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Training a new generation of researchers in Innovative Electrochemical OXidation processes

Photo-electrocatalytic (PEC) based Advanced Oxidation Process (AOP) for the Simultaneous Removal of Multiple Organic Micro-Pollutants From Wastewater Treatment Plant Effluent

Presented by: *Agha Zeeshan Ali*

Research team: *Prof. Dr. Ir. Jan Peter van der Hoek, Dr. Ir. Henri Spanjers & Yiqian Wu*

Department of Water Management, Faculty of Civil Engineering & Geosciences, TU Delft.

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Context

Organic Micro-Pollutants (OMPs)

Pharmaceuticals, personal care products, pesticides…

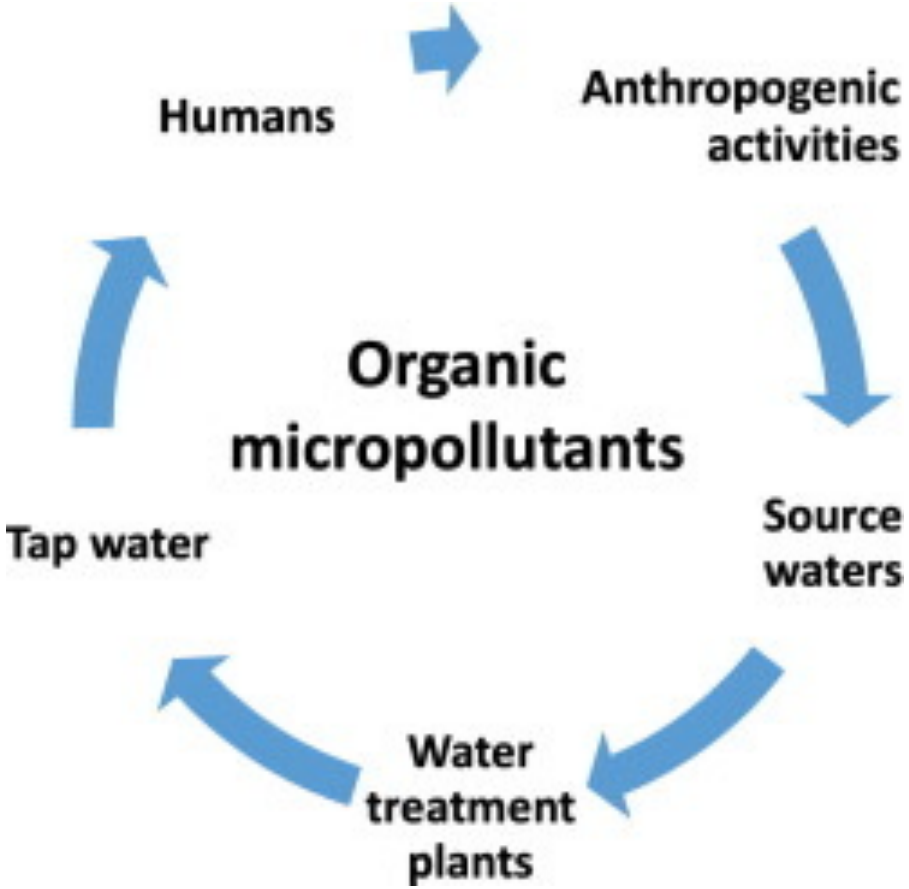
Characteristics

Low concentrations (ng L^{-1} - μg L^{-1}), potential health risks for humans

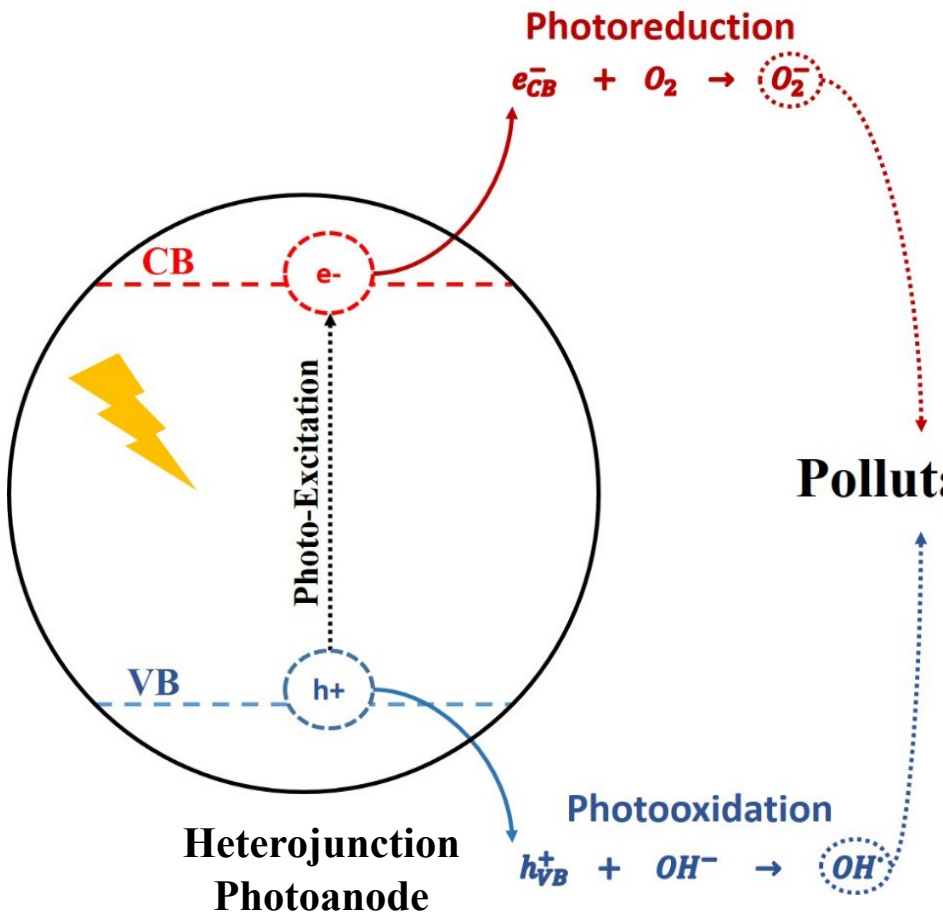
Selected OMPs

1. Benzotriazole (BTA)
2. Methyl Benzotriazole (MBTA)
3. Carbamazepine (CBZ)
4. Diclofenac (DIC)
5. Hydrochlorothiazide (HCTZ)
6. Sulfamethoxazole (SMX)
7. Propranolol (PRO)
8. Sotalol (SOT)
9. Trimethoprim (TMP)
10. Metoprolol (MP)
11. Clarithromycin (CLA)

