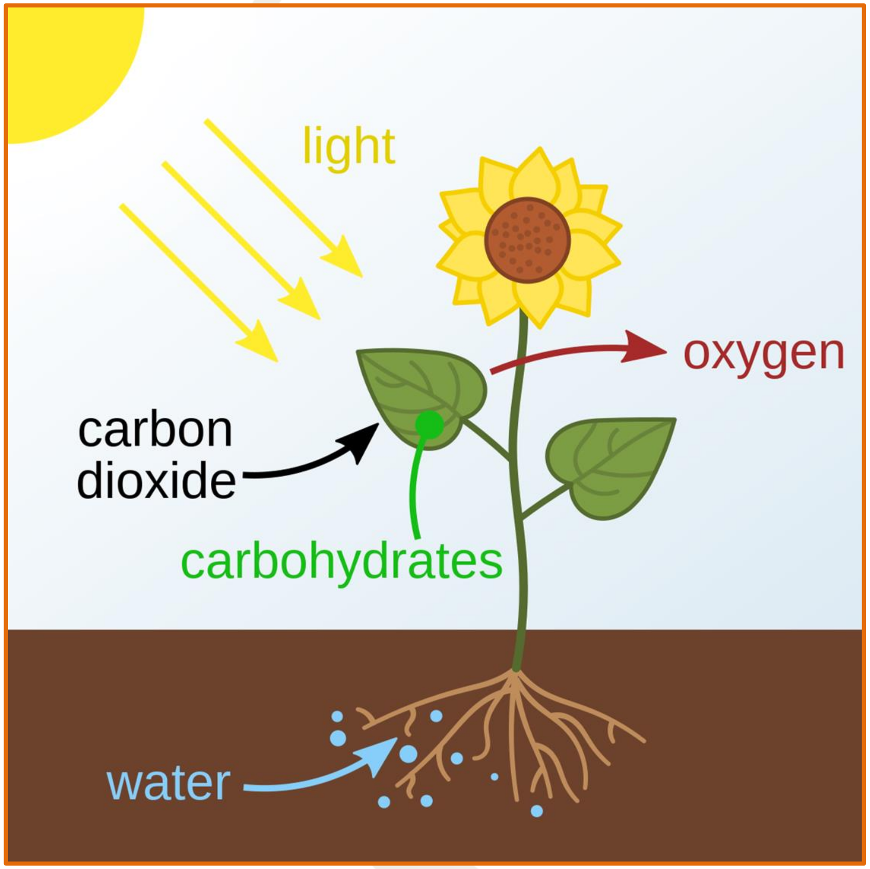
Photoelectrocatalysis



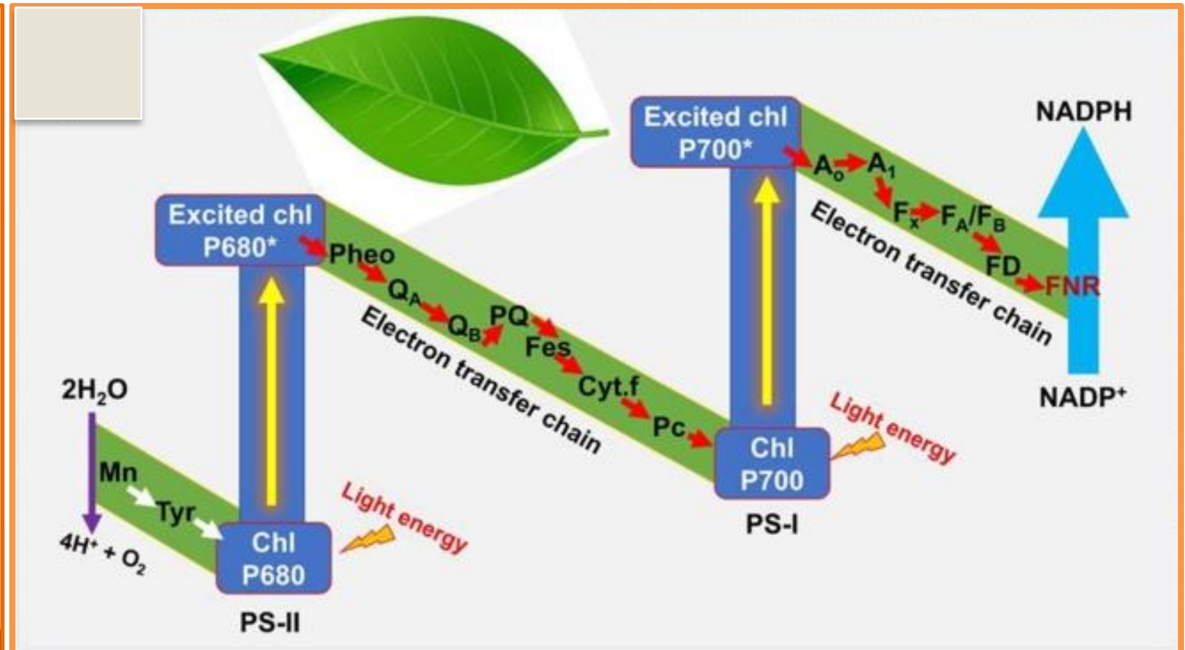
Catalysts 2020, 10(4), 439

Z-scheme photocatalysts_mimicking photosynthesis

Photosynthesis



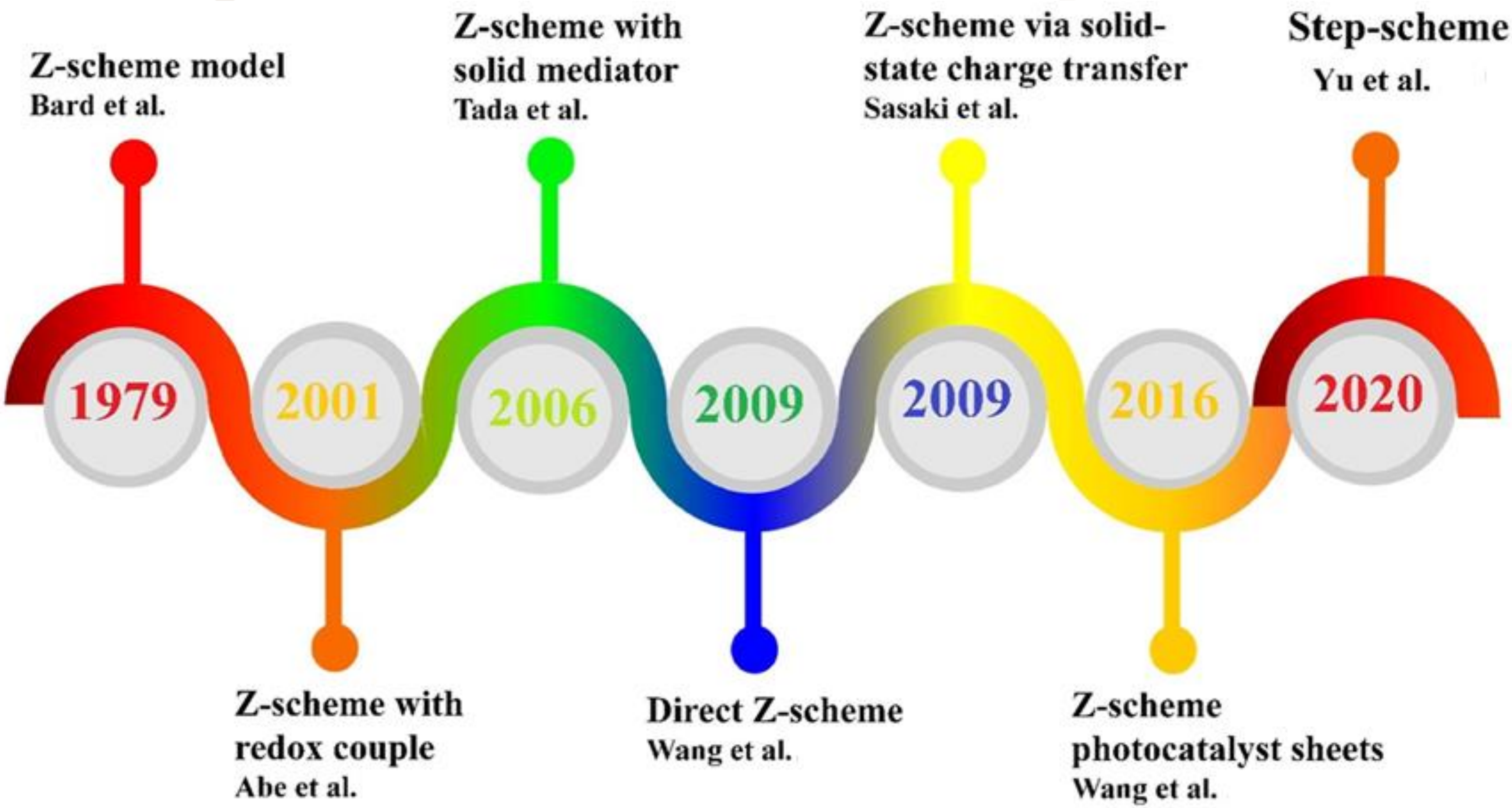
Z-scheme



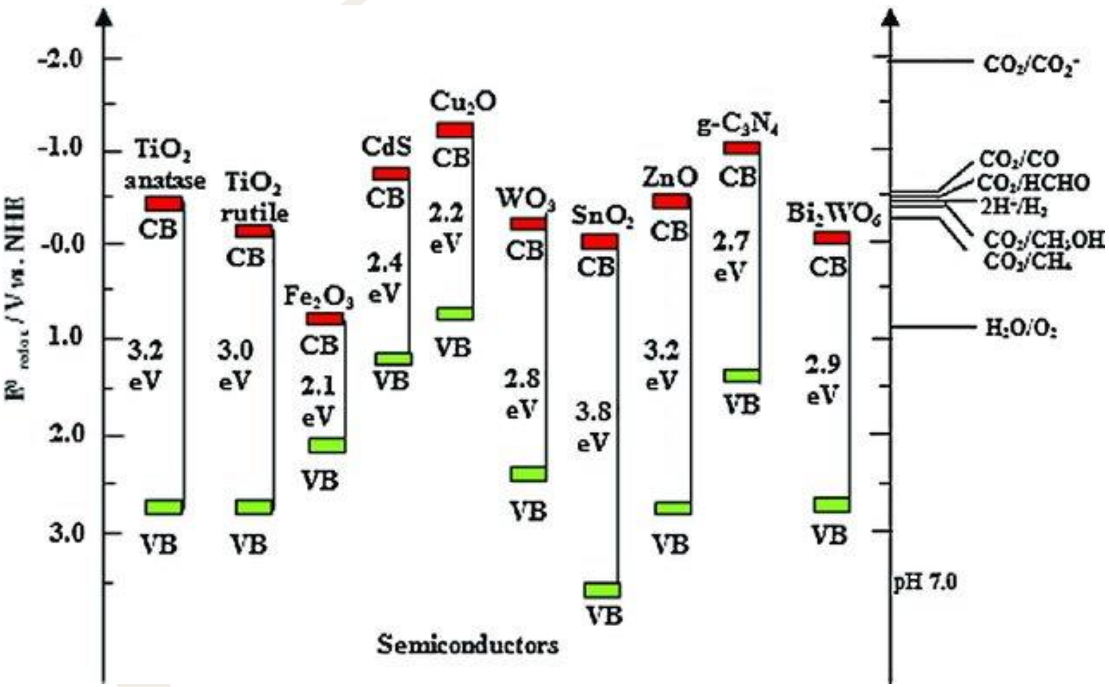
H_2O – Oxidation

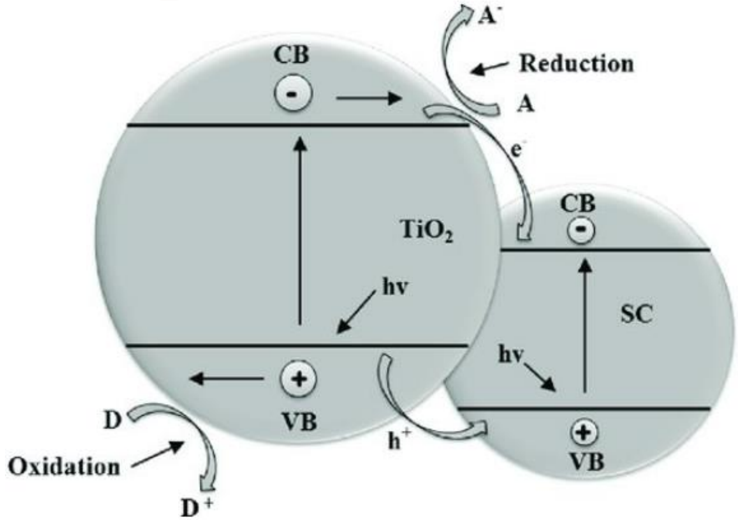
CO_2 - Reduction

Heterojunction (photo)electrocatalysts



Band position determination and alignment



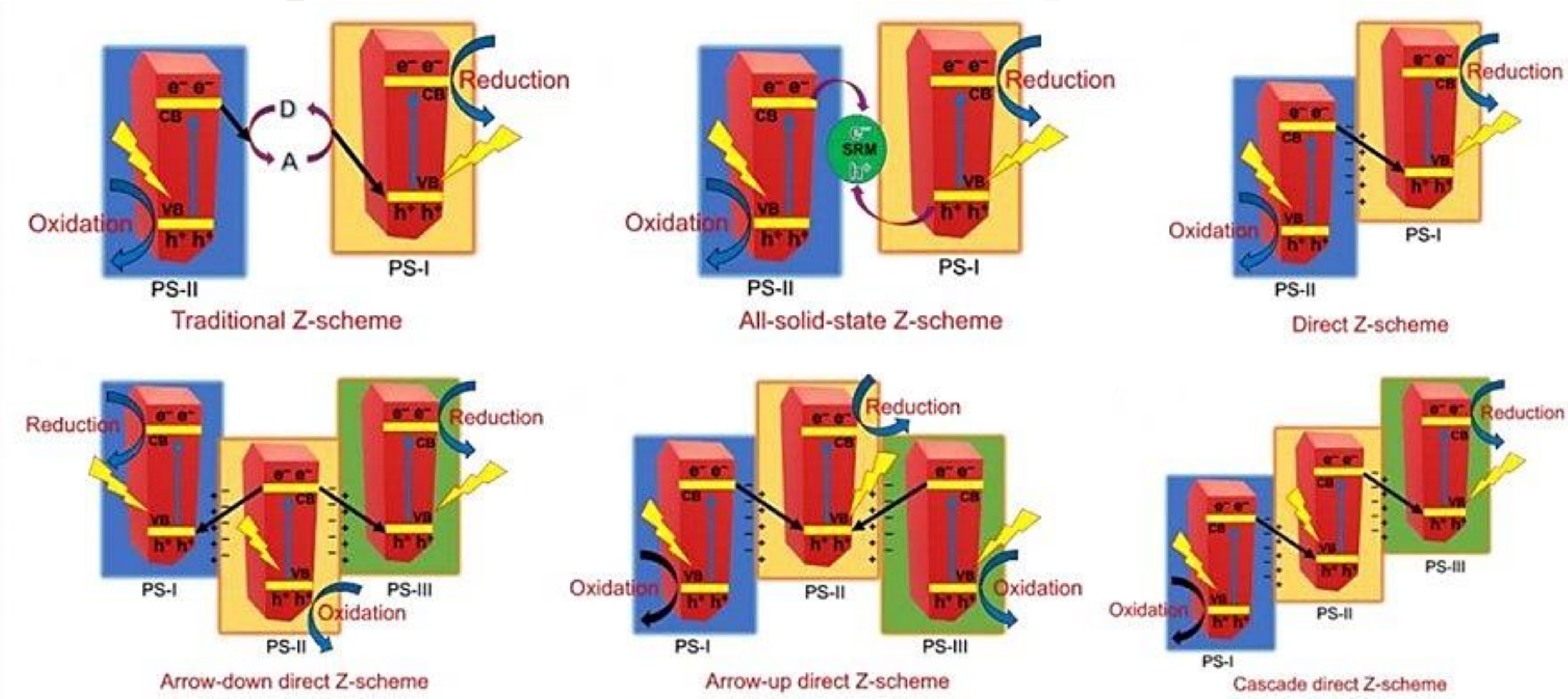


$E_{CB} = X - E^e - 0.5E_g$

$E_{VB} = E_{CB} + E_g$

- X → Electronegativity
- E_{CB} → Conduction band potential
- E_{VB} → Valence band potential
- E^e → Free electron energy
- E_g → Band gap energy

