

Supplementary Information

Spectro-Kinetic Modelling of Photocatalytic Oxidation of Heterocyclic Compounds in a Continuous-Flow Packed Bed Reactor

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S1. Determination of rate constant k_5 for $\cdot OH$ scavenging by $\cdot CR$

A general scavenging rate constant for $\cdot OH$ by CAB cation ($\cdot CR$) in aqueous solution is not known. However, reaction rates for similar heterocyclic cations as reported in literature^[1] is listed below:

1. Pyrrolidinium ion



2. Imidazolium ion



Dissolved organics in effluents from wastewater treatment plant are known to scavenge $\cdot OH$ radicals. The rate constant for dissolved organics quenching $\cdot OH$ radicals has been proposed to be in the range of $(0.2 - 1.4) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [2-4]. Table S2 lists some of the common aromatic organic compounds found in coking wastewater and their $\cdot OH$ scavenging rate constants from literature^[1,5].

Aniline	$1.4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$
Benzene	$7.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
Ethanol	$1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
Cresol	$1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$
Cyanide	$0.8 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$
Phenol	$1.4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$
Thiocyanate ion	$1.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$

Based on the above observations and structure property relationship with other heterocyclic ions, we assume a value of $1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ as the rate constant for the $\cdot\text{OH}$ scavenging by $\cdot\text{CR}$. On a μM basis, k_5 is calculated as $36 \times 10^6 \mu\text{M}^{-1} \text{ h}^{-1}$.

S2: Photon flux determination from discrete spectral irradiance

The discrete spectral irradiance was obtained from Newport^[6]. Photon flux can be calculated as:

$$q_p = \frac{I \times \lambda \times 5.03 \times 10^{15}}{6.02 \times 10^{17}}$$

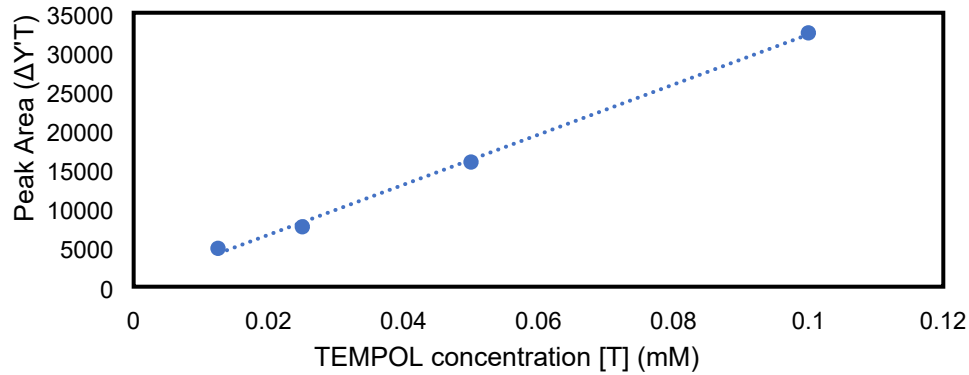
Wavelength, λ (nm)	Intensity, I (mW/m ² /nm)	Photon Flux, q_p ($\mu\text{mol}/\text{m}^2.\text{s}$)
250.74	17.45	0.04
299.82	119.97	0.30
350.55	162.79	0.48
400.74	203.85	0.68
449.26	200.60	0.75
499.45	251.19	1.05
550.74	217.37	1.00
600.37	213.91	1.07

The photon flux over the irradiant photoreactor area was determined to be $0.0376 \mu\text{mol}/\text{s}$.

S3: Peak intensity ratios and g-factor of ROS

EPR spectrum	Peak intensity ratio	g-factor	Reference
DMPO-OH	1:2:2:1	2.0023	[7]
DMPO-OOH	1:1:1:1:1:1	2.004	[8]
DMPO-OCR	1:1:1:1:1:1	2.0027	[9]

S4: Calibration plot of TEMPOL



$$\Delta H/\Delta t = 100/60 = 2.$$

S5: Rate constant k_o for photocatalyst activation:

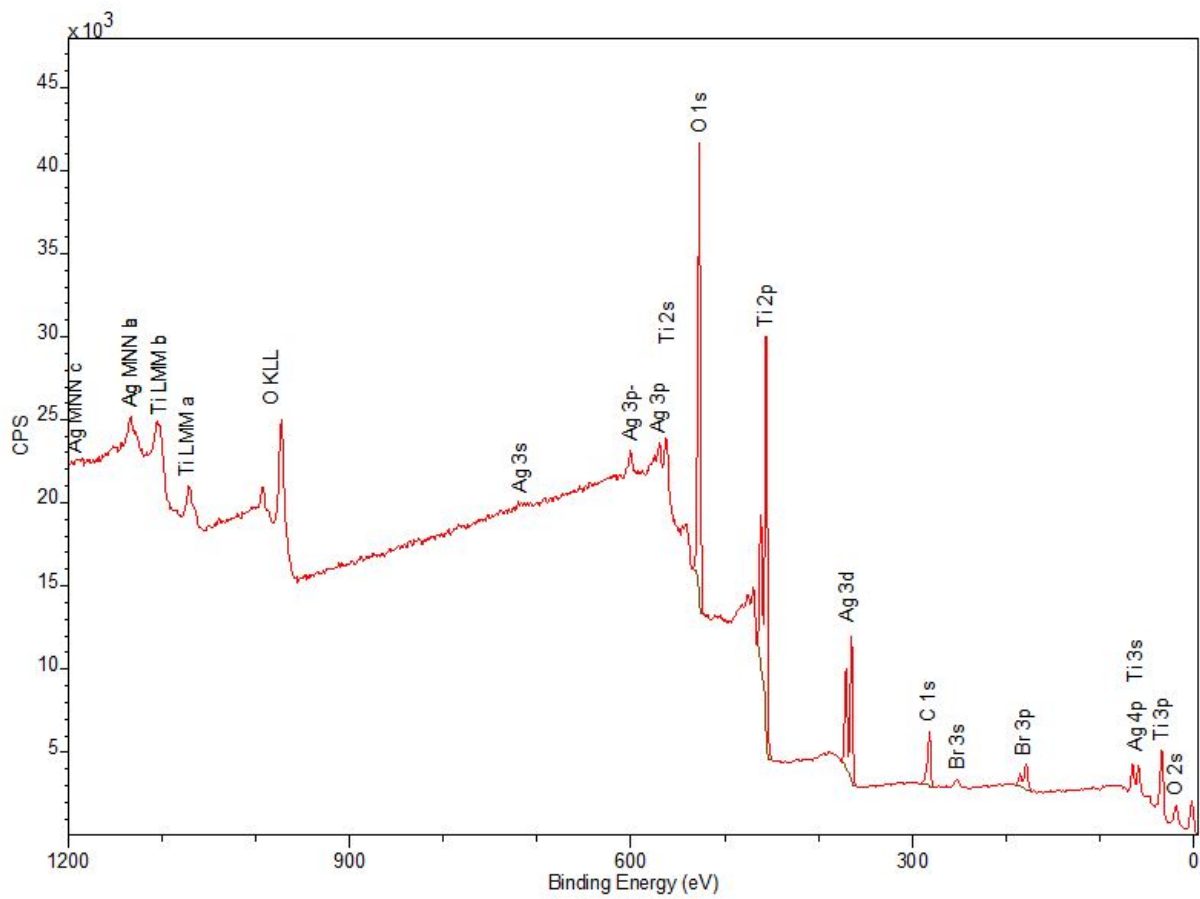
The value of k_o was estimated using the following equation by assuming photocatalyst particles are spherical in shape:

$$k_o = \frac{1}{4} \Phi Q_{abs} S_{BET}$$

Where Φ is the quantum efficiency, Q_{abs} is the absorption efficiency, and S_{BET} is the BET surface area of the catalyst. Using experimental data from our earlier study^[10], k_o was estimated as $\sim 6 \text{ m}^2, \text{g}^{-1}$.

1.