10 μg L^{-1} (each) in WWTP effluent



ZnO-GQD-$BiVO_4$ Photoanode



Band Gap Energies

Zinc Oxide (ZnO) 3.0 – 3.2 eV

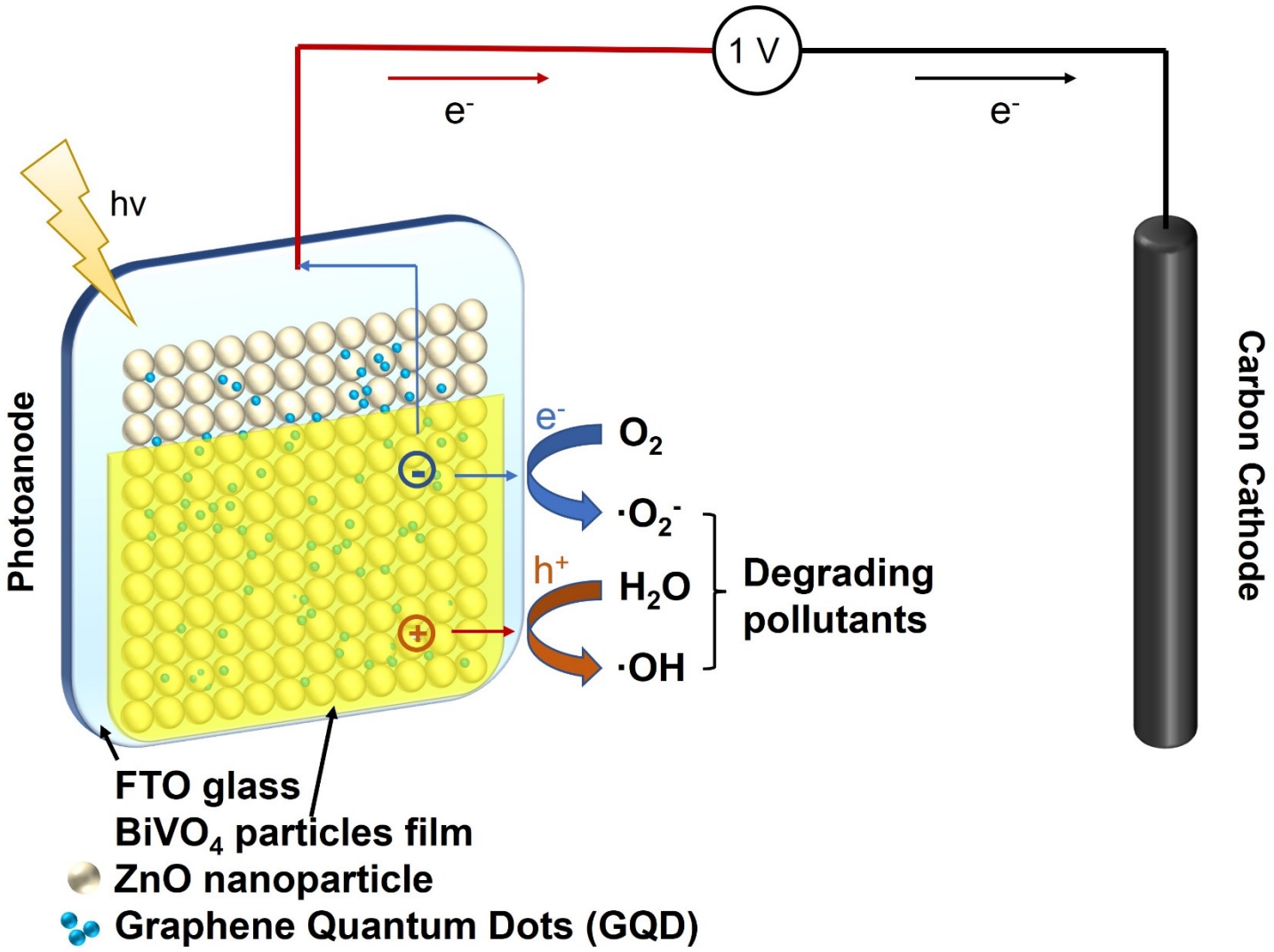
Bismuth Vanadate ($BiVO_4$) ~2.4 eV

} Covering UV-Visible Range

Pollutants ⇨ Degradation

"Low rate of recombination in heterojunction photoanode"