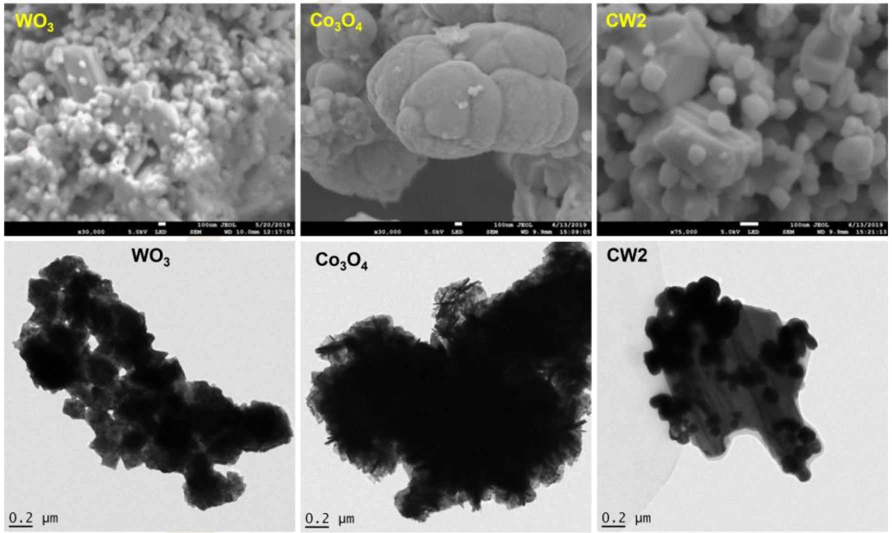
Charge Transfer Mechanisms

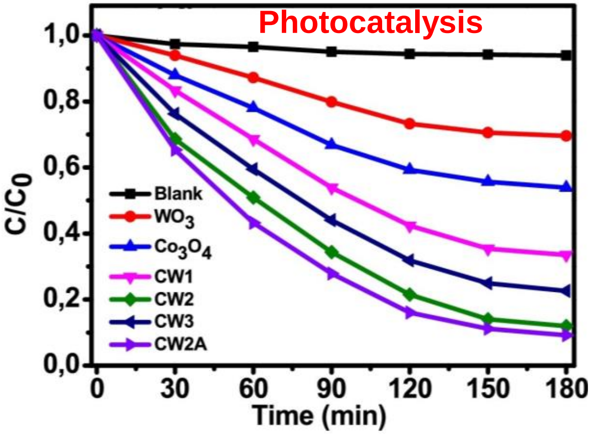


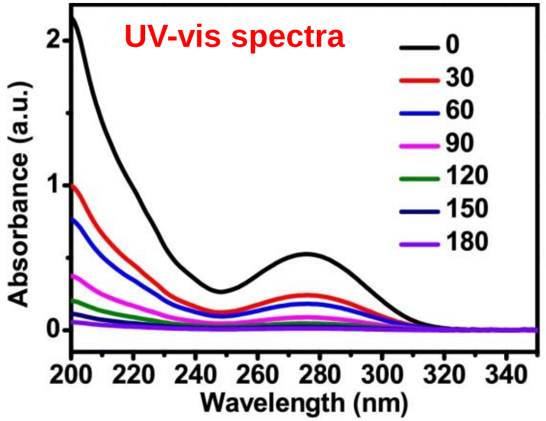
- ➢ **Charge separation for efficient oxidation/ reduction process**
- ➢ **Use of low energy photons to activate the photocatalysts**

p-n heterojunction mechanisms

Diclofenac degradation







Journal of Environmental Chemical Engineering
Volume 8, Issue 2, April 2020, 103560
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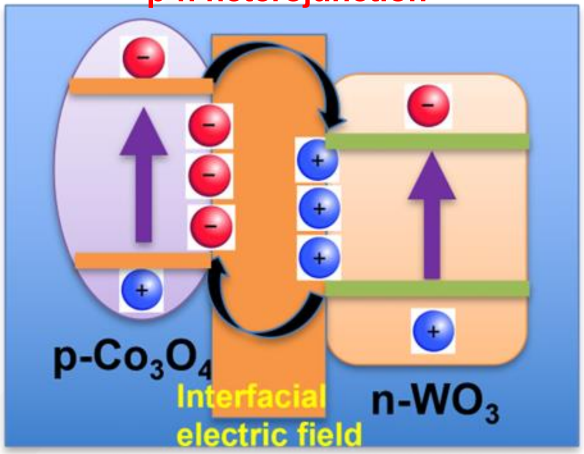
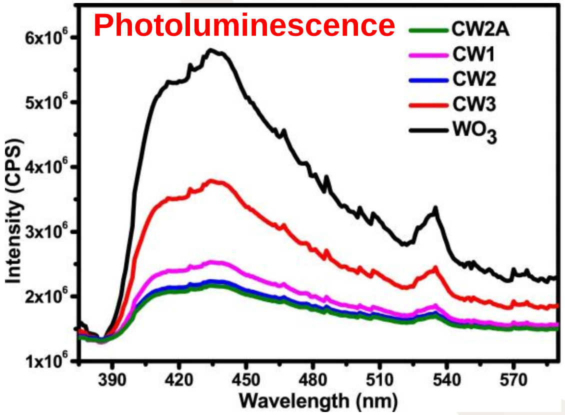
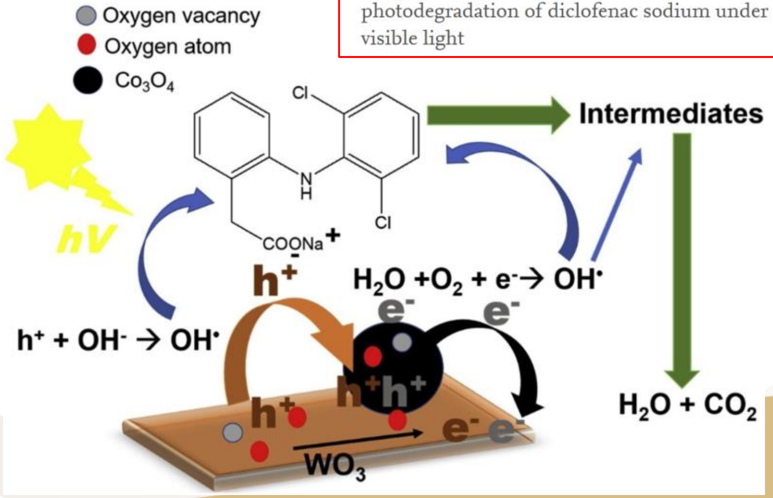
Cobalt (II/III) oxide and tungsten (VI) oxide p-n heterojunction photocatalyst for photodegradation of diclofenac sodium under visible light

p-n heterojunction

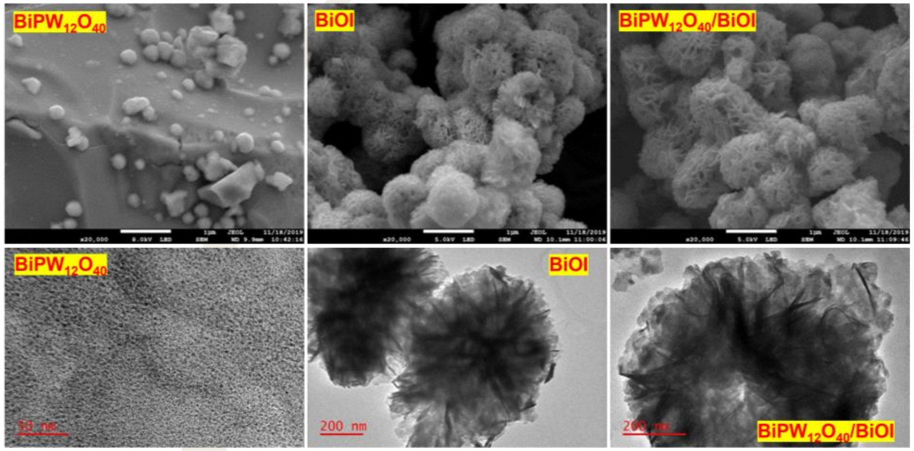


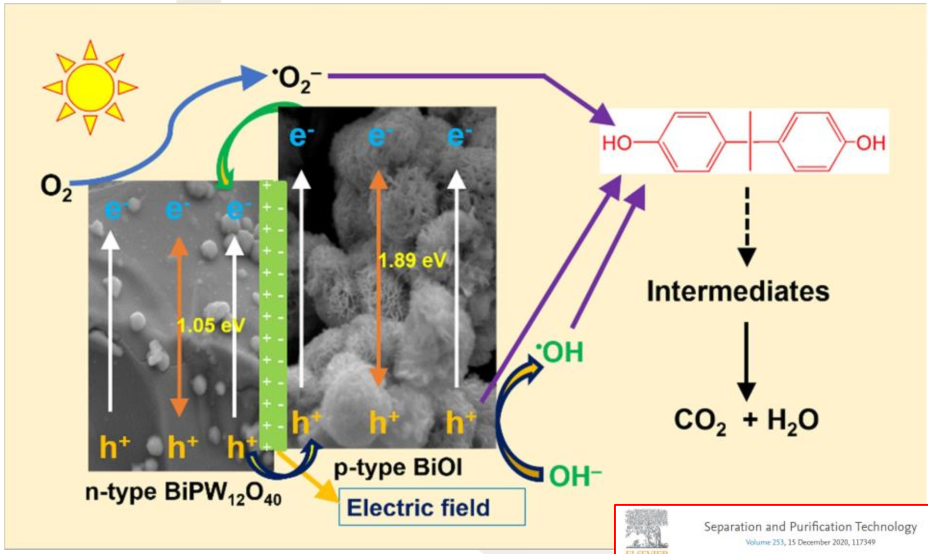


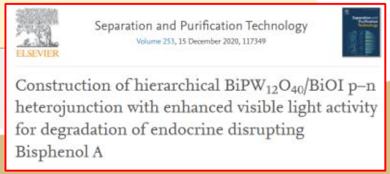


p-n heterojunction mechanisms

Photodegradation of bisphenol A and Acid Black 25

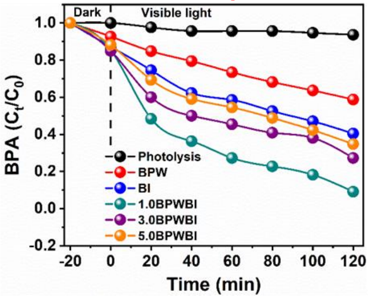




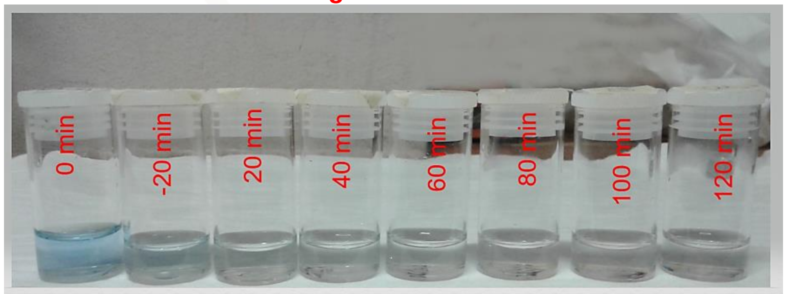

Separation and Purification Technology
Volume 253, 15 December 2020, 117349

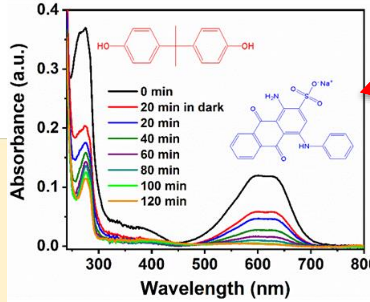
Construction of hierarchical BiPW$_{12}$O$_{40}$/BiOI p–n heterojunction with enhanced visible light activity for degradation of endocrine disrupting Bisphenol A

Photocatalysis



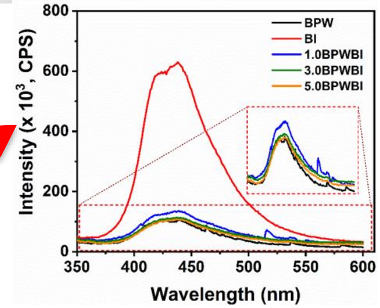
Change of colour



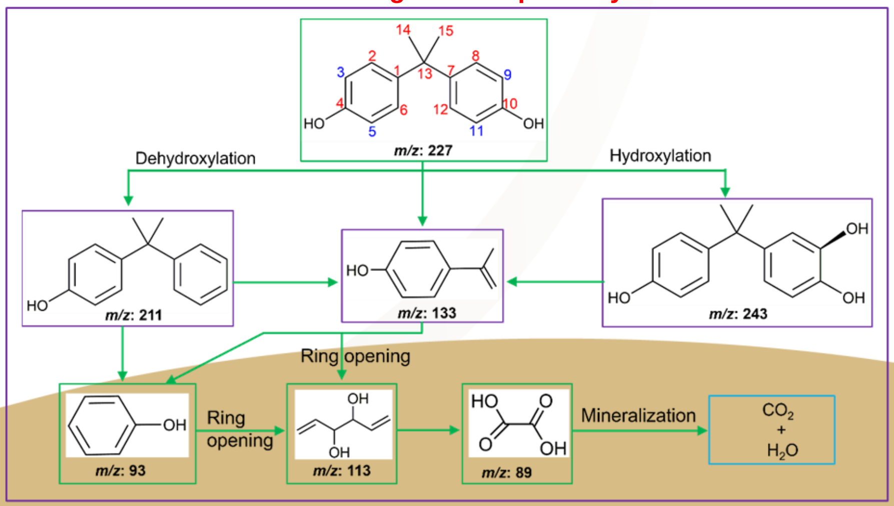


UV-vis spectra of both BPA and AB 25

Photoluminescence

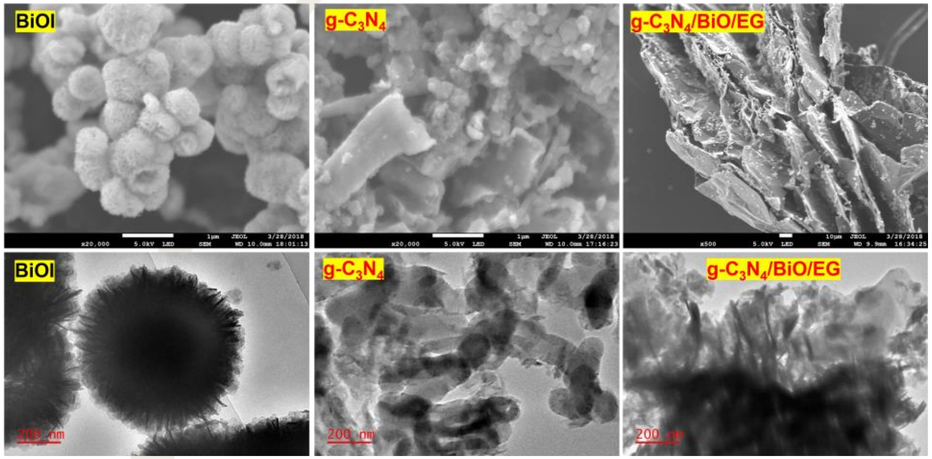


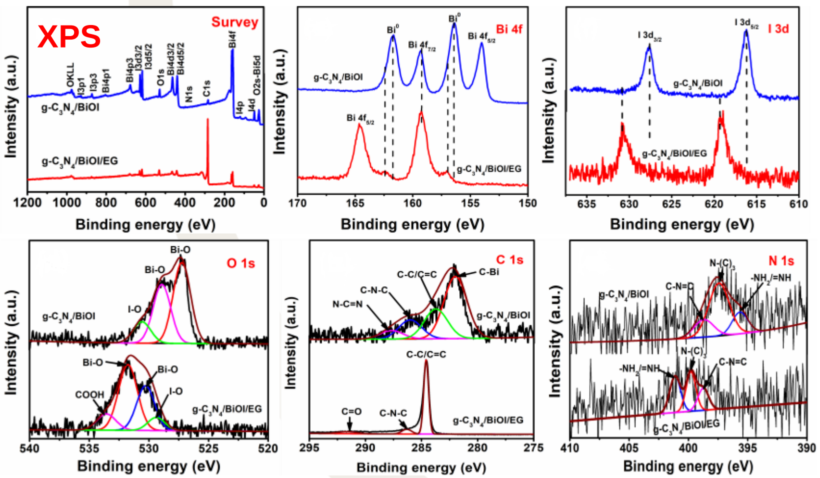
Degradation pathway

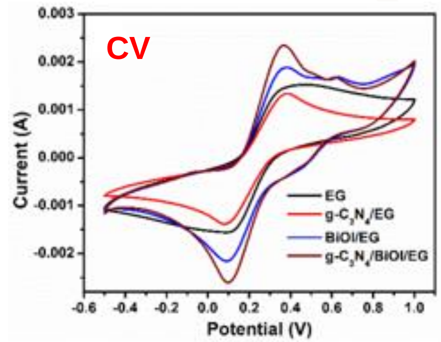


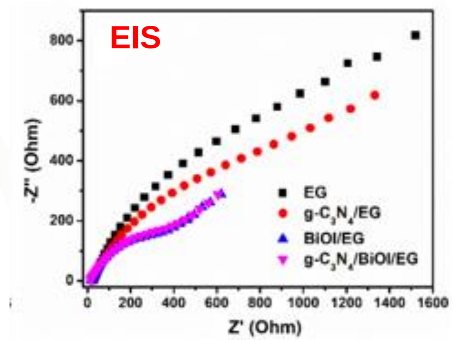
p-n heterojunction in PEC

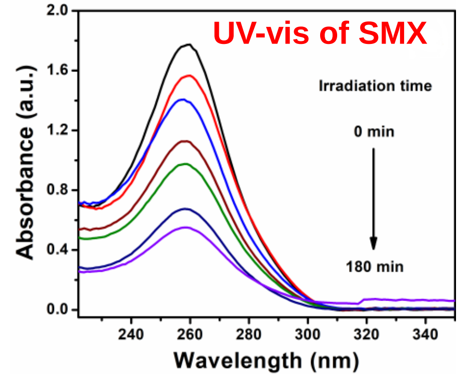
Photoelectrodegradation of sulfamethoxazole