S6: XPS survey spectra of reduced Ag/AgBr/TiO₂:



S7: Atomic percentages of Ti, O, Ag, Br calculated from XPS

Element	Relative Atomic %
Ti 2p	22.7
O 1s	49.7
Ag 3d	3.3
Br 3p	3.2

S8: Band edge calculation:

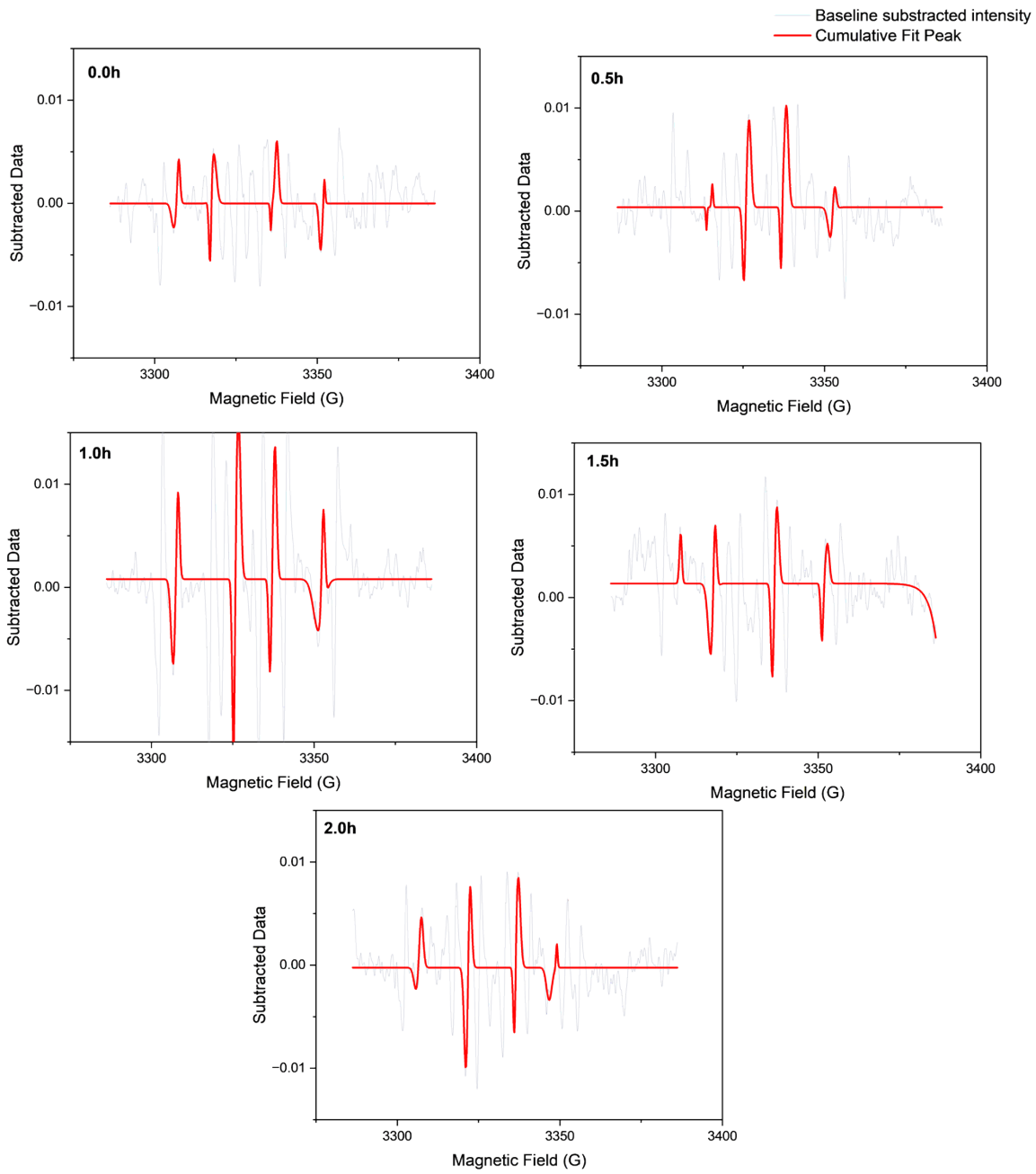
The position of the valence band, VB and the conduction band, CB can be determined, if the values of both the ionization energy and electron affinity are known. Conduction band potential is calculated as:

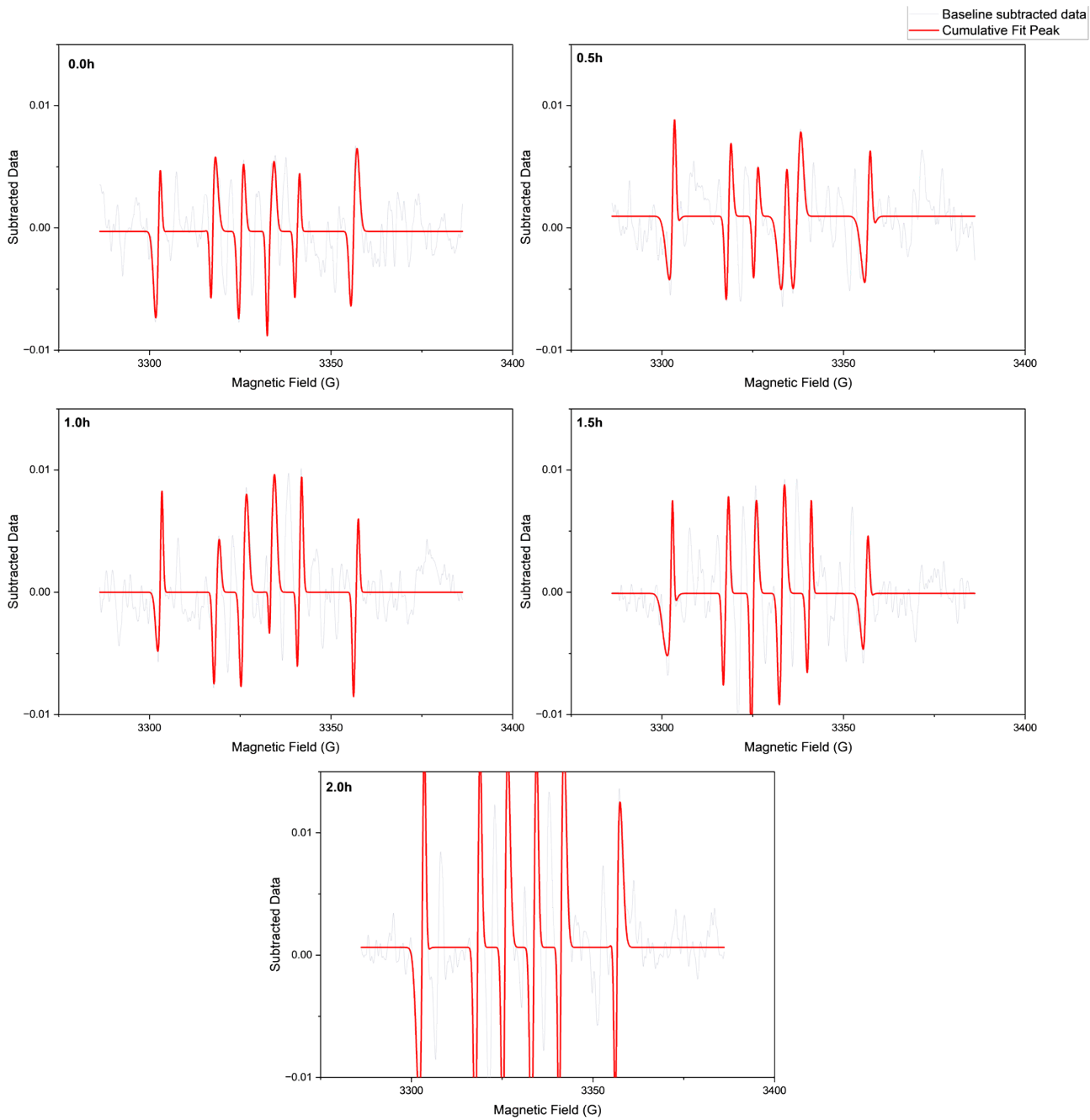
$$E_{CB}^0 = E_{VB}^0 - E_g$$

Where, E_{VB}^0 is the valence band potential of photocatalyst^[11] determined by VB XPS.

Photocatalyst	Optical bandgap	CB potential	VB potential
TiO ₂	3.21	-0.34	2.87
Ag/AgBr/TiO ₂	2.78	-0.32	2.46

S9: Peak Deconvolution





S10: AQE reported in other photocatalytic system

Photocatalytic system	AQE	Reference
Sc-Doped Rutile TiO ₂	30%	[12]
Core-shell heterostructure of TiO ₂ nanofibers with carbon quantum dots.	52%	[13]
Pt nanoparticle-loaded P25 TiO ₂	56%	[14]
PtCu-TiO ₂ sandwich photocatalyst	99.2%	[15]

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