Photo-electrocatalytic Advanced Oxidation Process

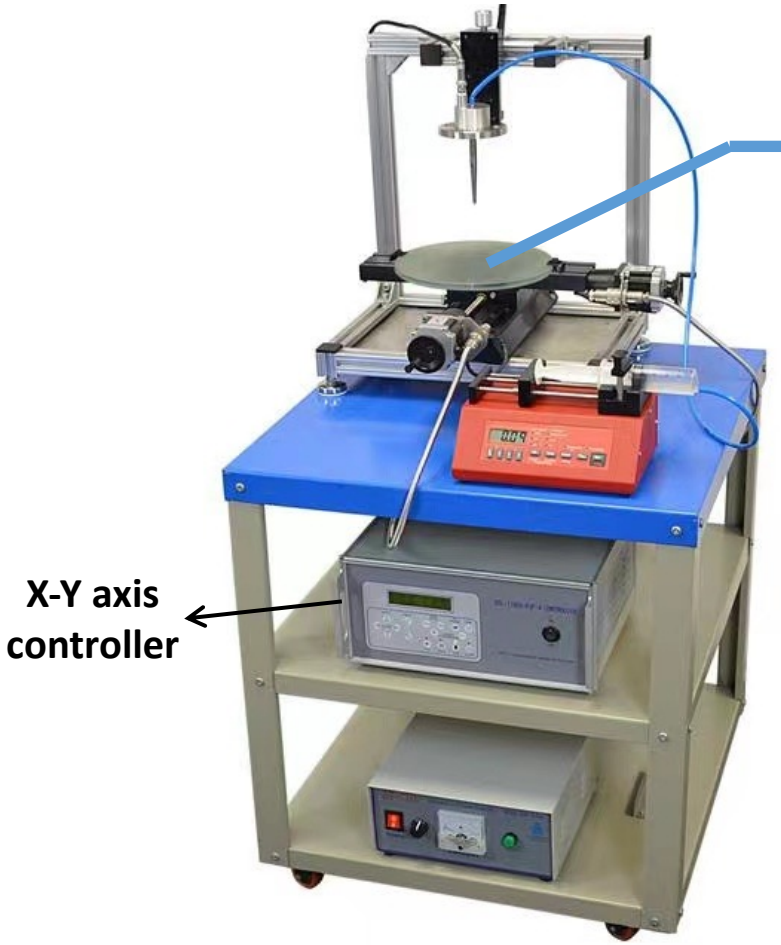


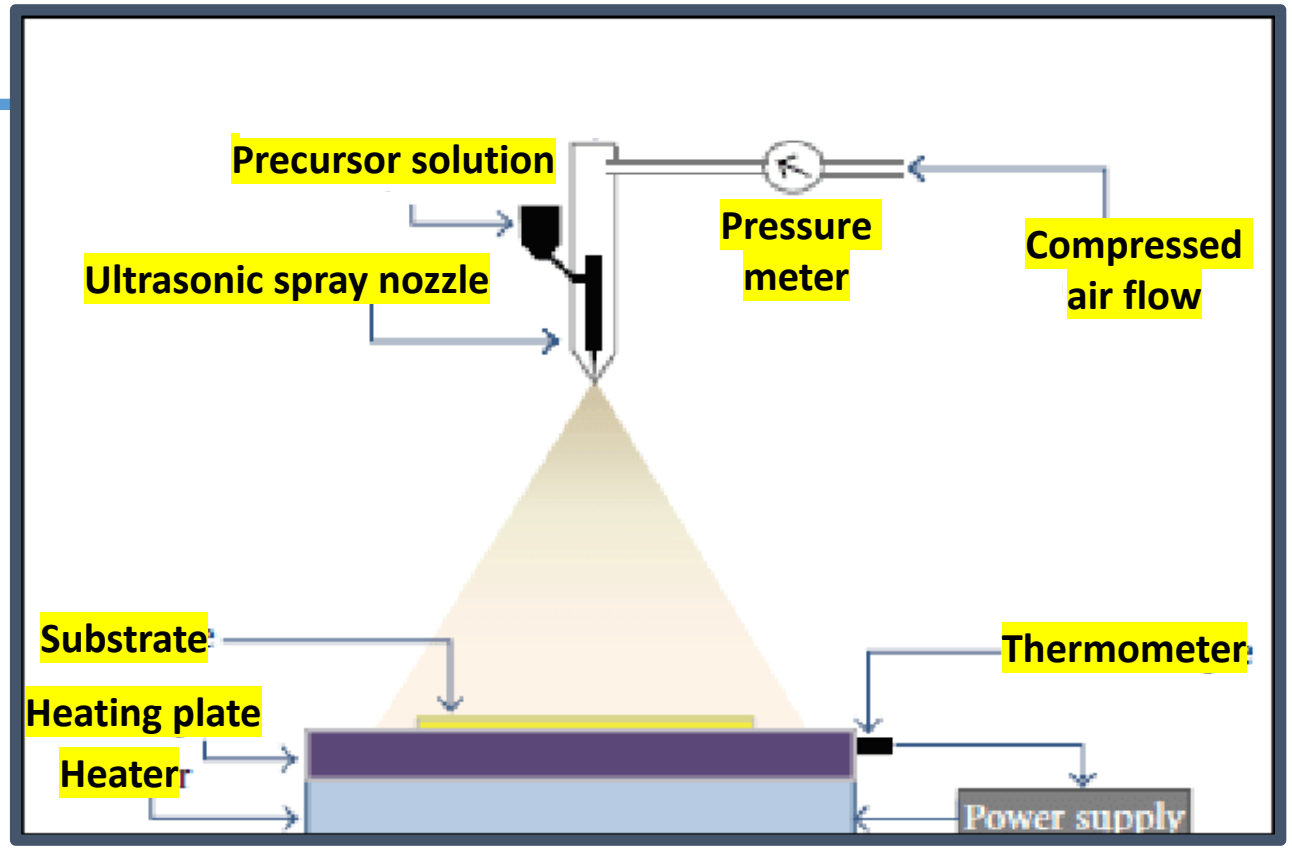
Research Objectives

- *Fabricate a visible light driven heterojunction photoanode.*
- *Fabricated photoanode able to produce reactive species.*
- *Reduce the rate of recombination in heterojunction photoanode as compared to pristine bismuth vanadate.*
- *Higher removal efficiency of heterojunction photoanode.*