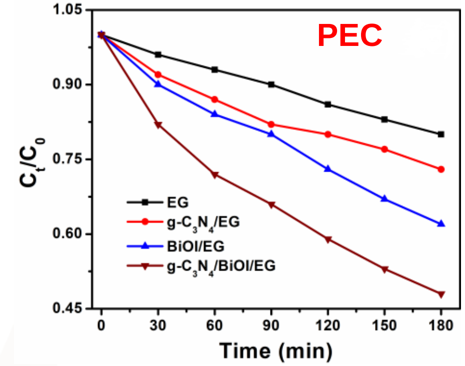


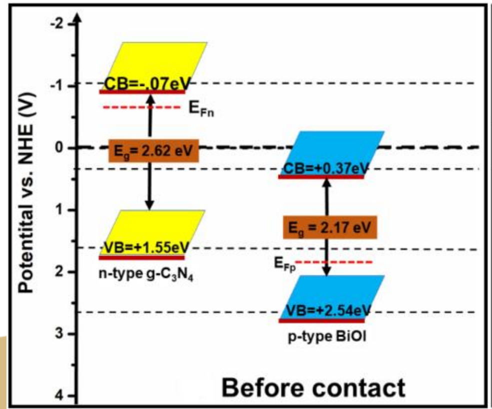


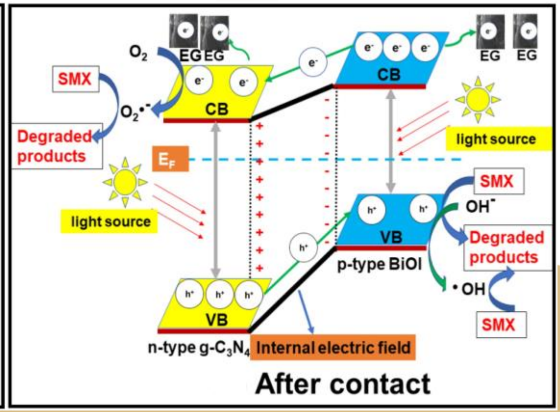












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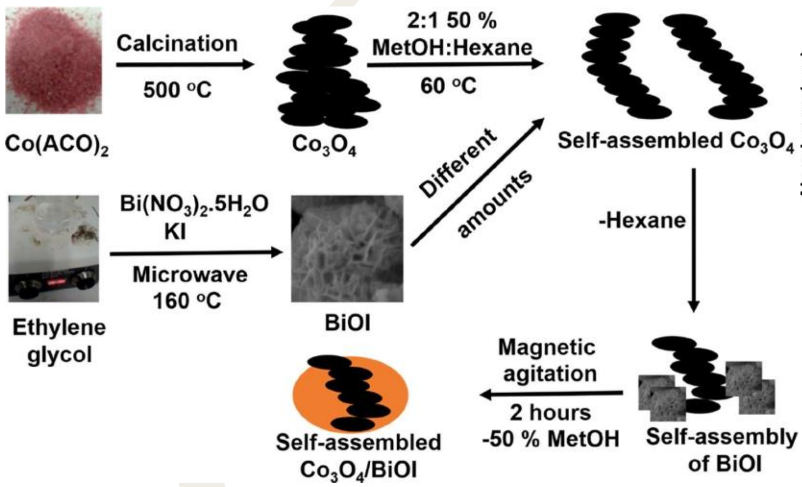
Applied Surface Science
Volume 483, 31 July 2019, Pages 506-520

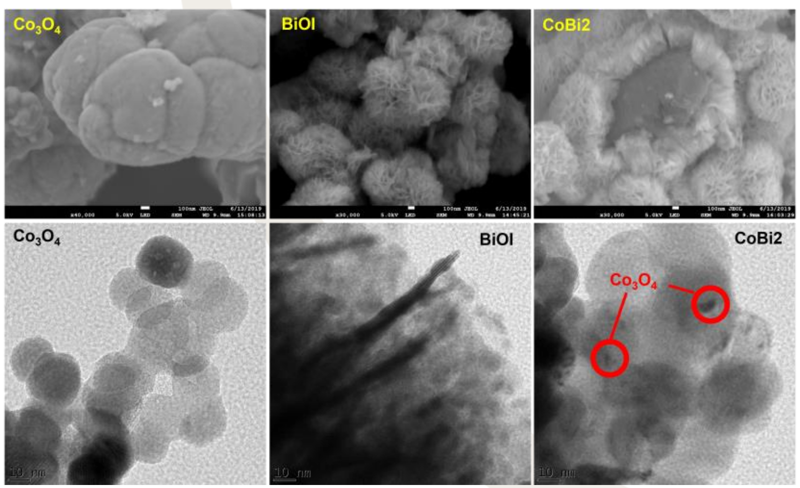
Full length article

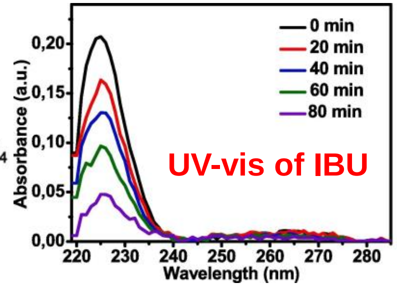
Photoelectrocatalytic degradation of sulfamethoxazole on g-C3N4/BiOI/EG p-n heterojunction photoanode under visible light irradiation

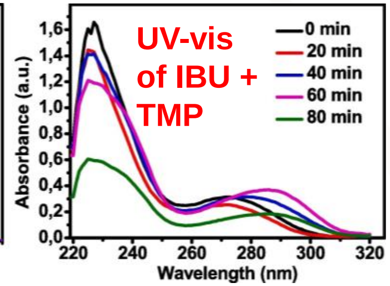
Direct Z-scheme photocatalysis

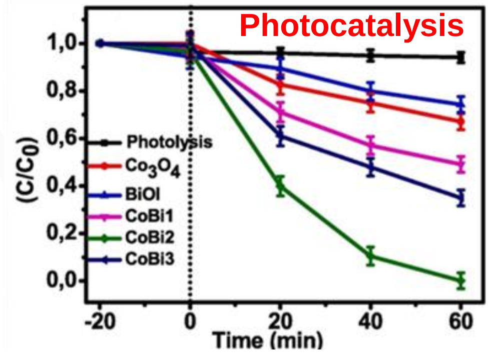
Degradation of ibuprofen in the presence of trimethoprim

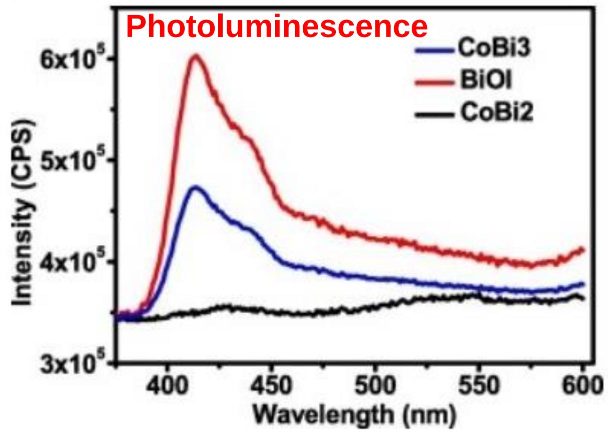


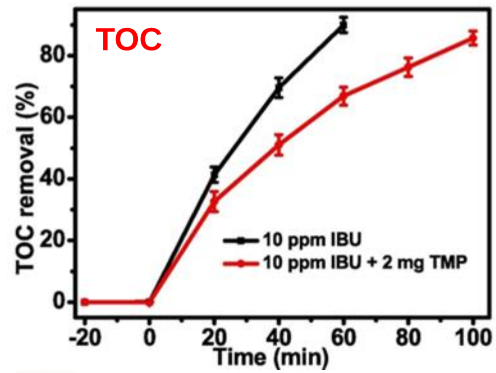


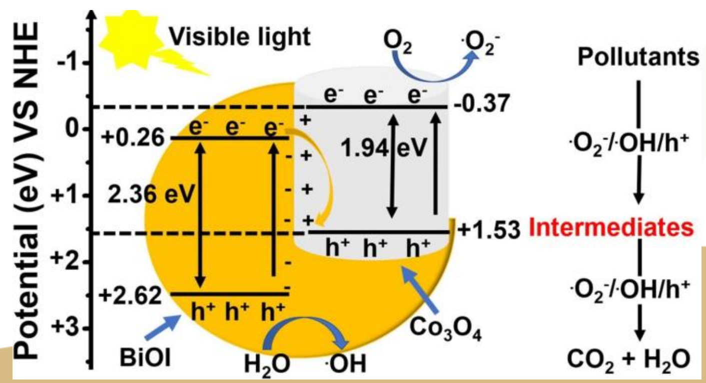


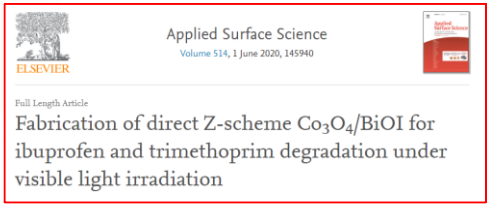






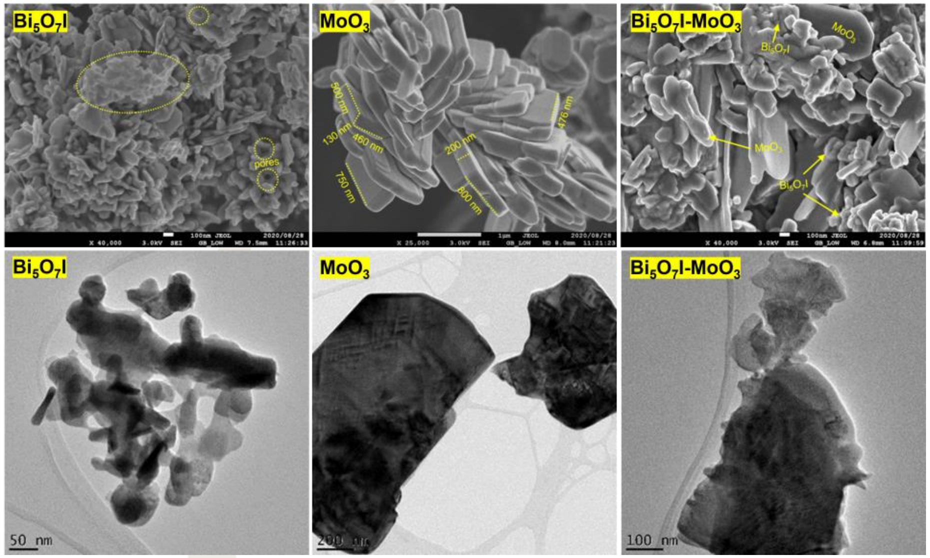


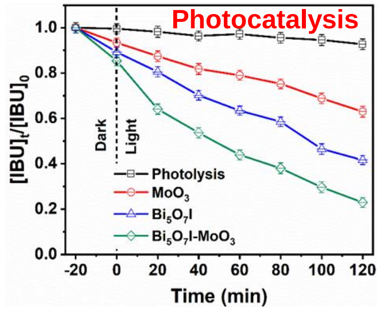


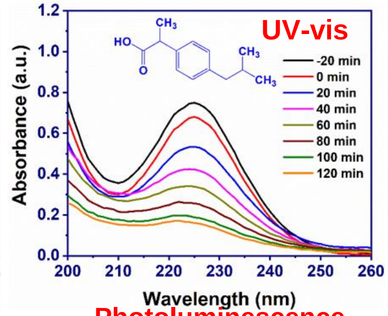

Applied Surface Science
Volume 514, 1 June 2020, 145940
Full Length Article
Fabrication of direct Z-scheme Co_3O_4/BiOI for ibuprofen and trimethoprim degradation under visible light irradiation

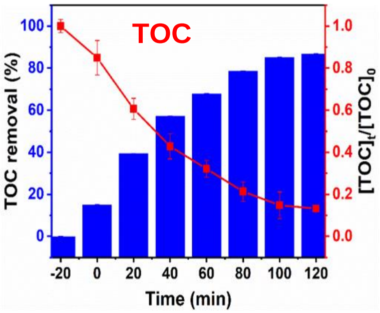
Direct Z-scheme photocatalysis

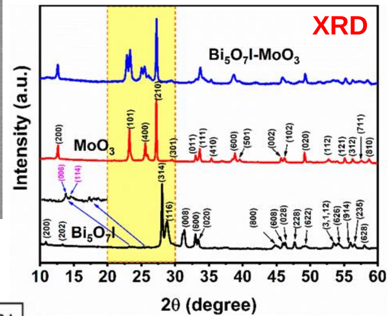
Degradation of ibuprofen

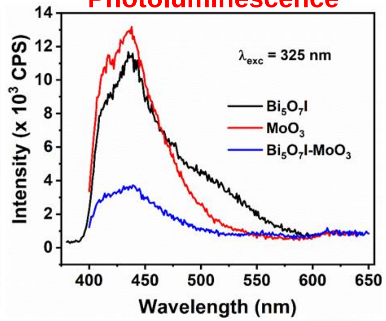


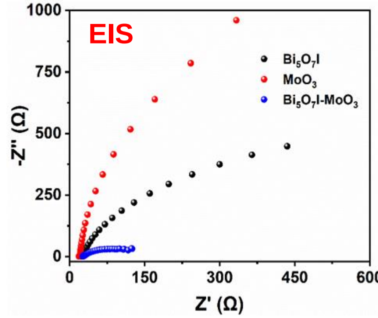




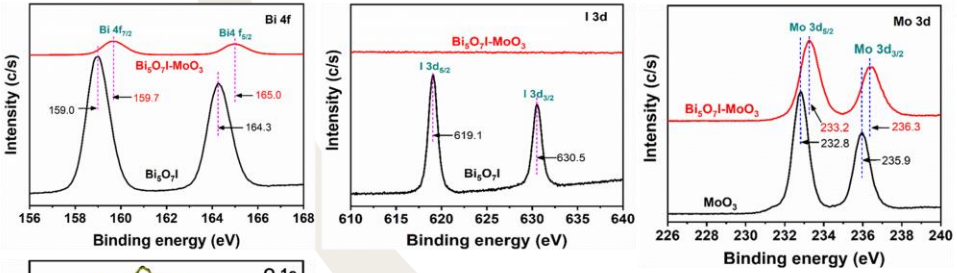


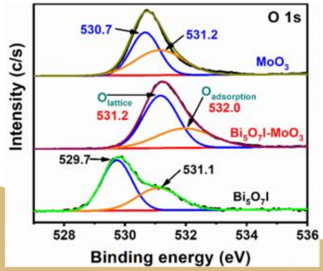






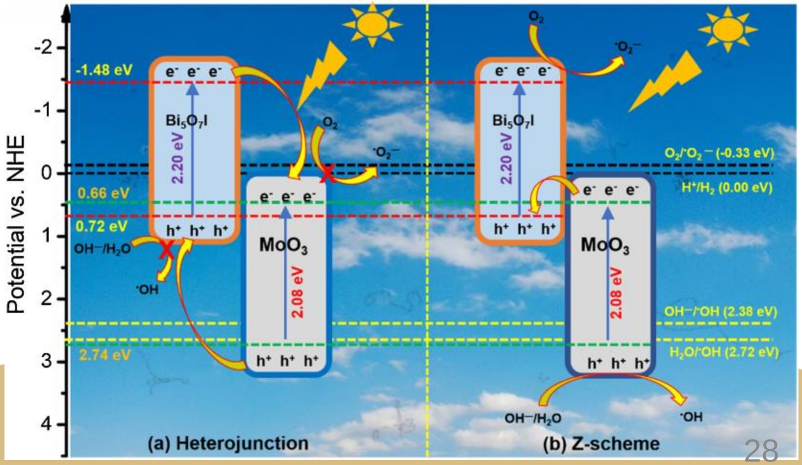
XPS





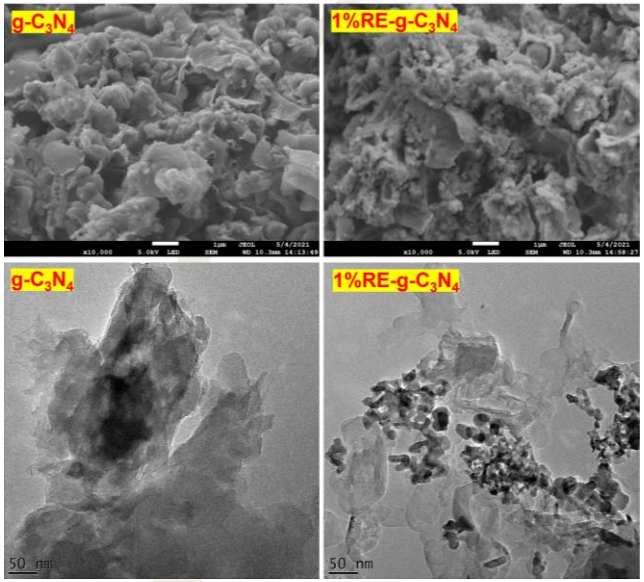
ELSEVIER
Colloids and Surfaces A: Physicochemical and Engineering Aspects
Volume 612, 5 March 2021, 126004

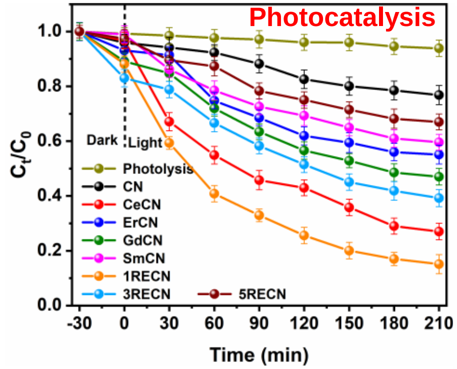
Synthesis of Bi$_5$O$_7$I-MoO$_3$ photocatalyst via simultaneous calcination of BiOI and MoS$_2$ for visible light degradation of ibuprofen