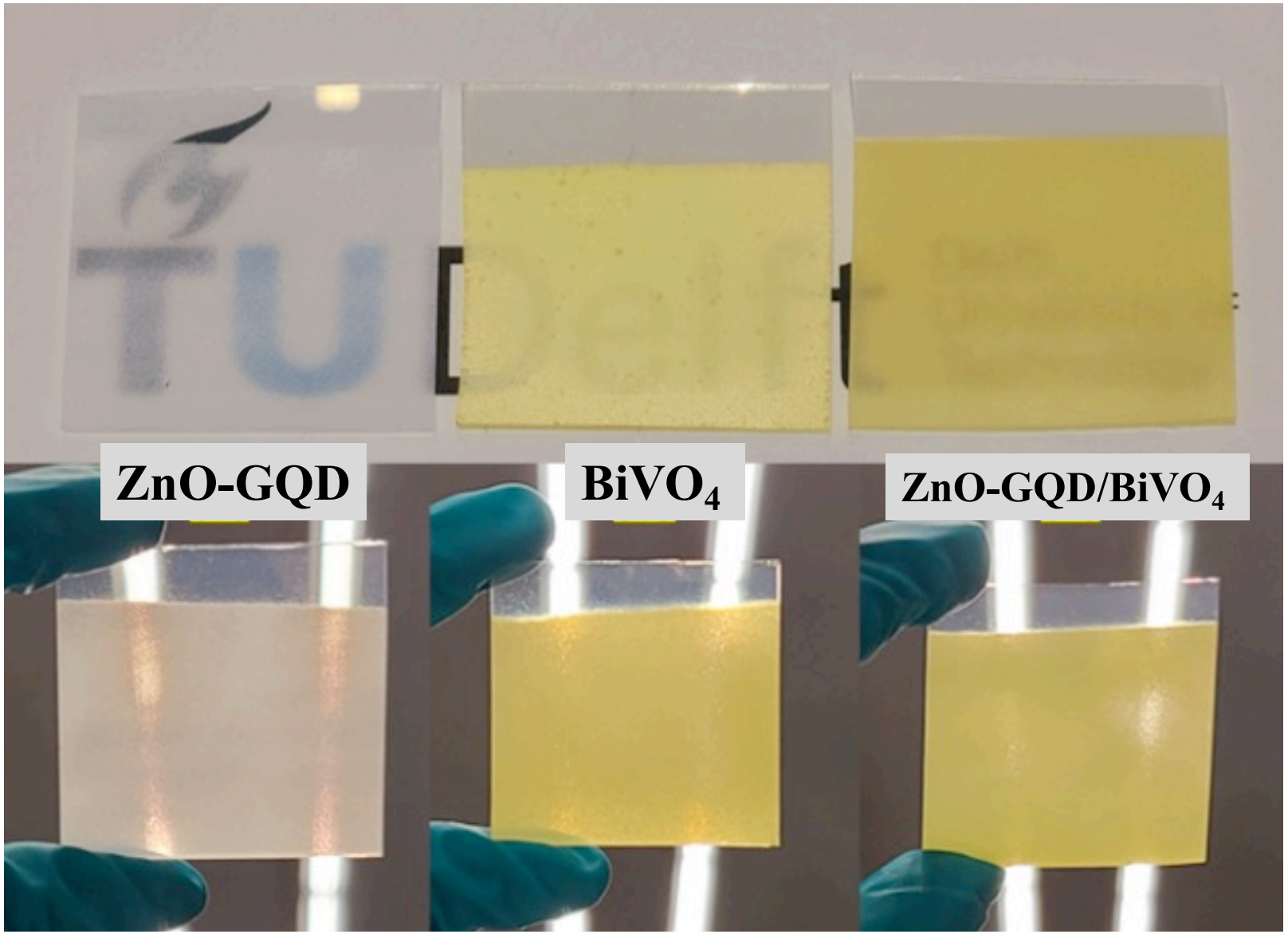
Fabrication of Photoanodes

Ultrasonic Spray Pyrolysis (USP)





Fabricated Photoanodes



Structural Characterization

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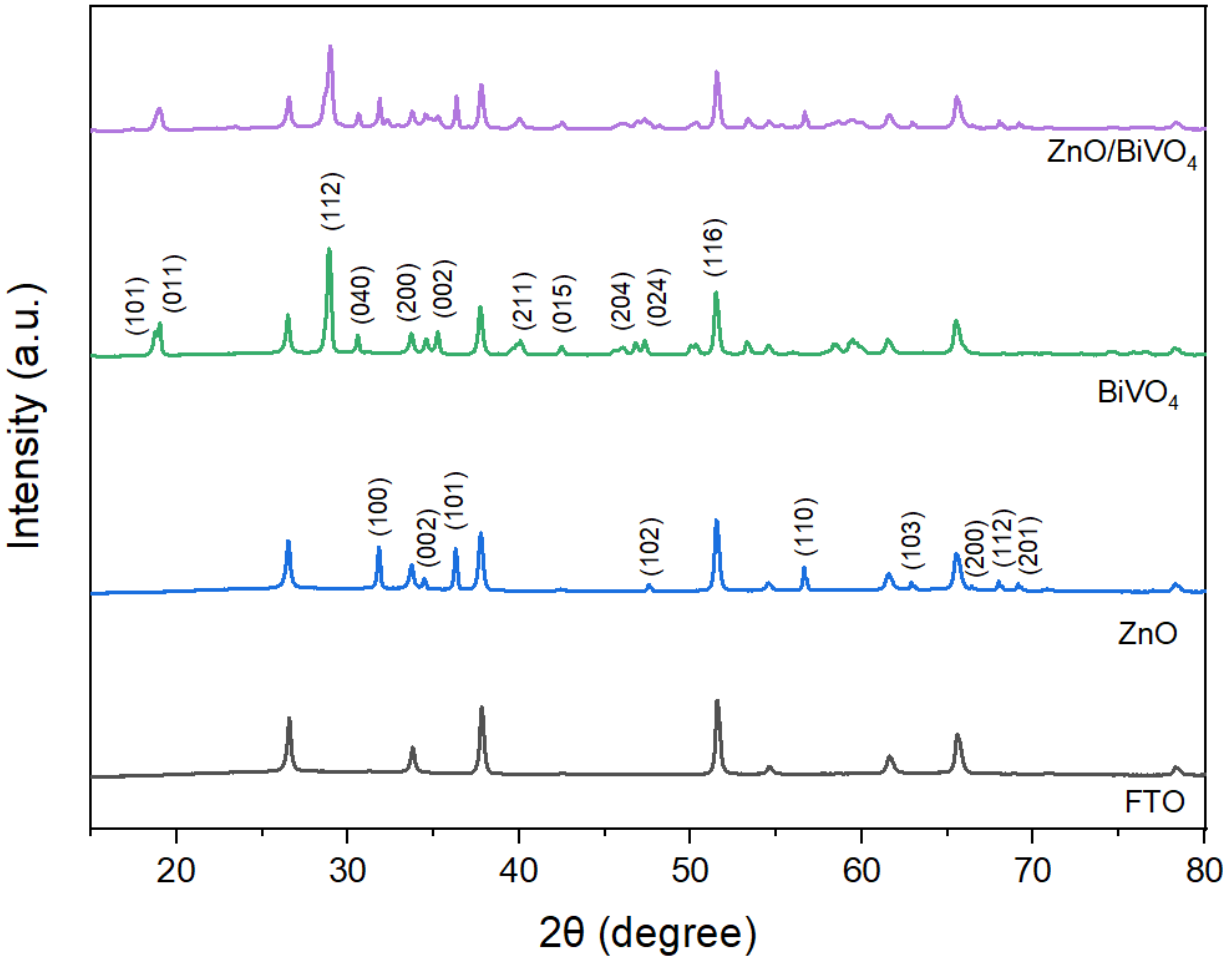
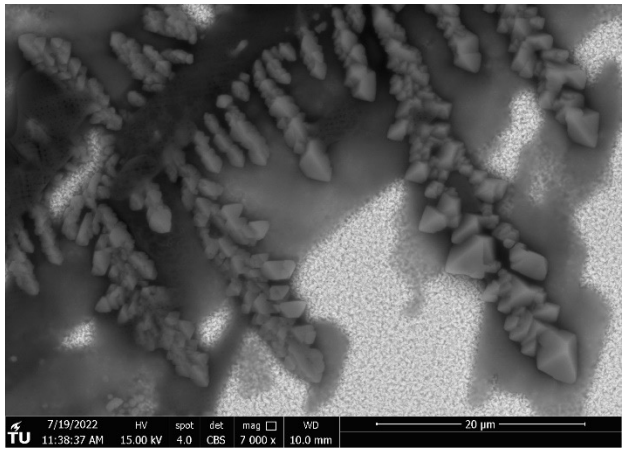
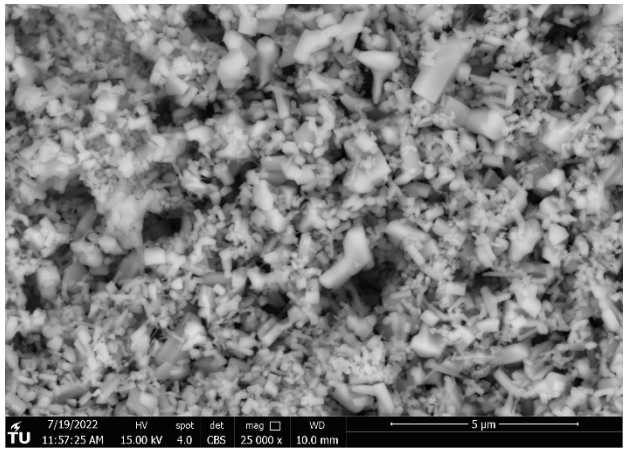
X-Ray Diffraction (XRD)