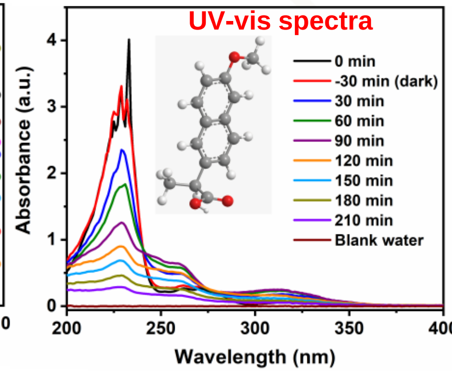


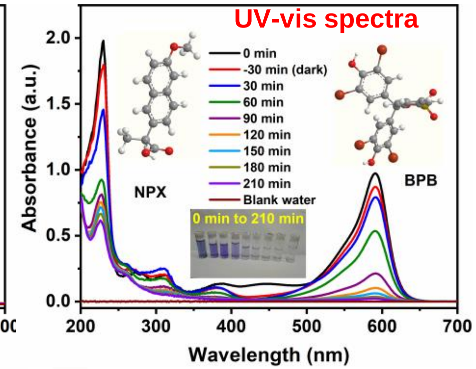
Direct Z-scheme photocatalysis

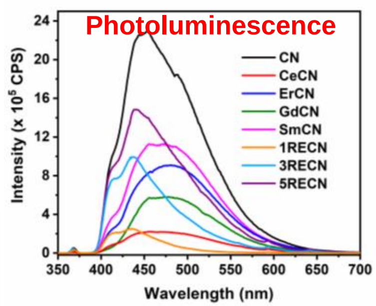
Degradation of naproxen

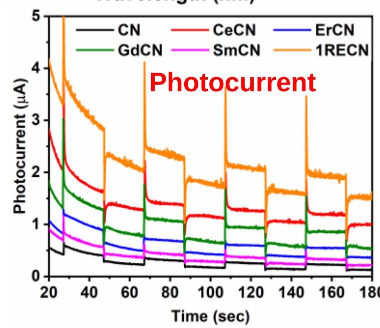


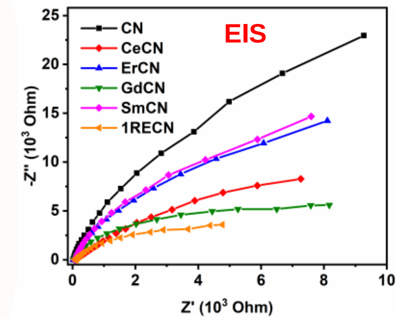


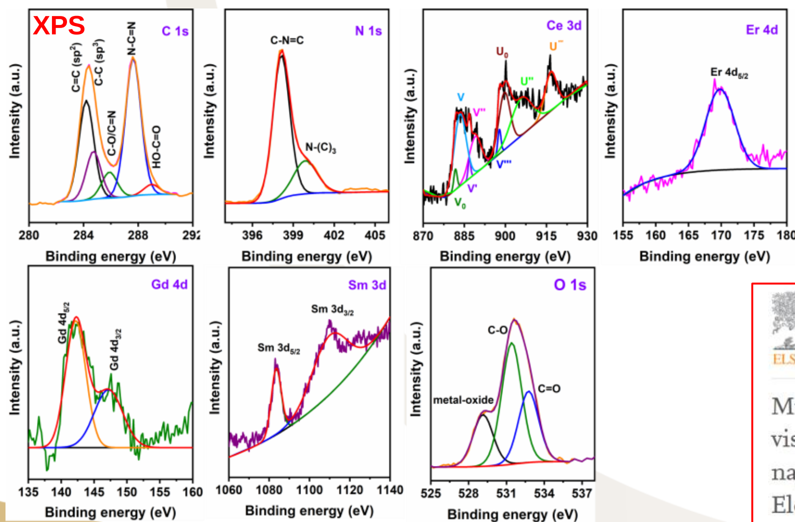








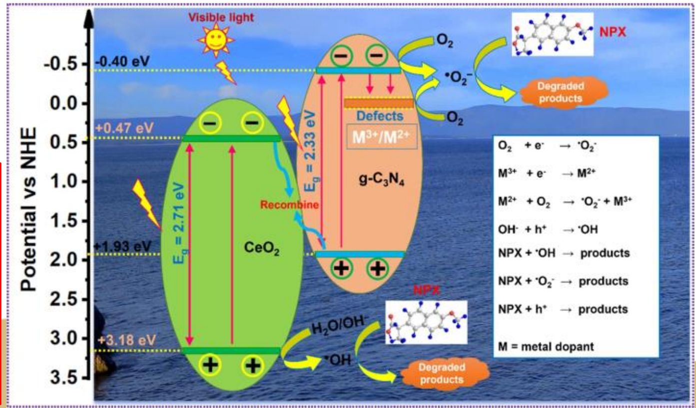




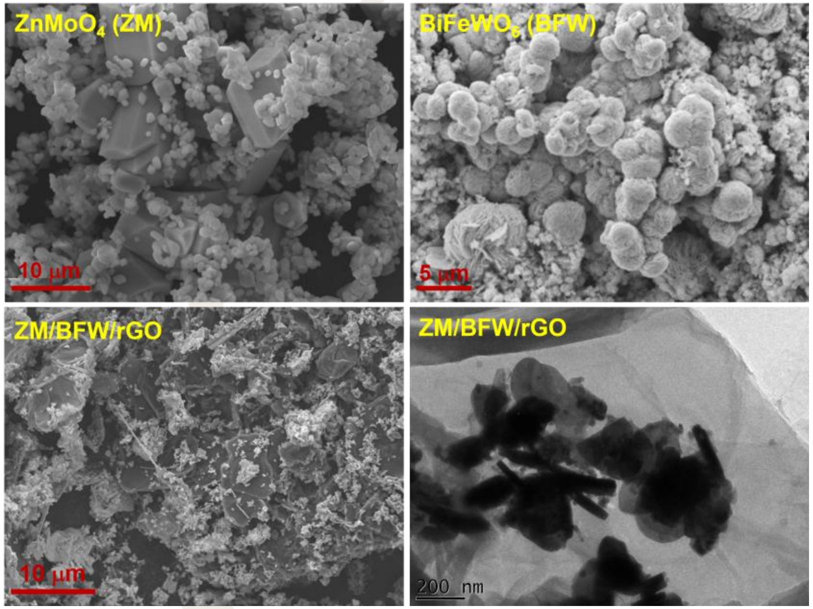
Separation and Purification Technology

Volume 282, Part B, 1 February 2022, 120089

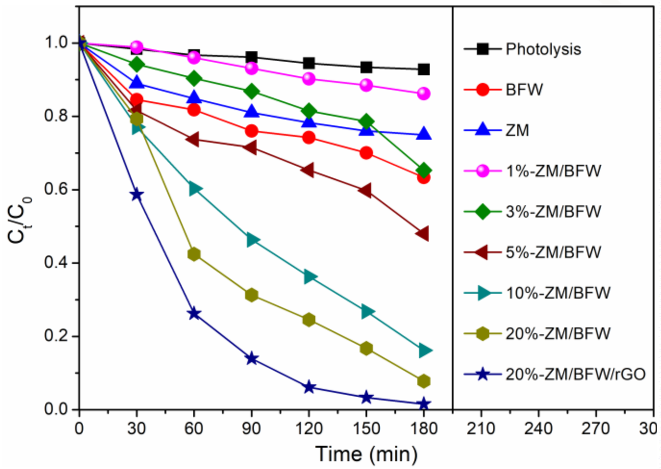
Multi-elemental doped g-C₃N₄ with enhanced visible light photocatalytic Activity: Insight into naproxen Degradation, Kinetics, effect of Electrolytes, and mechanism



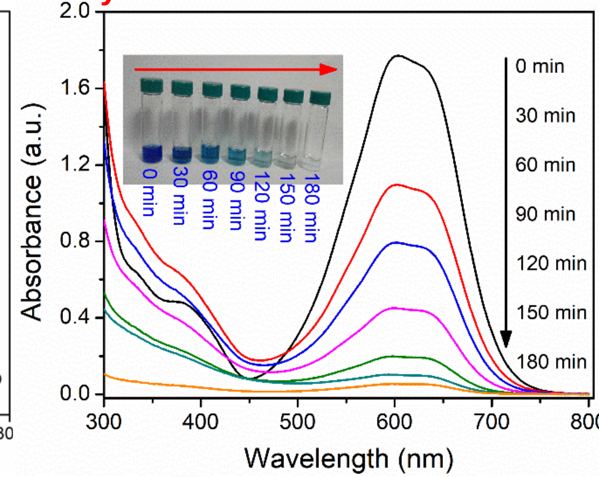
All solid Z-scheme mechanism for dye removal

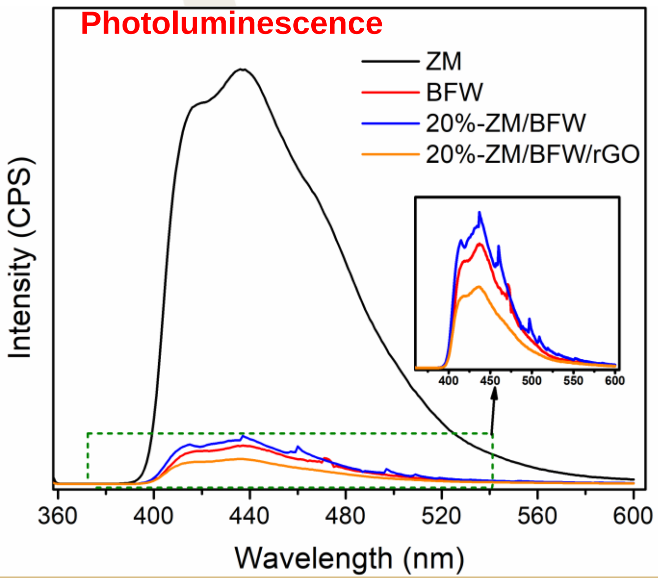


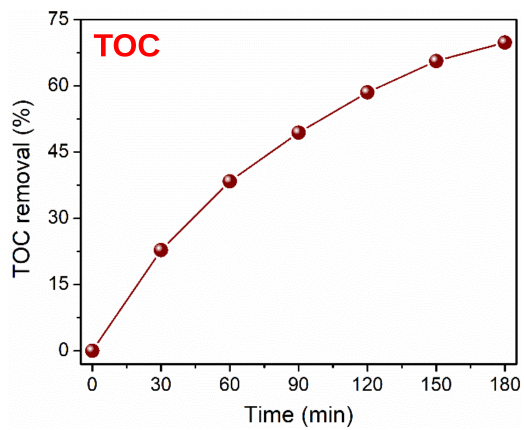
Degradation of acid blue 25

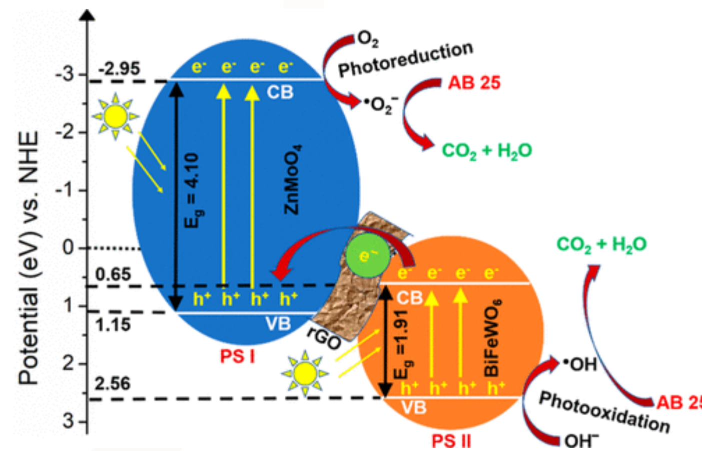


Photocatalysis









THE JOURNAL OF PHYSICAL CHEMISTRY C
Article
Cite This: J. Phys. Chem. C 2019, 123, 20605−20616
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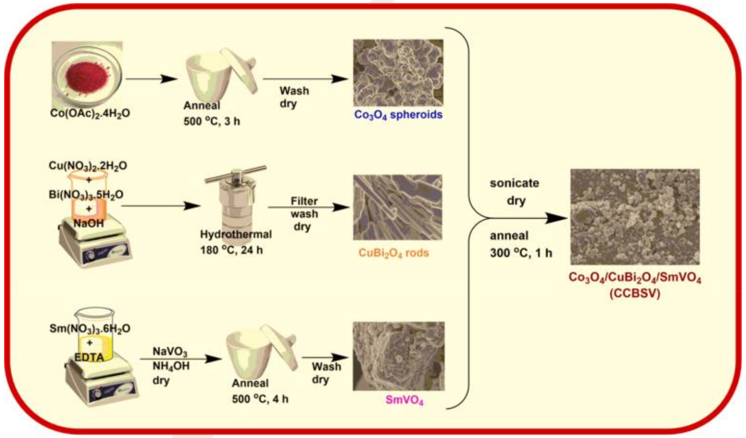
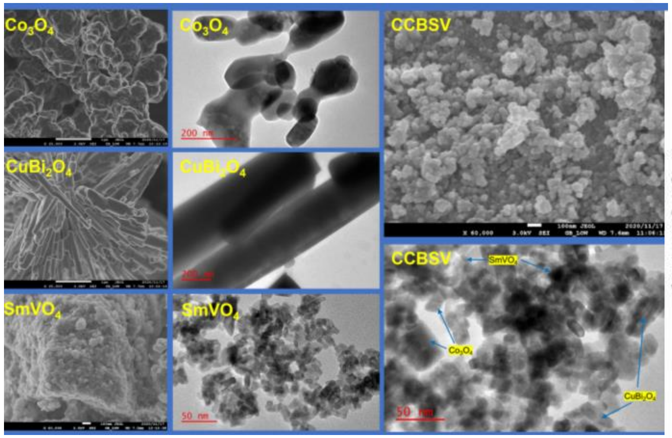
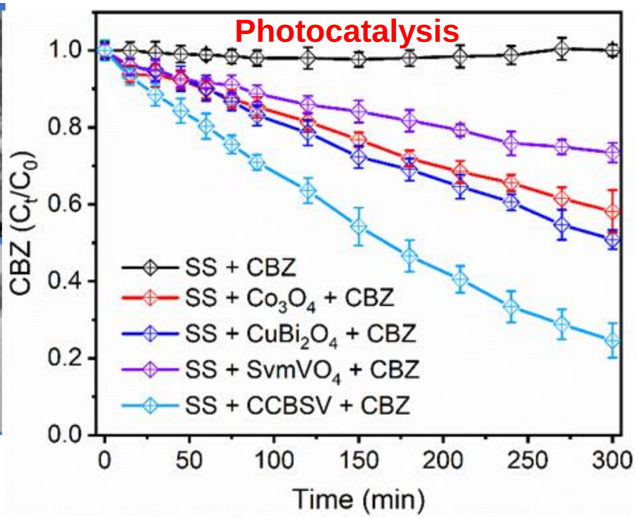
Visible Light Driven $ZnMoO_4/BiFeWO_6$/rGO Z-Scheme Photocatalyst for the Degradation of Anthraquinonic Dye