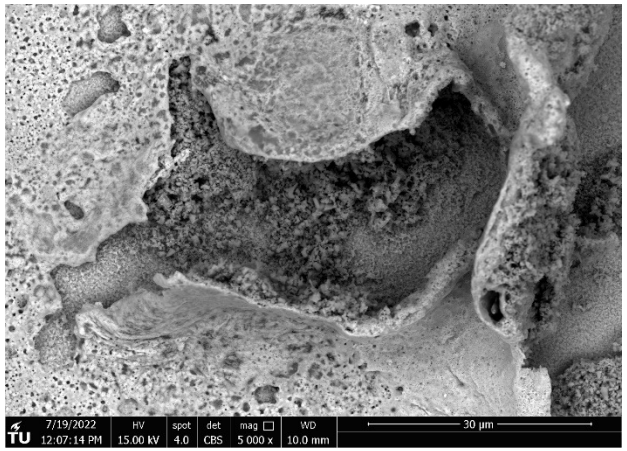
Scanning Electron Microscopy (SEM)

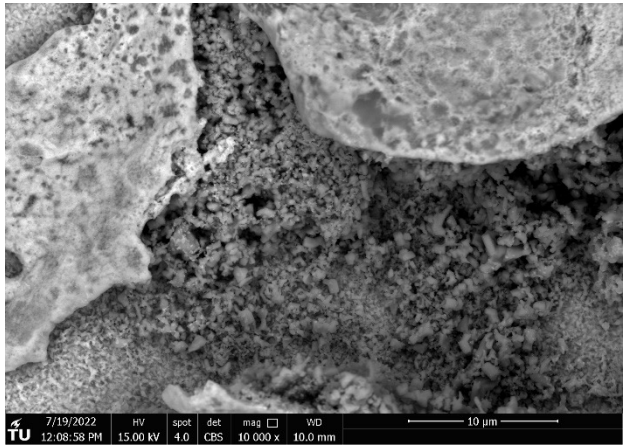


GQD



ZnO





ZnO-GQD/$BiVO_4$

Optical Characterization

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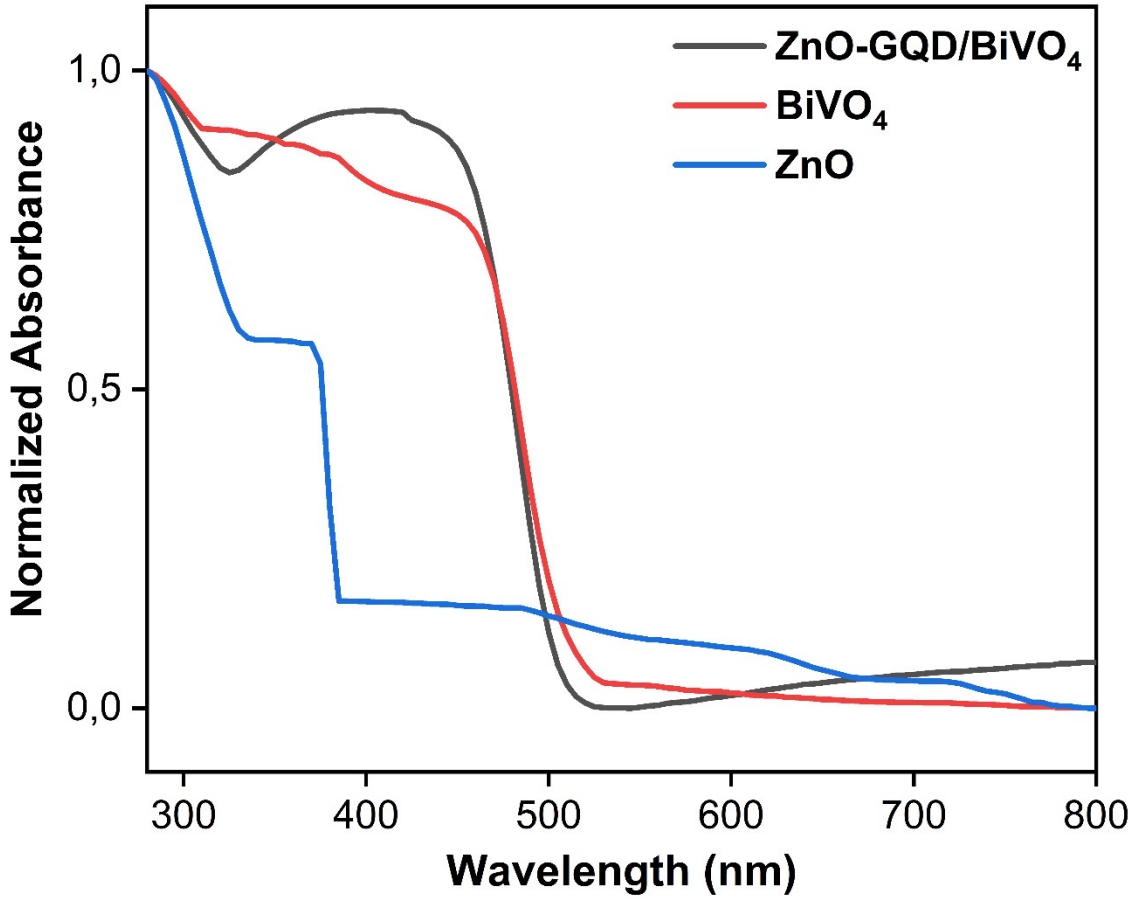
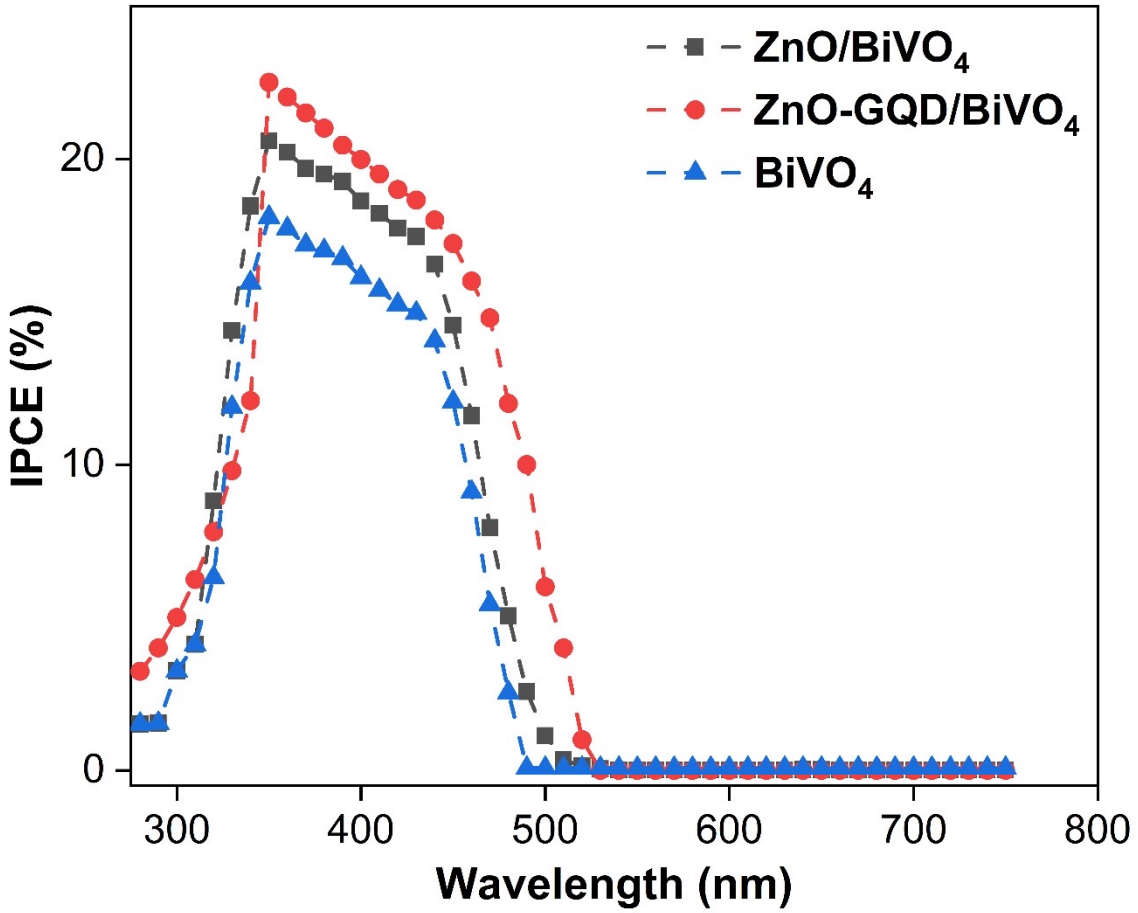
UV-Visible Absorbance Spectroscopy



- *Visible light driven photoanodes with absorbance edge around 530 nm*

Quantum Efficiency Measurement



- *Heterojunction photoanode showed $IPCE_{max}$ of around 23% at λ=350 nm*

Photo-electrocatalytic Removal of OMPs

- **Photoanode:** ZnO-GQD/$BiVO_4$
- **Surface Area of Photoanode:** 14.7 cm^2
- **Volume:** 160 mL
- **Time:** 3 hr (180 min)
- **Electrolyte: 10 µg L^{-1}** of each **OMP** + 0.1 M Na_2SO_4 in WWTP effluent at pH 7.5.
- **Solar simulated light** (AM 1.5) with intensity of 60 W m^{-2} calibrated between 300 – 400 nm.
- **1V vs Ag/AgCl** as external bias to reduce the rate of recombination.

	TOC (mg L^{-1})	COD (mg L^{-1})	NO_3-N
Original Spiked Effluent	11.99	32.5	1.88
After 3 hr of Removal Experiment	6.2	27.8	2.26

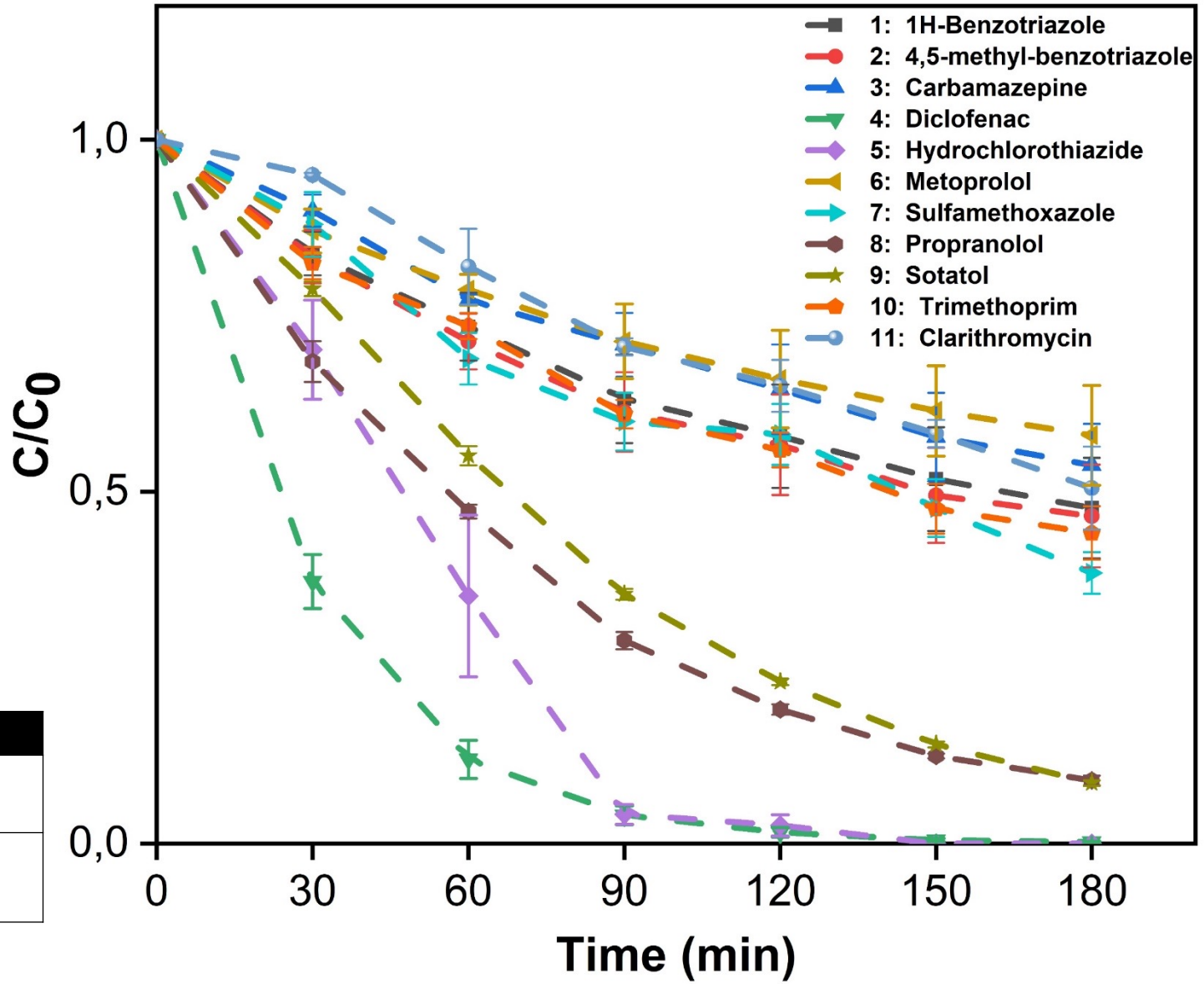
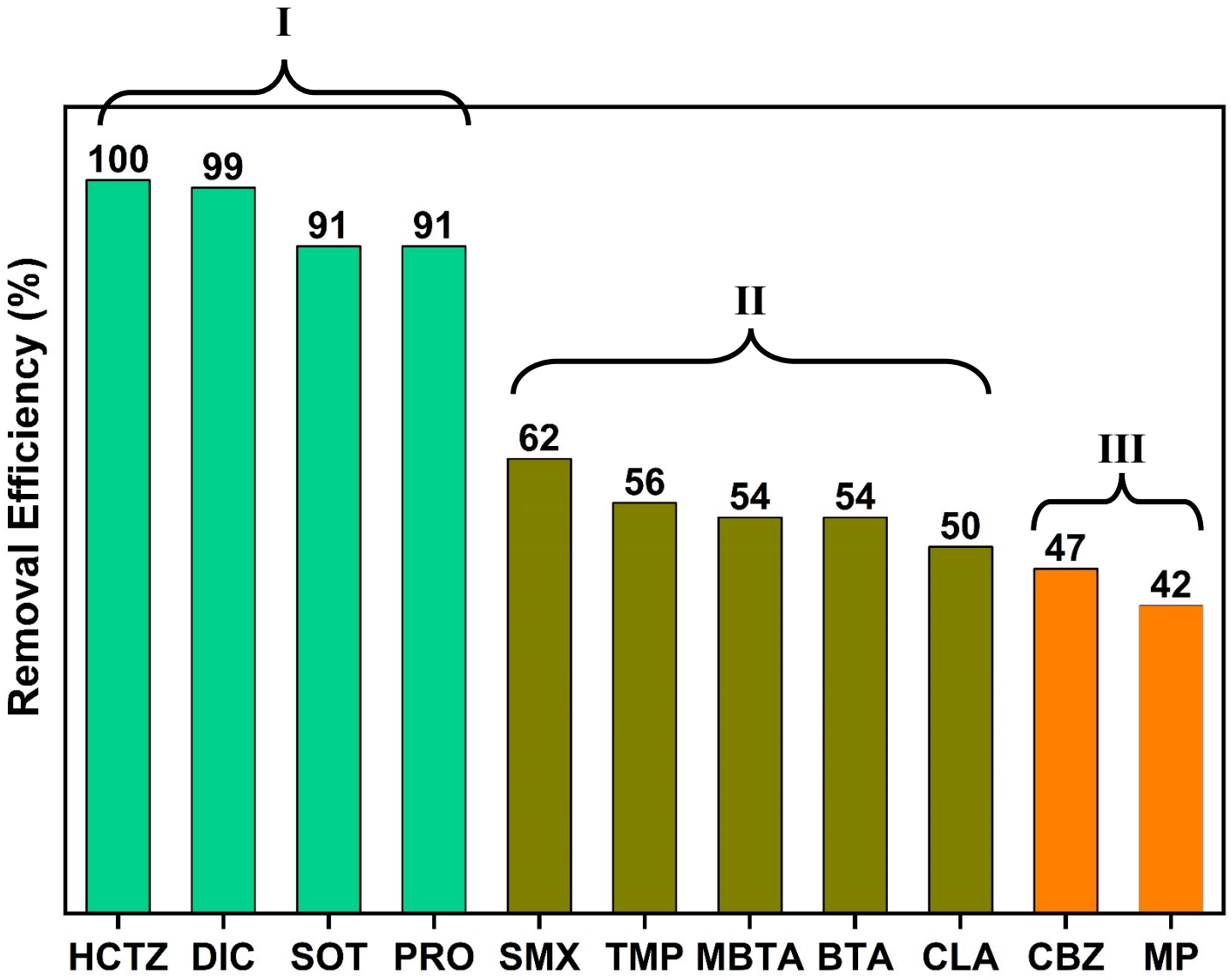