Dual Z-scheme mechanism

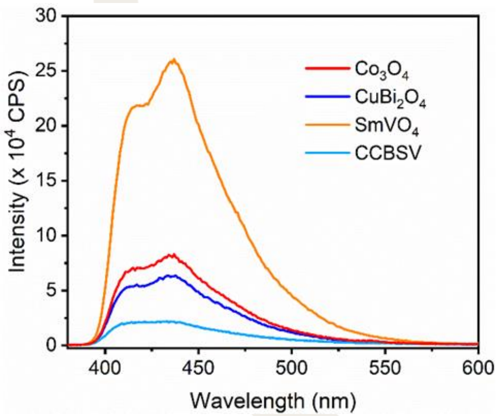
Degradation of carbamazepine







Photoluminescence



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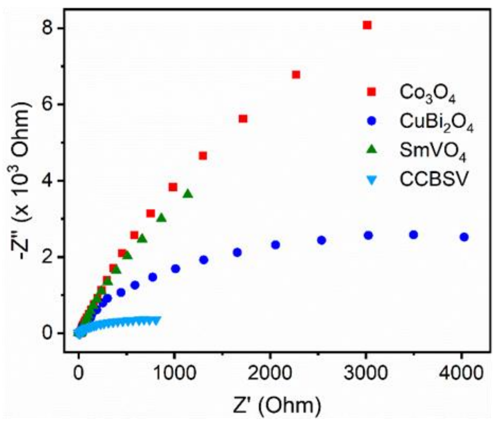
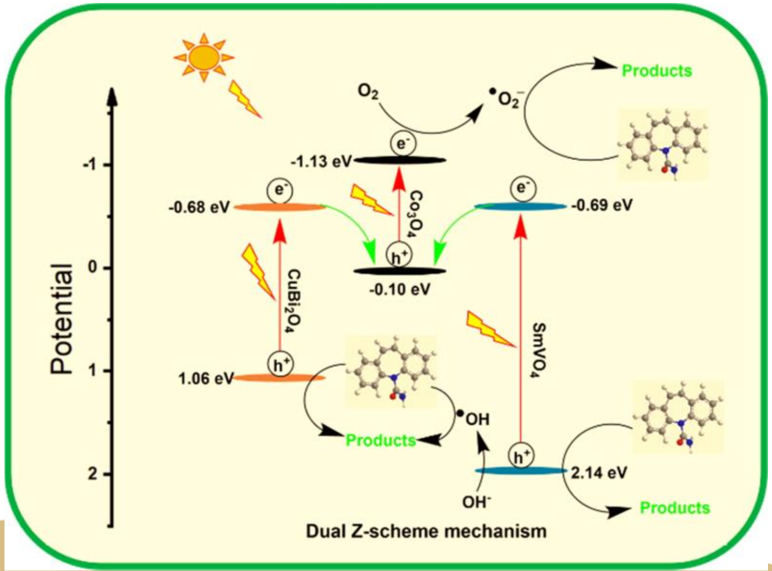
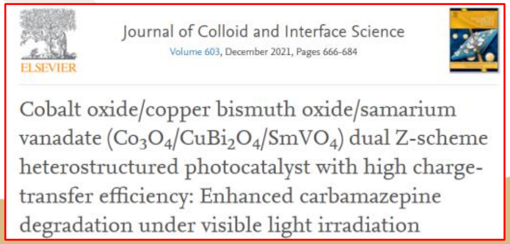
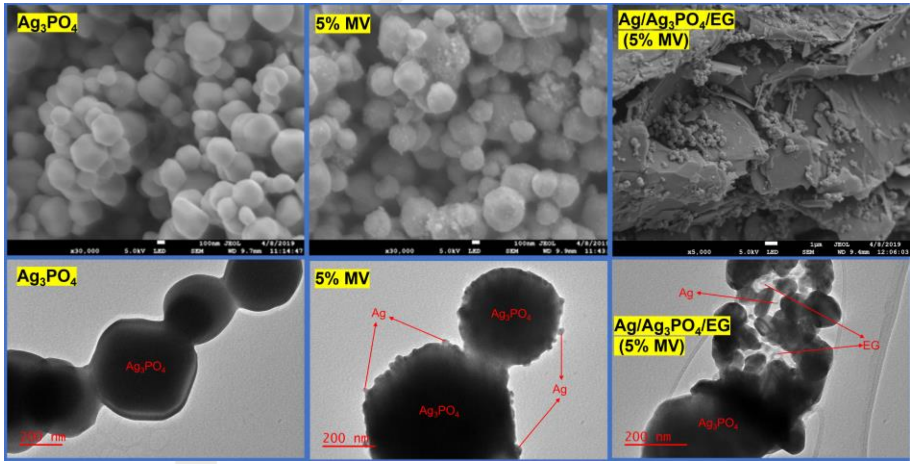


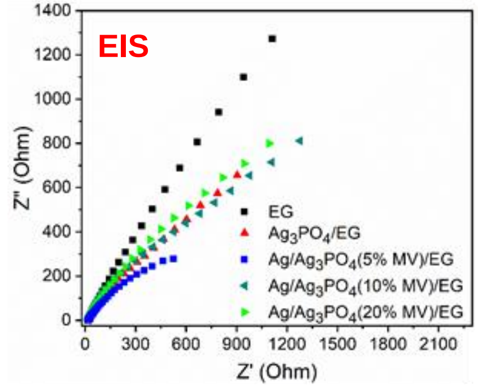


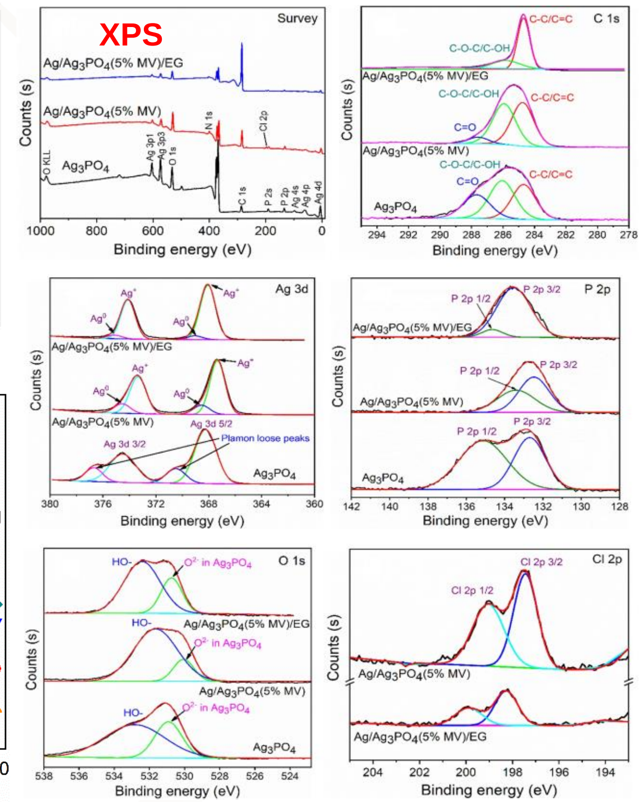

Journal of Colloid and Interface Science
Volume 603, December 2021, Pages 666-684

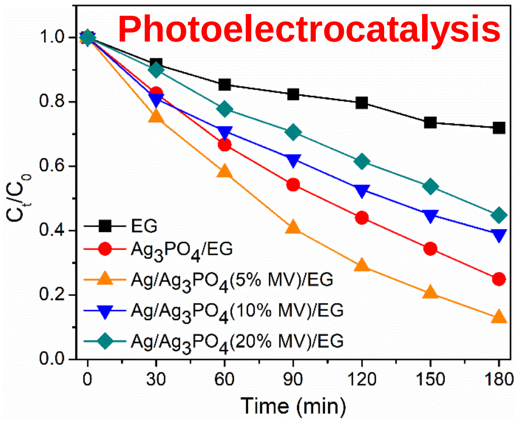
Cobalt oxide/copper bismuth oxide/samarium vanadate ($Co_3O_4/CuBi_2O_4/SmVO_4$) dual Z-scheme heterostructured photocatalyst with high charge-transfer efficiency: Enhanced carbamazepine degradation under visible light irradiation

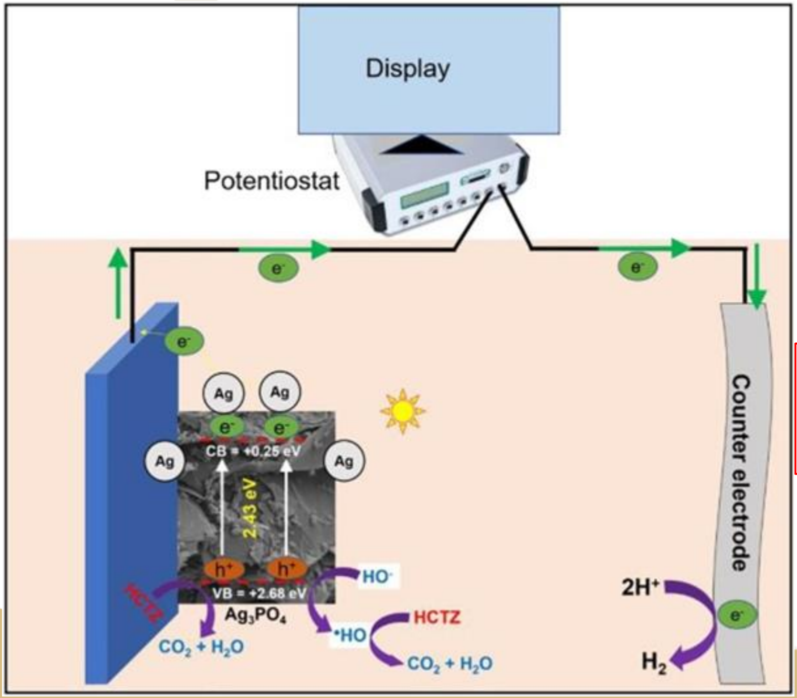
Z-scheme anode - degradation of hydrochlorothiazide

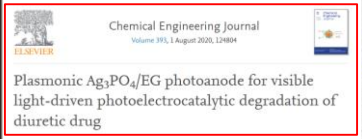




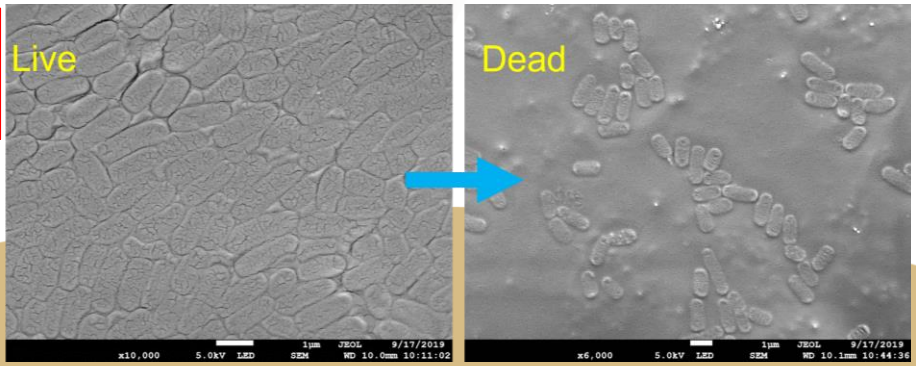






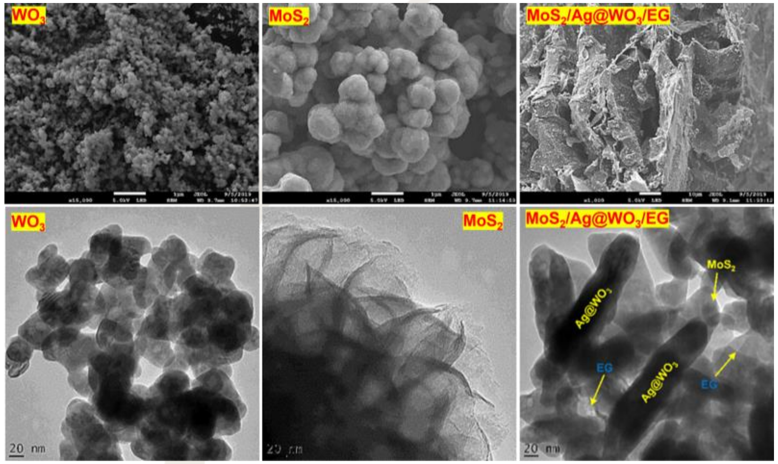

Chemical Engineering Journal

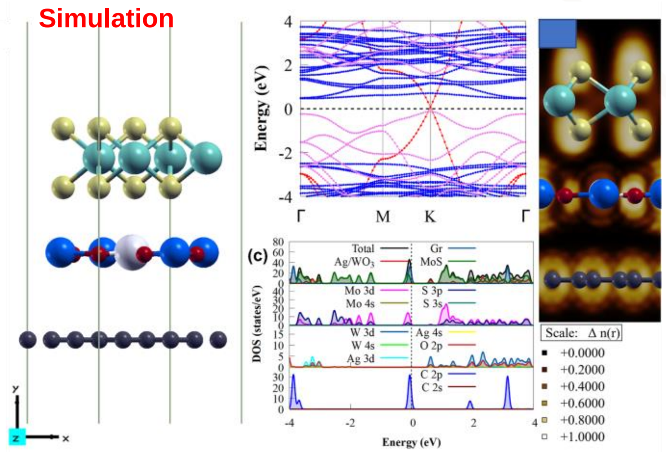
Plasmonic Ag_3PO_4/EG photoanode for visible light-driven photoelectrocatalytic degradation of diuretic drug

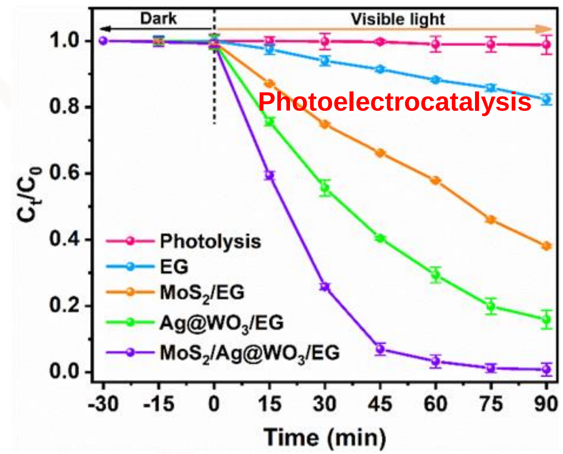


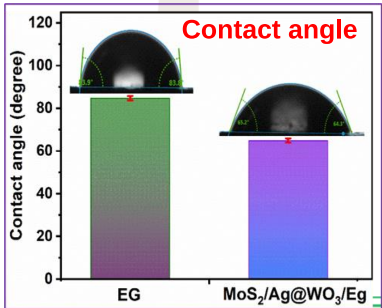
DFT in PEC: Z-scheme mechanism

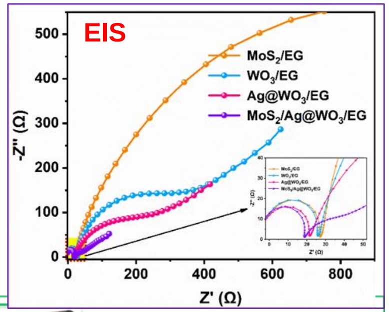
Photoelectrodegradation of bisphenol A

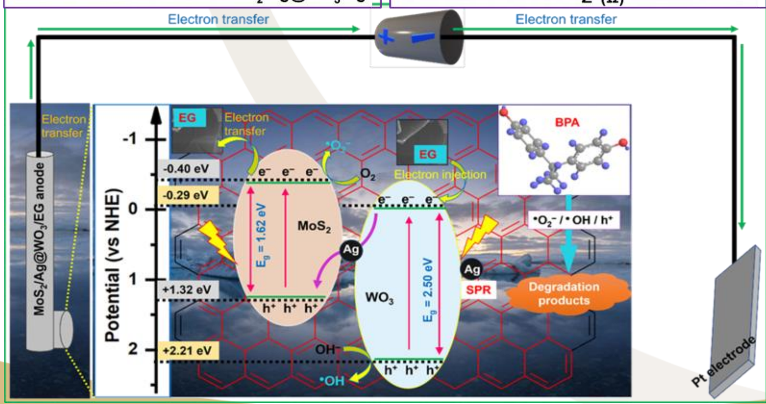


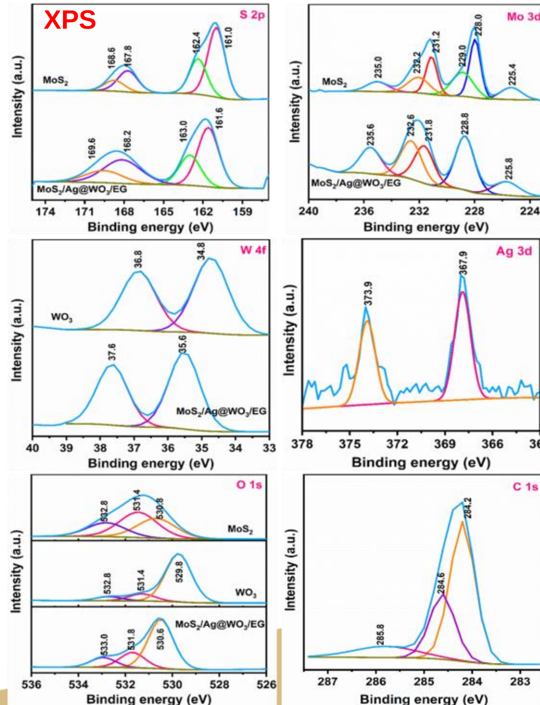






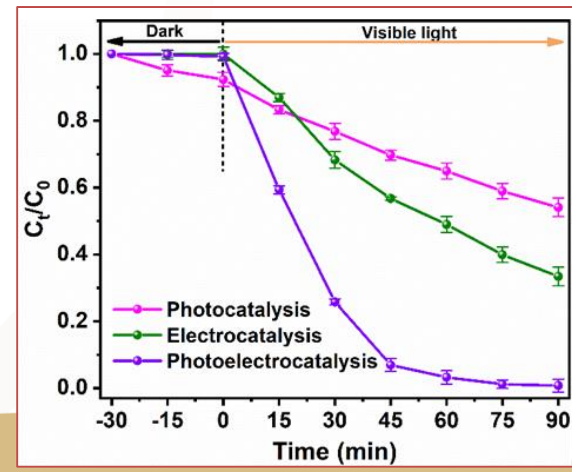






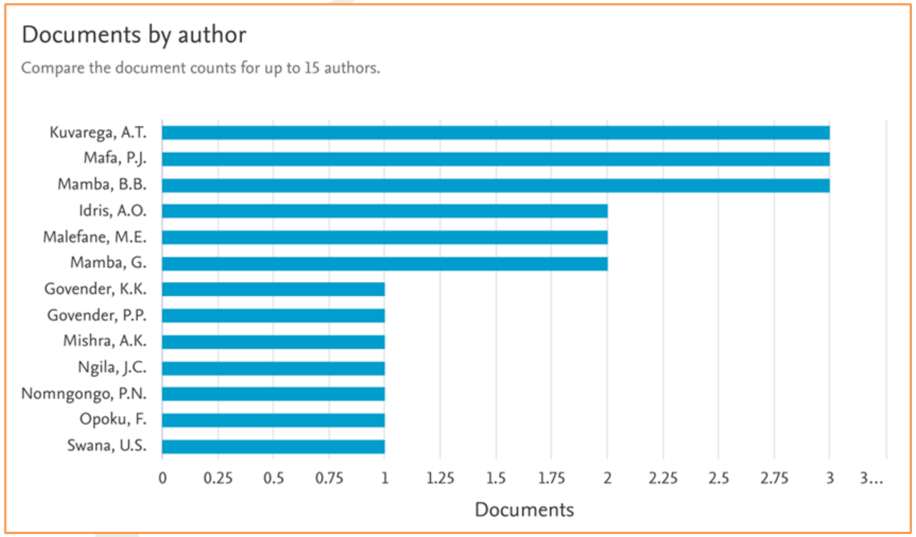
Photoelectrocatalysis: Synergism of process