Photo-electrocatalytic Removal of OMPs



Compounds	Removal Efficiency (%)
Hydrochlorothiazide (HCTZ), Diclofenac (DIC), Sotalol (SOT) and Propranolol (PRO)	More than 80%
Sulfamethoxazole (SMX), Trimethoprim (TMP), Methyl Benzotriazole (MBTA), Benzotriazole (BTA) and Clarithromycin (CLA)	Between 50 and 80%
Carbamazepine (CBZ) and Metoprolol (MP)	Between 40 and 50%

Photo-electrocatalytic Removal of OMPs

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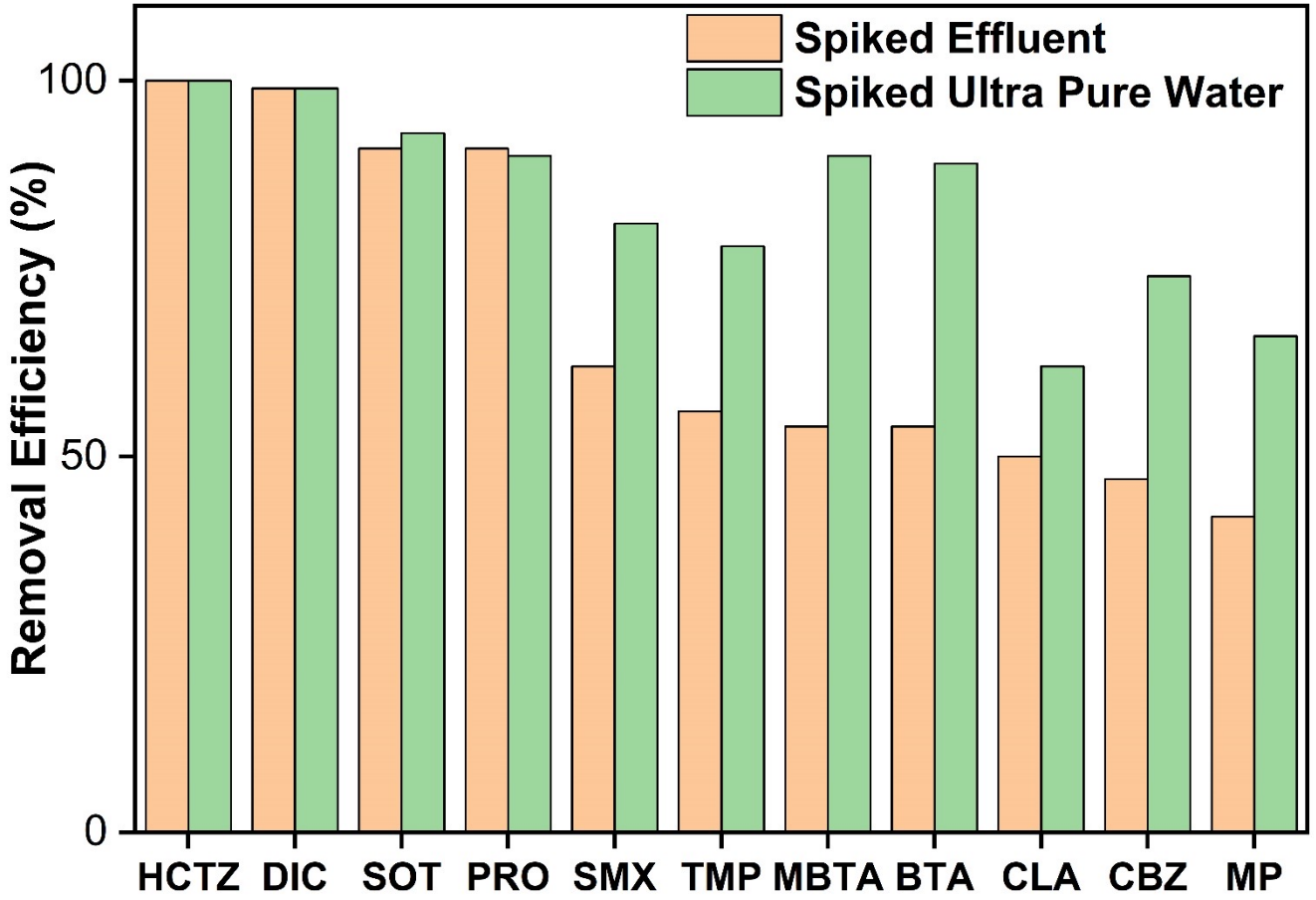
Comparison Of Removal Efficiencies In WWTP Effluent & Ultra-Pure Water



Fitting equation: $\frac{C}{C_0} = e^{-kt}$

OMP	Rate Coefficient (K) in Spiked Effluent (x 10^{-3} min^{-1})	Rate Coefficient (K) in Spiked Ultra-Pure Water (x 10^{-3} min^{-1})
Hydrochlorothiazide (HCTZ)	29.86	43.62
Diclofenac (DIC)	34.44	29.71
Sotalol (SOT)	12.39	11.81
Propranolol (PRO)	13.64	11.25
Sulfamethoxazole (SMX)	5.22	7.83
Trimethoprim (TMP)	5.11	7.35
Methyl Benzotriazole (MBTA)	5.06	9.70
Benzotriazole (BTA)	4.77	9.96
Clarithromycin (CLA)	2.66	6.33
Carbamazepine (CBZ)	4.17	7.00
Metoprolol (MP)	3.68	5.82

Conclusion

1. Ultrasonic spray pyrolysis proved to be an effective method for the batch fabrication of thin film photoanodes.
2. The fabricated heterojunction photoanodes showed superior photoelectrocatalytic properties.
3. Targeted OMPs had different degradation behaviors, and competition was observed during the photoelectrocatalytic degradation process of multiple OMPs.
4. More in depth analysis is required to explain the difference in the removal rate of OMPs during simultaneous removal of multiple OMPs

Thank you for your time, suggestions & comments are welcome!