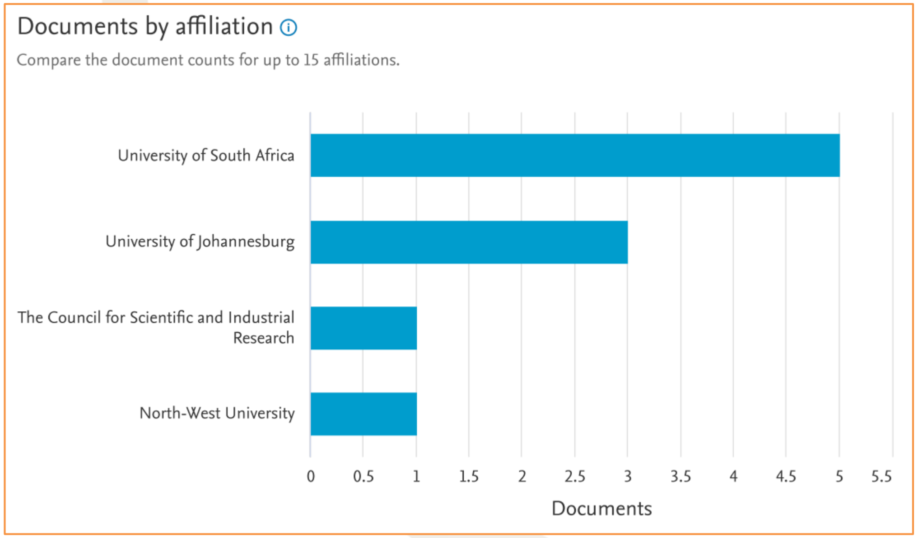
$$S = \left(k_{PEC} - (k_{PC} + k_{EC})\right)/k_{PEC}$$

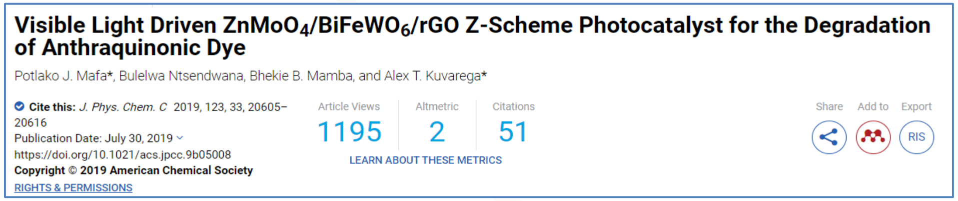


Article under review in Chemical Engineering Journal

Z-scheme research







Visible Light Driven $ZnMoO_4/BiFeWO_6$/rGO Z-Scheme Photocatalyst for the Degradation of Anthraquinonic Dye

Potlako J. Mafa*, Bulelwa Ntsendwana, Bhekie B. Mamba, and Alex T. Kuvarega*

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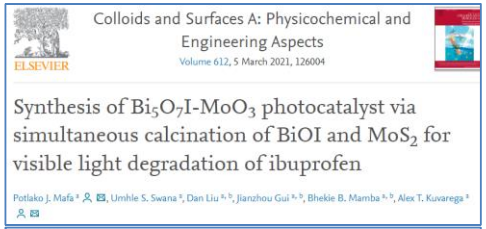
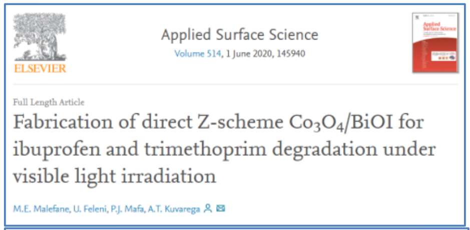


Colloids and Surfaces A: Physicochemical and Engineering Aspects
Volume 612, 5 March 2021, 126004

Synthesis of Bi_5O_7I-MoO_3 photocatalyst via simultaneous calcination of BiOI and MoS_2 for visible light degradation of ibuprofen

Potlako J. Mafa, Umhle S. Swana, Dan Liu, Jianzhou Gui, Bhekie B. Mamba, Alex T. Kuvarega

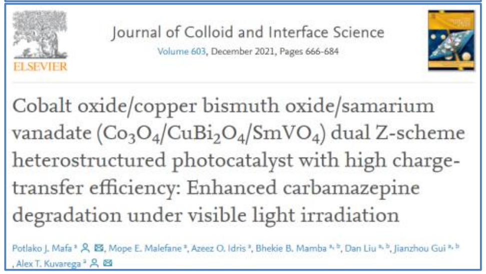


Applied Surface Science
Volume 514, 1 June 2020, 145940

Full Length Article

Fabrication of direct Z-scheme Co_3O_4/BiOI for ibuprofen and trimethoprim degradation under visible light irradiation

M.E. Malefane, U. Feleni, P.J. Mafa, A.T. Kuvarega



Journal of Colloid and Interface Science
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Separation and Purification Technology
Volume 282, Part B, 1 February 2022, 120089

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Potlako J. Mafa, Mope E. Malefane, Azeez O. Idris, Dan Liu, Jianzhou Gui, Bhekie B. Mamba, Alex T. Kuvarega

Chemical Engineering Journal
Volume 452, Part 2, 15 January 2023, 138894

Review

Modulation of Z-scheme photocatalysts for pharmaceuticals remediation and pathogen inactivation: Design devotion, concept examination, and developments

Mope Edwin Malefane, Potlako John Mafa, Thabo Thokozani Innocent Nkambule, Muthumuni Elizabeth Managa, Alex Tawanda Kuvarega

Magnetic nanoparticles

$CoFe_2O_4$

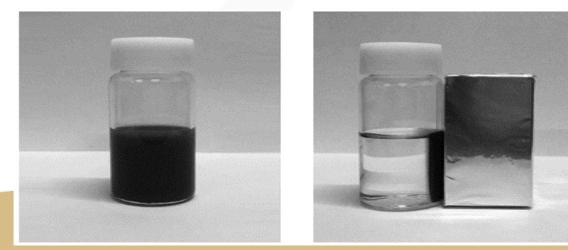
$CoFe_2O_4$

- Chemical stability
- Narrow band gap
- Visible light driven
- Moderate saturation magnetization
- High electron hole recombination

Doping and Coupling →

$Zn_xCo_{1-x}Fe_2O_4$/N-CQDs

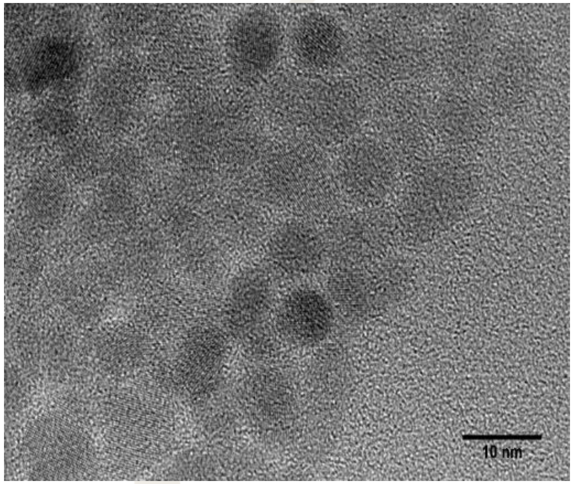
➢ Photocatalytic activity

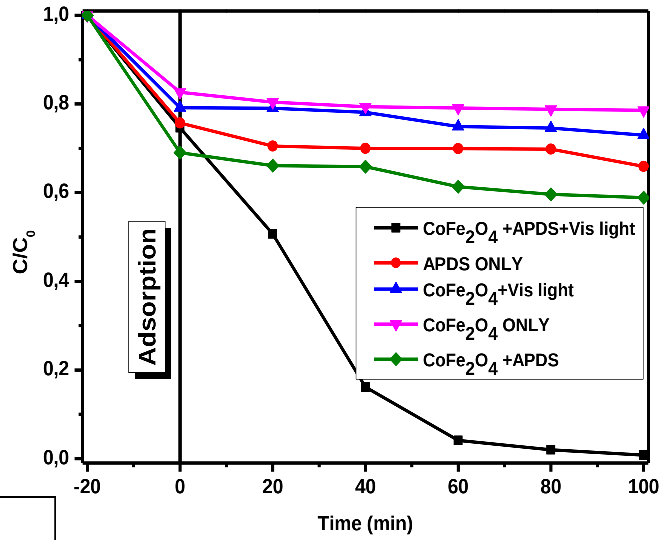


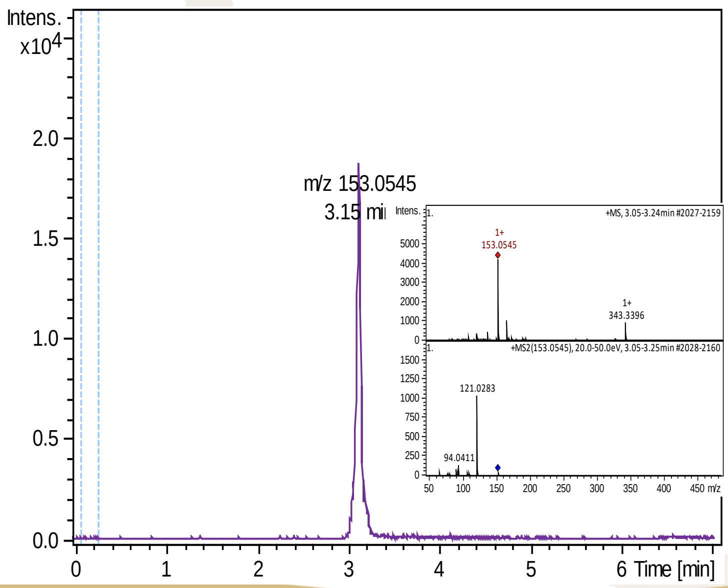
Recoverable

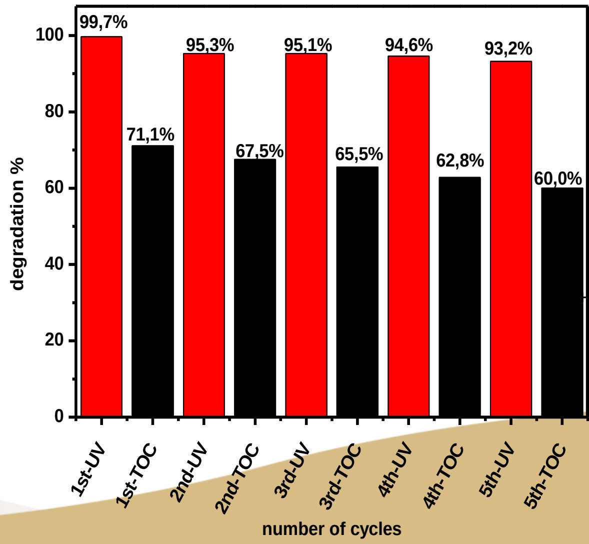
Magnetic nanoparticles

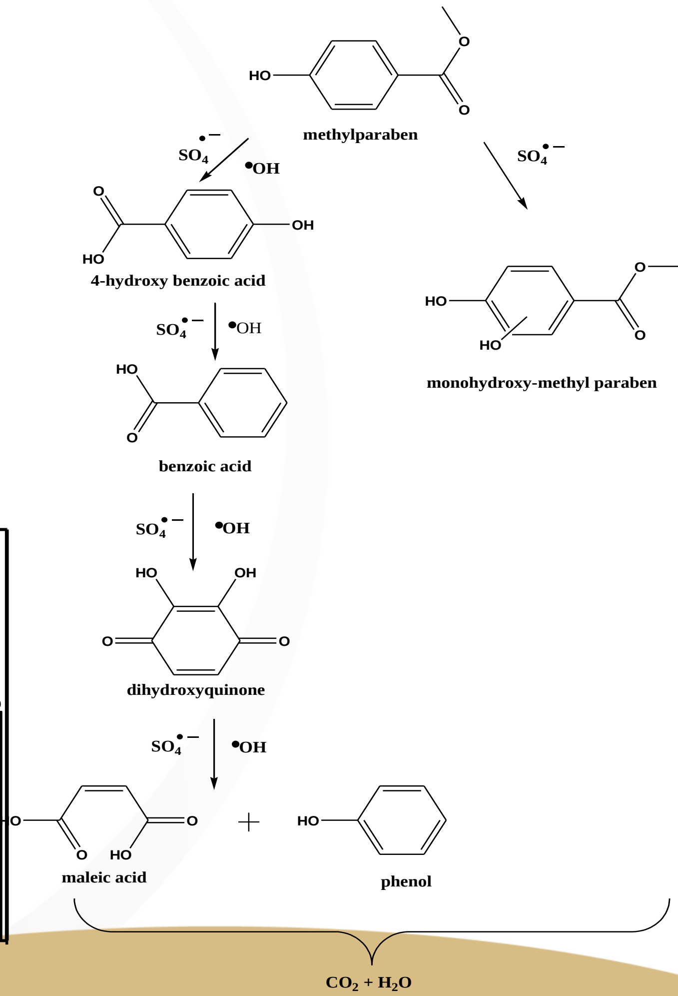
Persulphate-assisted photodegradation methylparaben



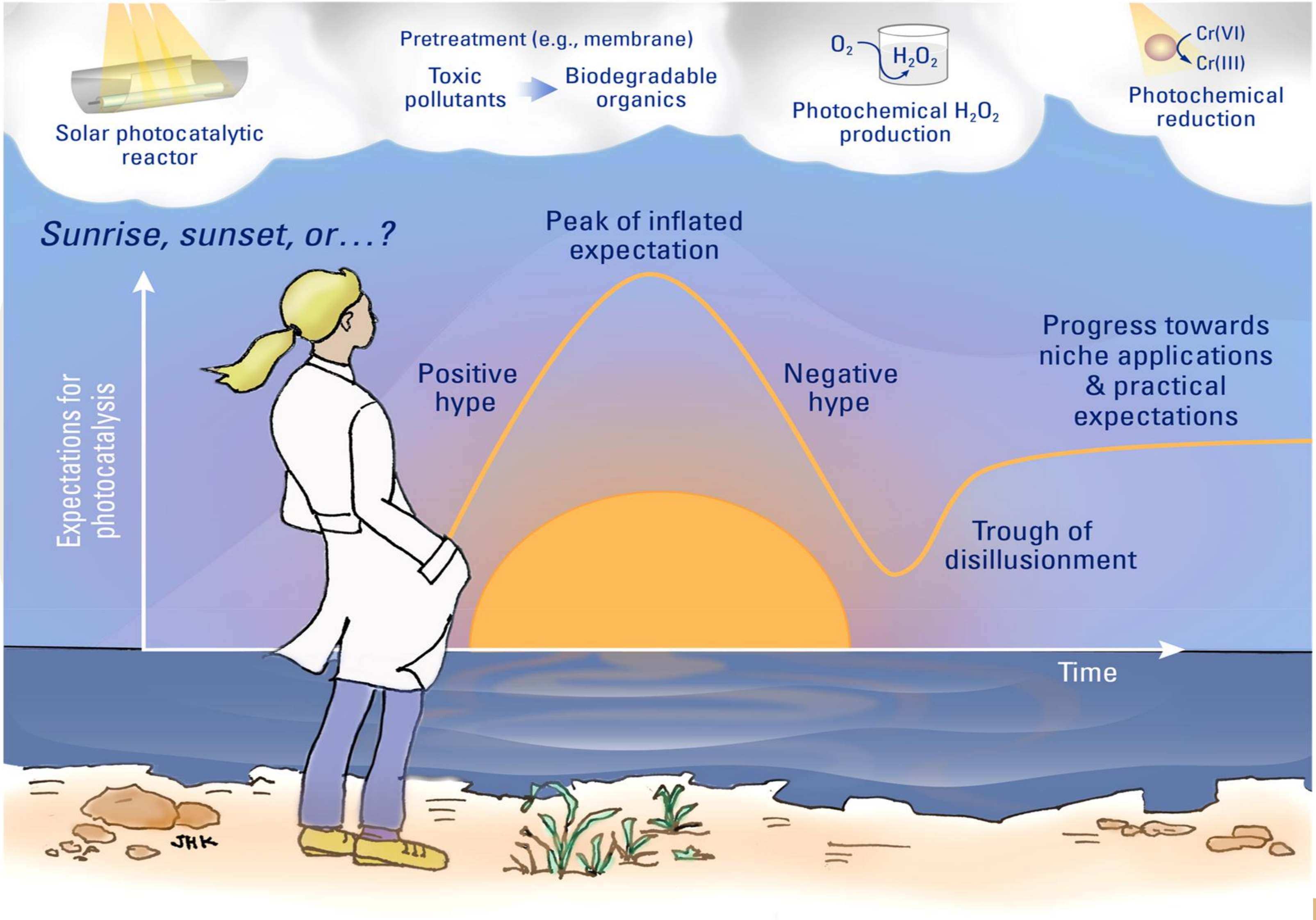








Future Trajectory of AOP Water Treatment



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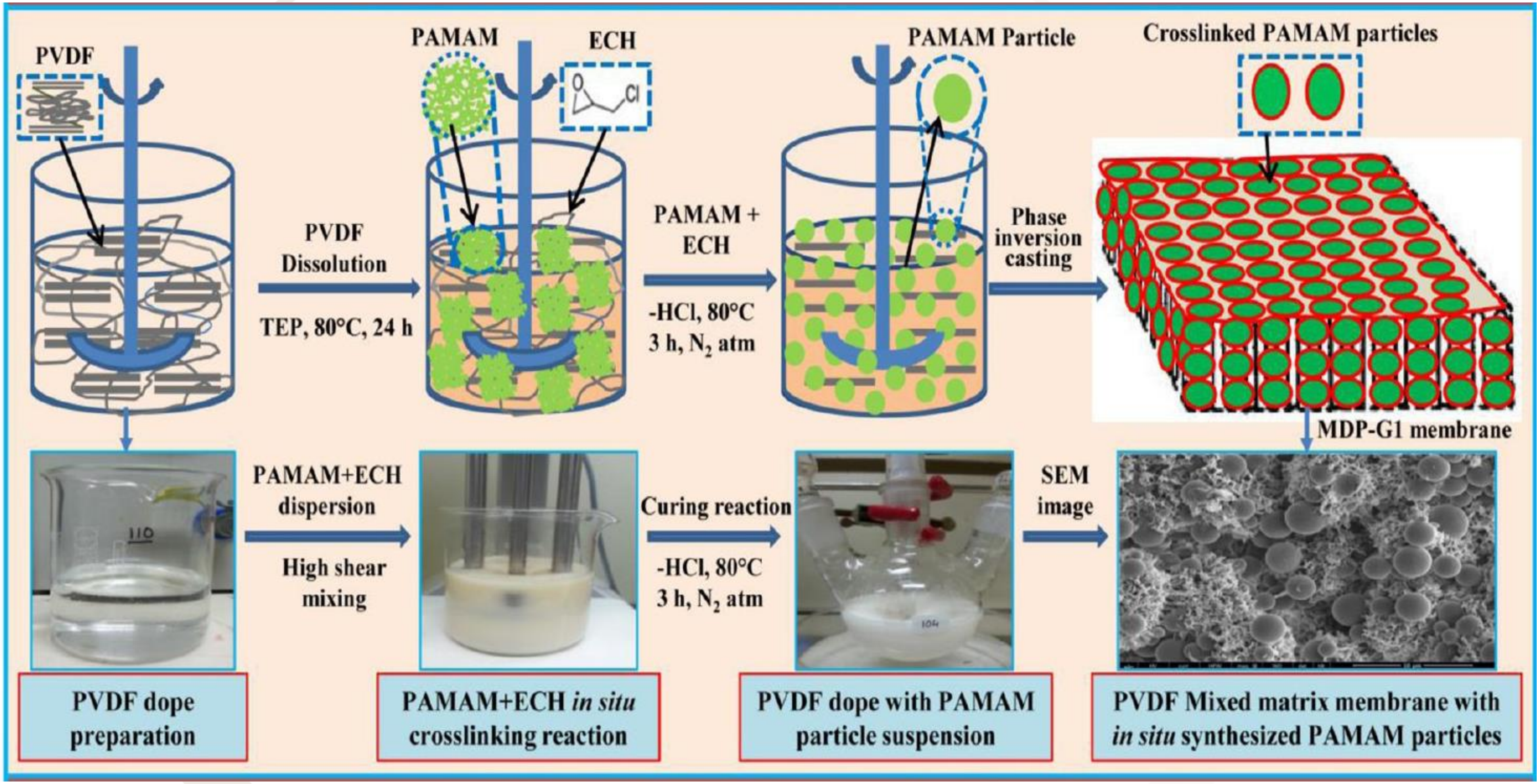
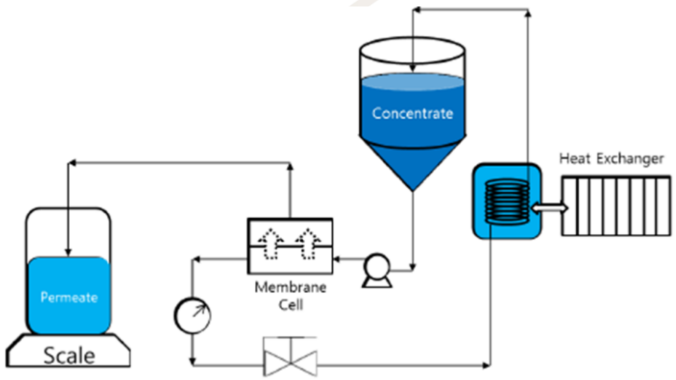
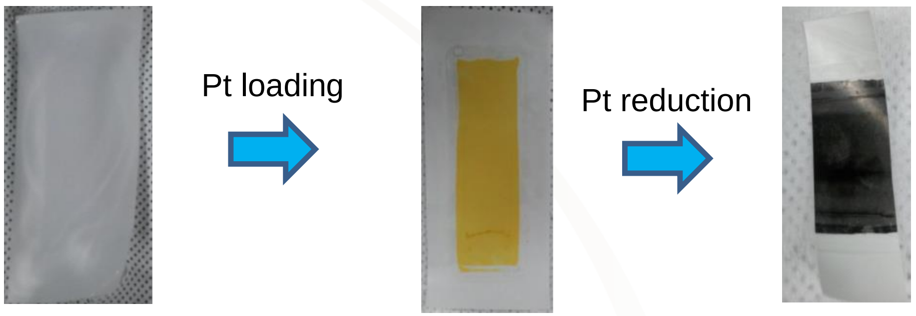
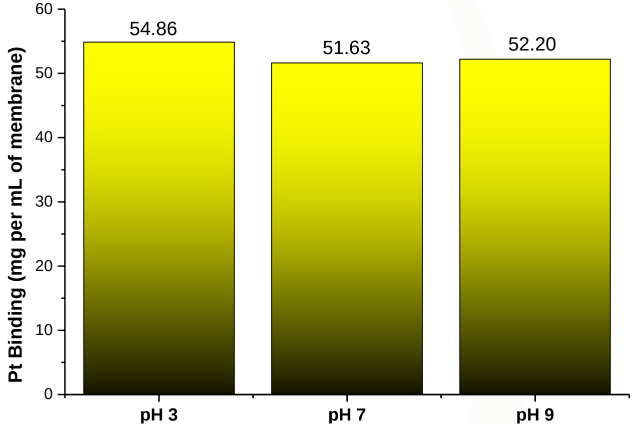
Catalytic membranes

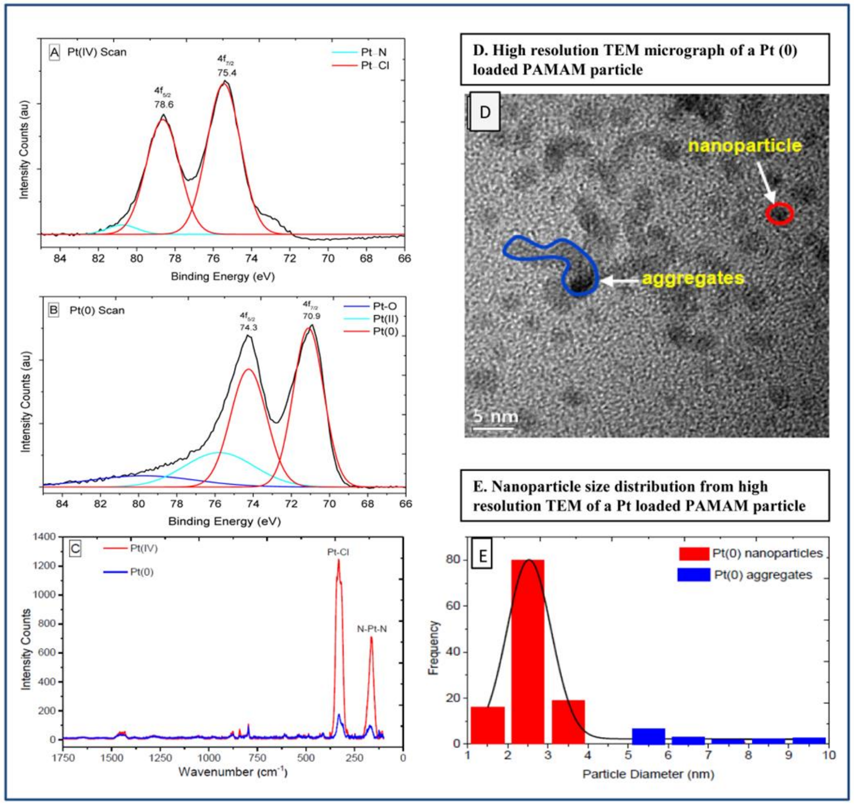


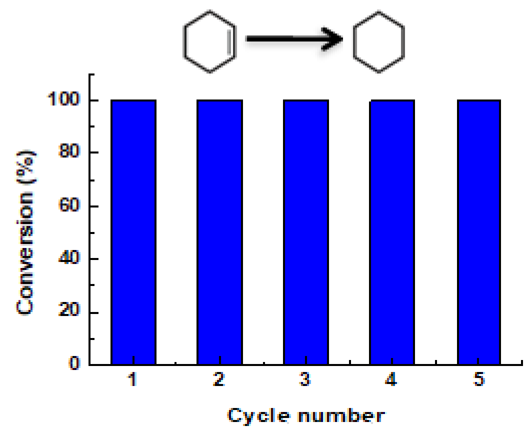
Catalytic hydrogenation of alkenes

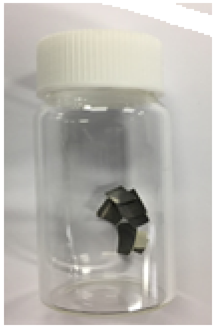






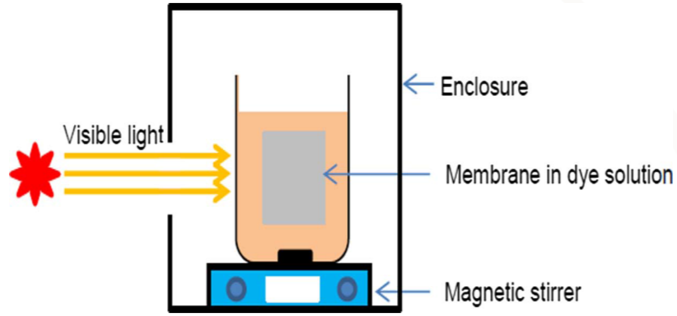


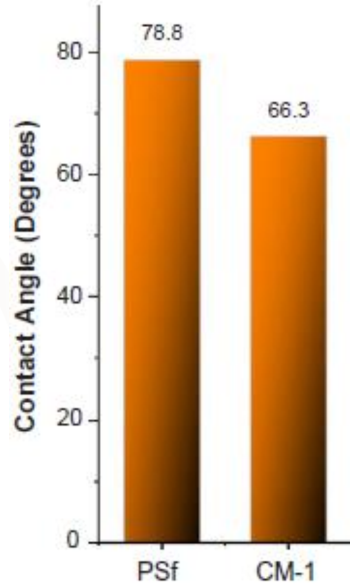


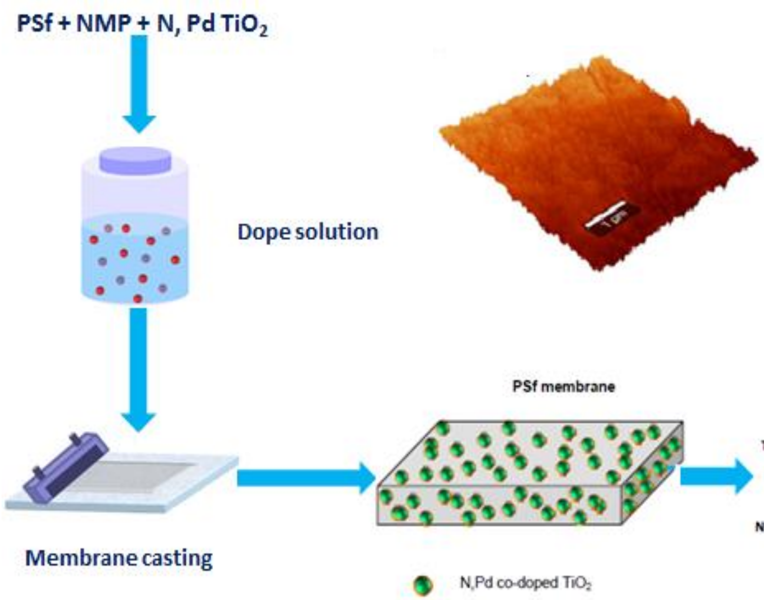


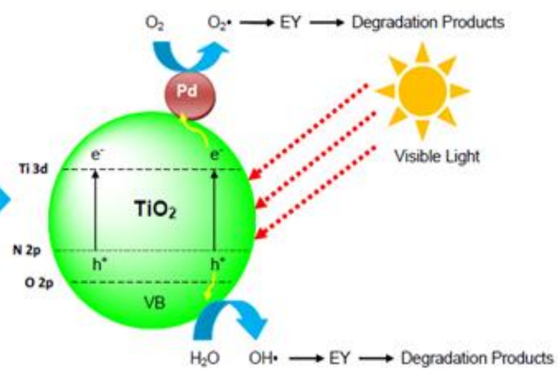
Visible light active photocatalytic membranes

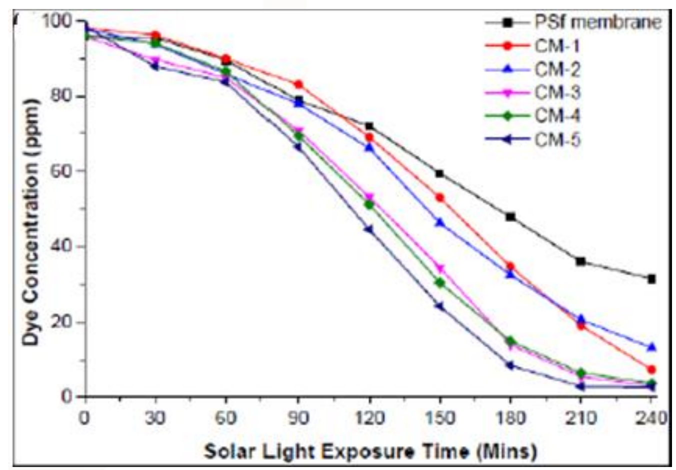
PSf	N,Pd co-doped TiO_2 (Weight % in PSf)	NMP
18 wt%	0.0	82.00 v%
18 wt%	0.5	81.91 v%
18 wt%	1.0	81.82 v%
18 wt%	2.0	81.64 v%
18 wt%	4.0	81.28 v%
18 wt%	7.0	80.74 v%



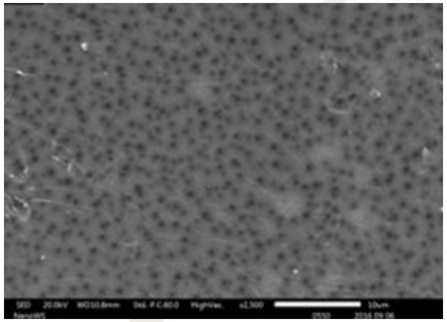




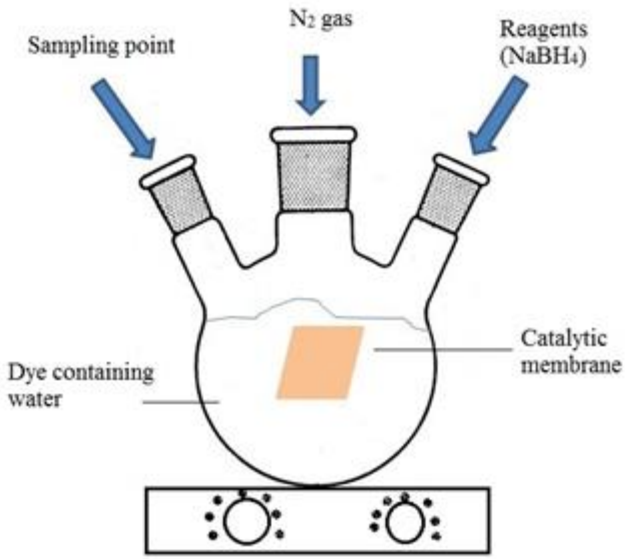


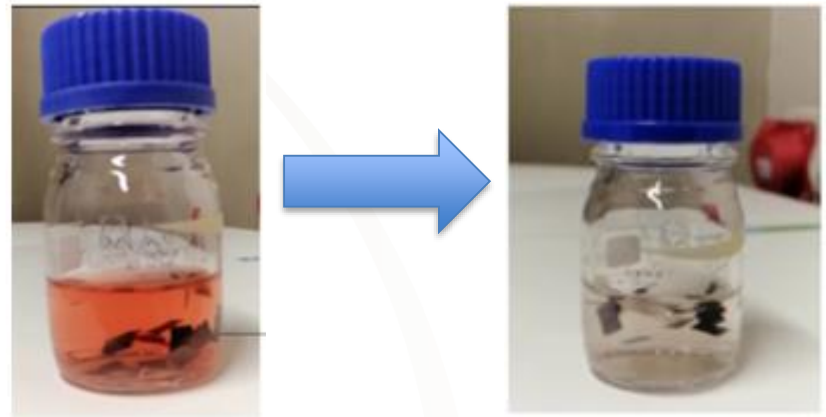


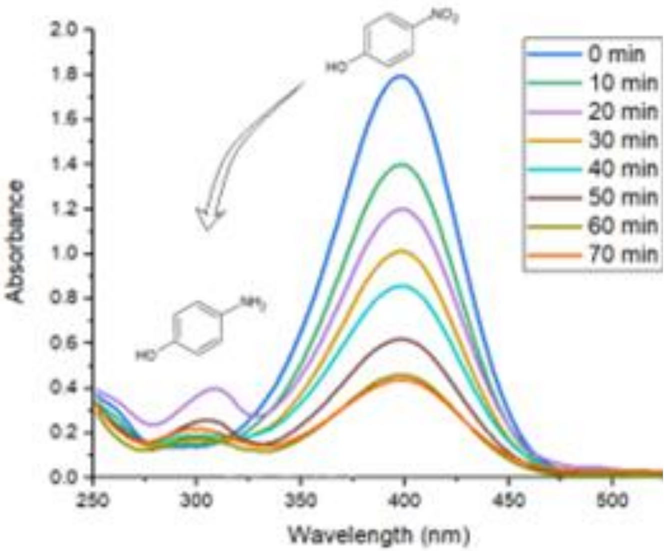
Catalytic antimicrobial membranes

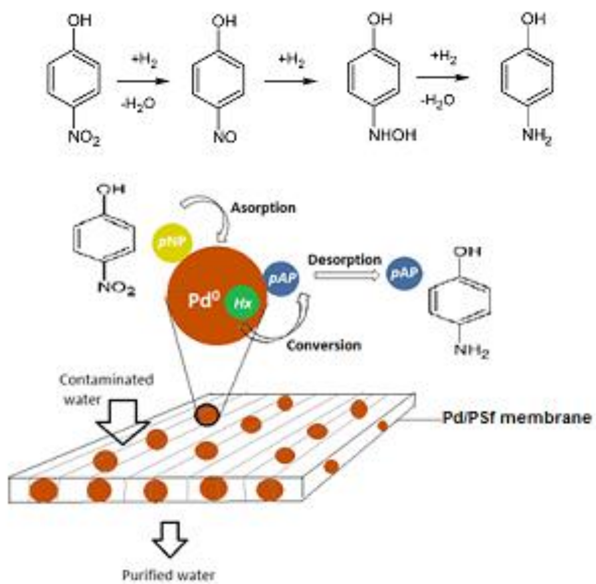


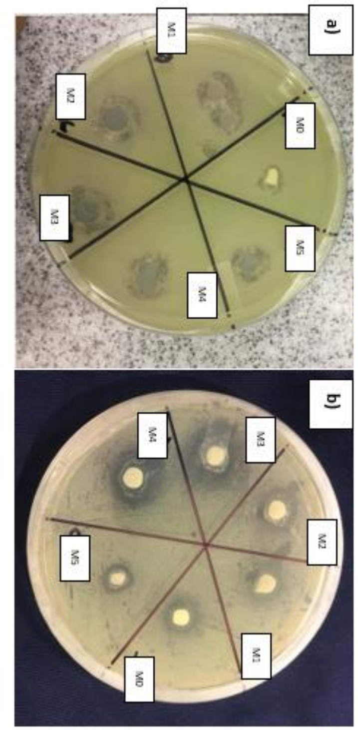
PES membrane
with Ag or AgPd









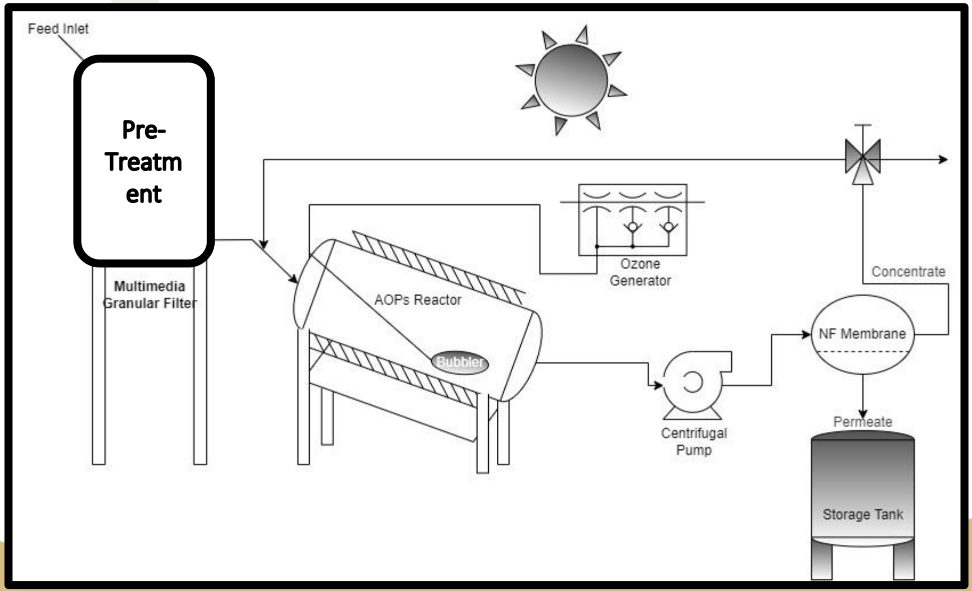


E. Coli

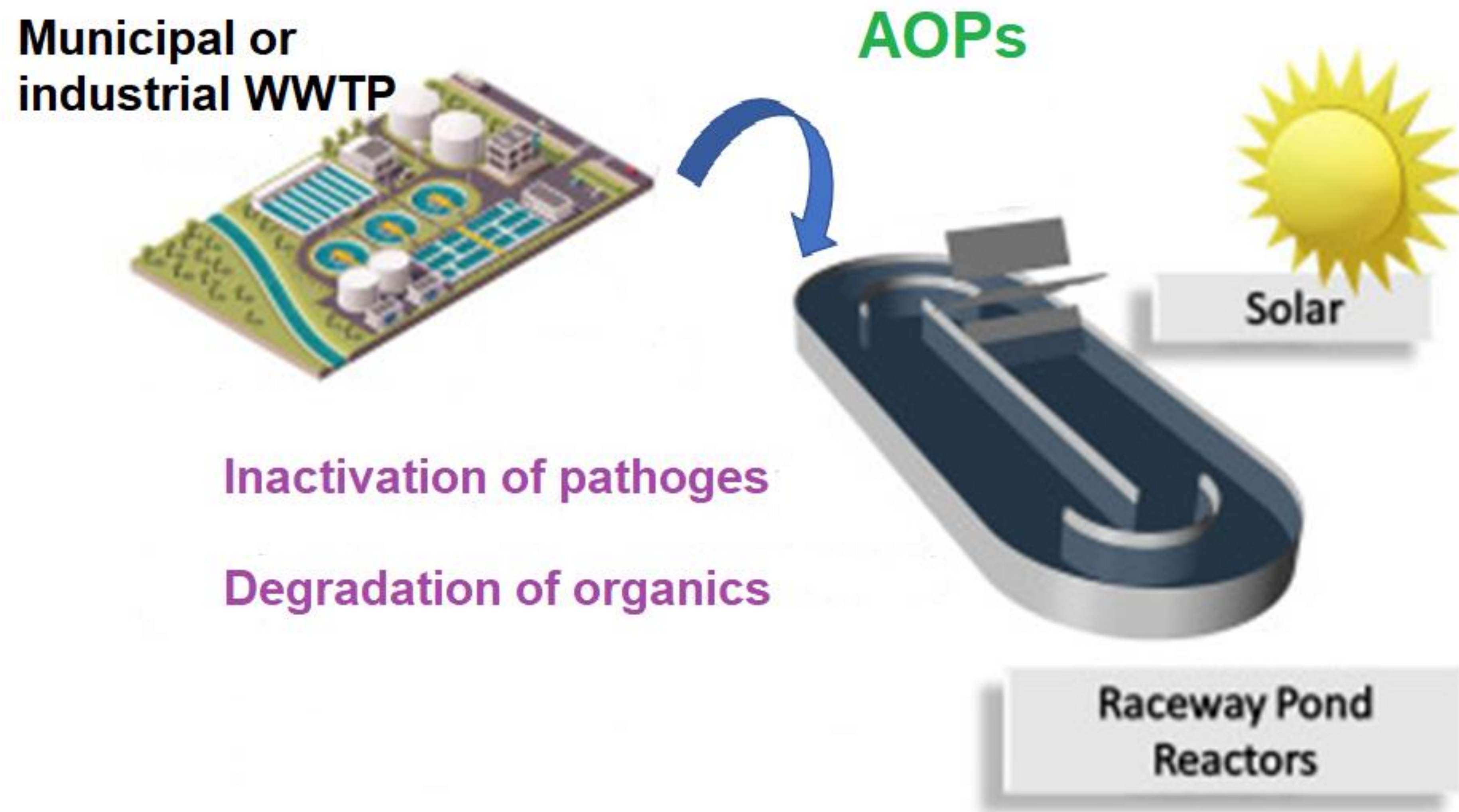
B. Cereus

The Future: Integrated AOP/Membrane Technology

SODIS Reactor

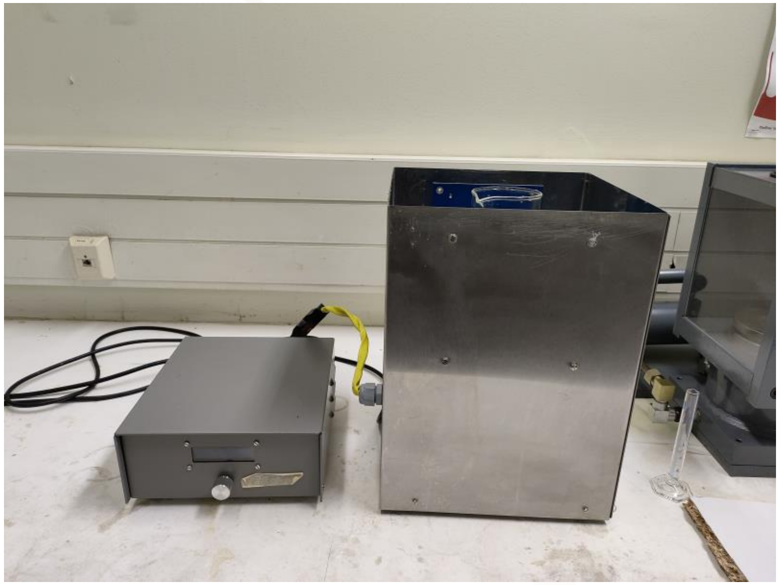


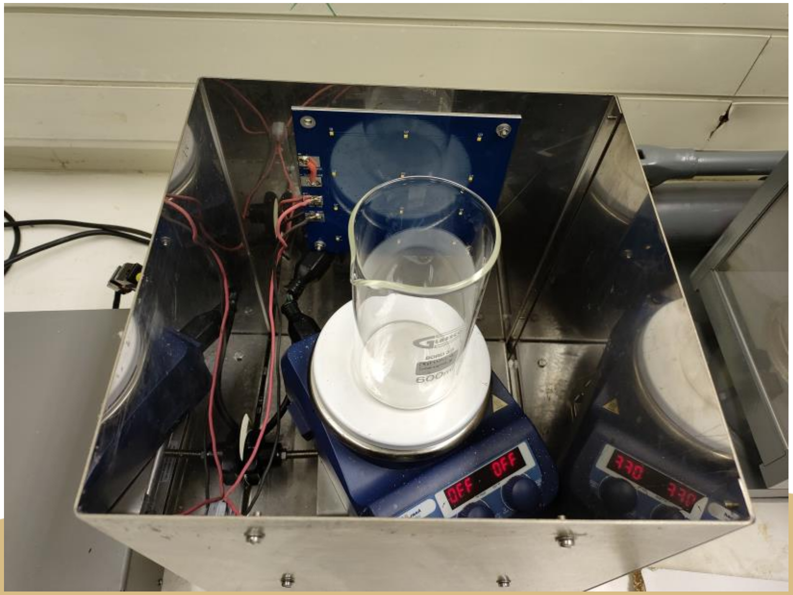
The Future: Raceway Pond Reactors for AOPs



Science of The Total Environment, 2021, 800, 149653

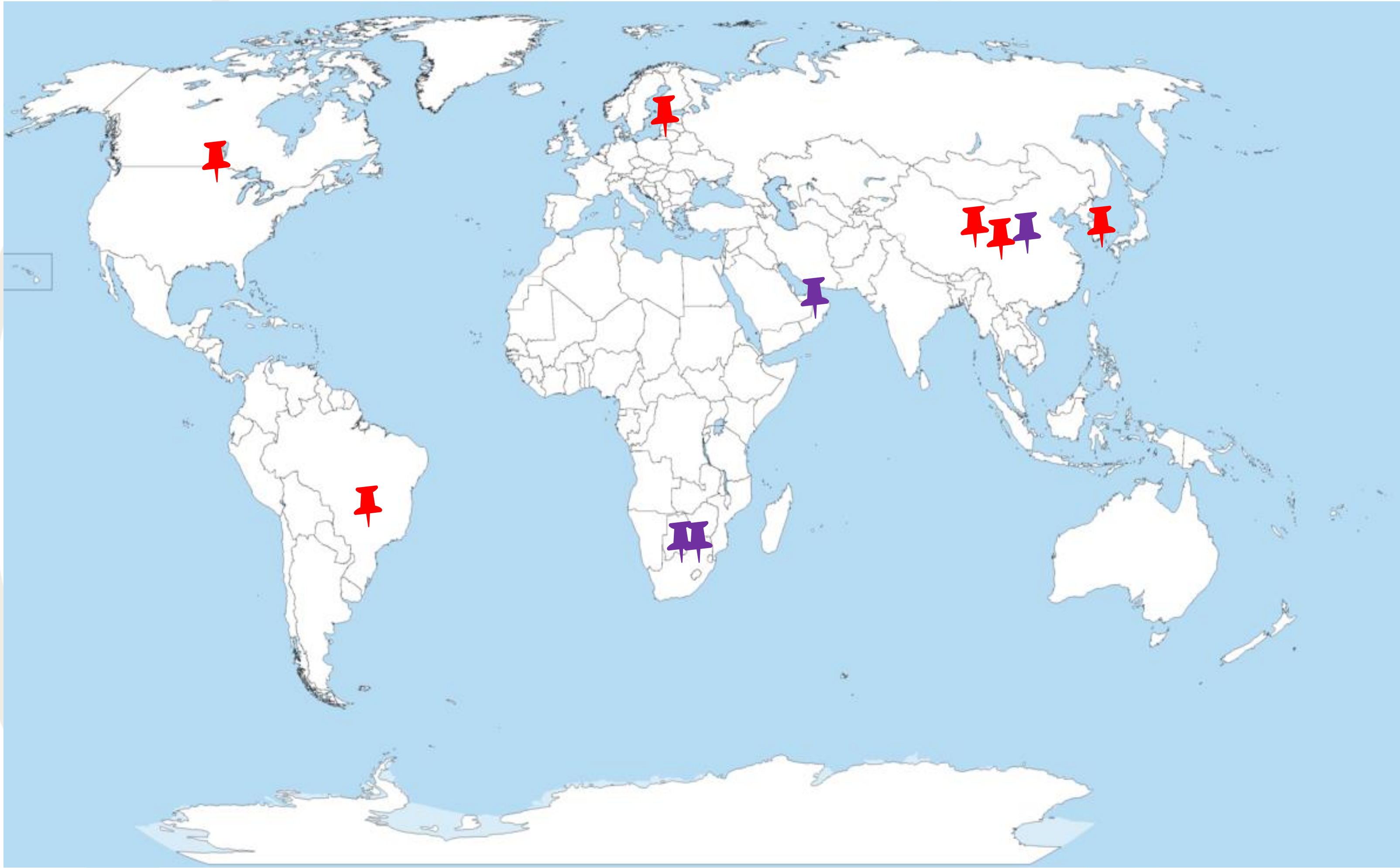
The Future: Small Scale Reactors for AOPs





Custom made visible light LED Reactors

Collaborations



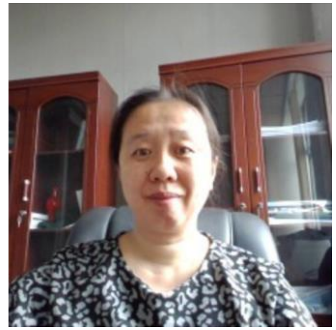
Established Collaborations

Future Planned Collaborations

Acknowledgements

Prof BB Mamba

Prof MS Diallo



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Prof S Rengaraj

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Prof D Onwudiwe

Prof H Zhang

Prof J Li

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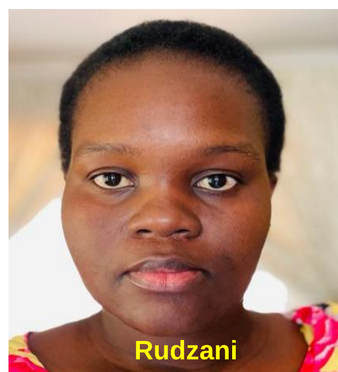

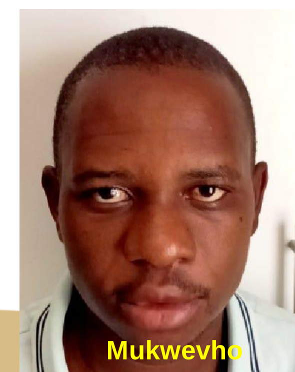

In loving memory

May their souls continue to rest in peace

Prof Kebede K. Kefeni **Mr Kagiso "Kg" Mokalane** **Dr Unathi Sidwaba**


thank you
danke
рахмат
謝謝
ngiyabonga
teşekkür ederim
gracias
merci
obrigado
bedankt
dziękuję
спасибо
Баярлалаа
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go raibh maith agat
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terima kasih
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