Photocatalysis of the Aminophosphonate EDTMP

Insights into Kinetics and Degradation Mechanisms of EDTMP via Doped TiO_2 Photocatalysts

Julia Schowarte

EDTMP Degradation

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- **photochemical** Degradation of EDTMP
  - **additives** H_2O_2, Metals…
  - few publications on industrial phosphonates

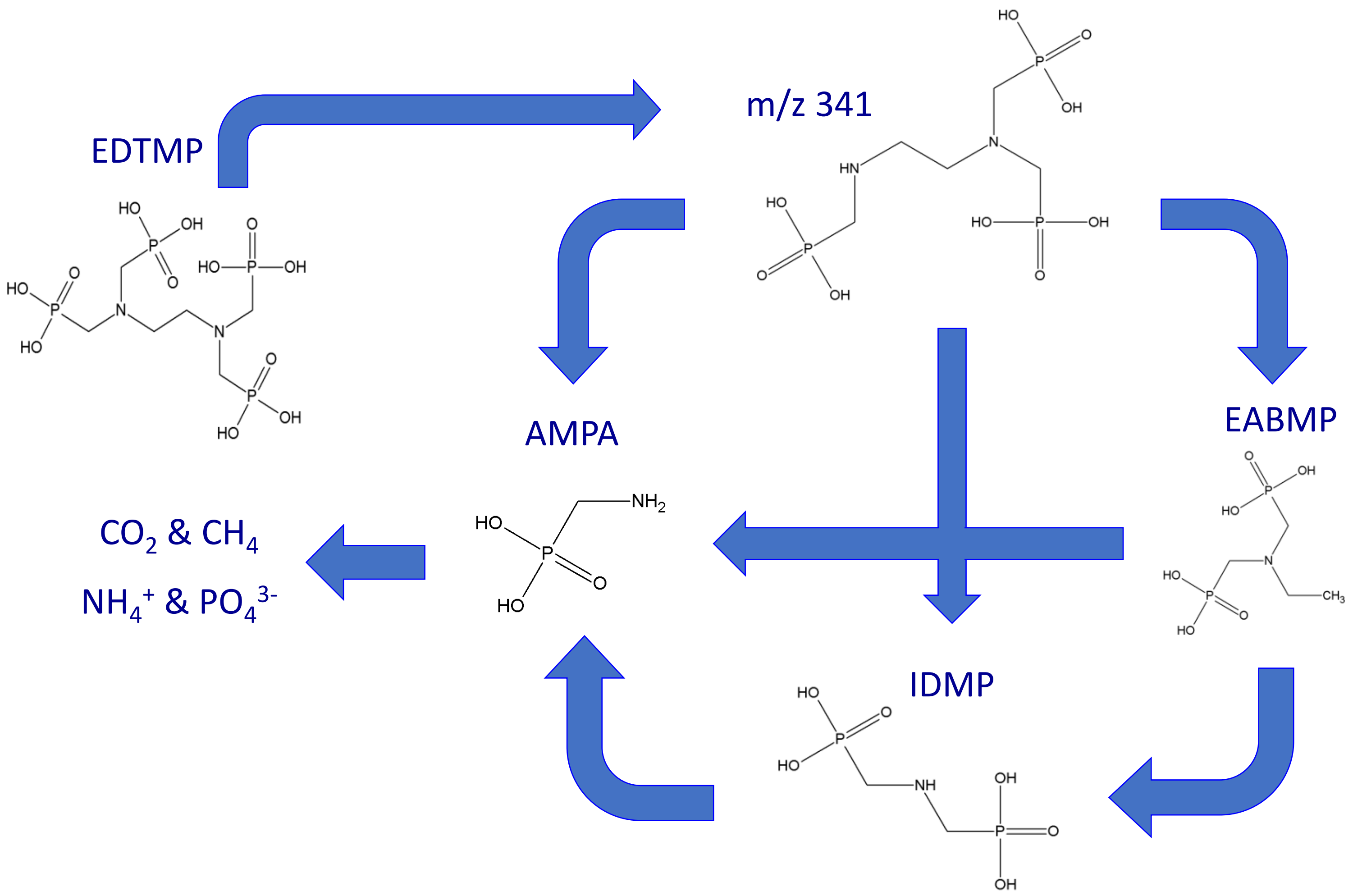

Fig. 1. Photochemical degradation pathway of EDTMP.

https://doi.org/10.1016/j.jphotochem.2019.112192
https://scholar.google.de/scholar?q=photocatalysis+persistent+chemicals

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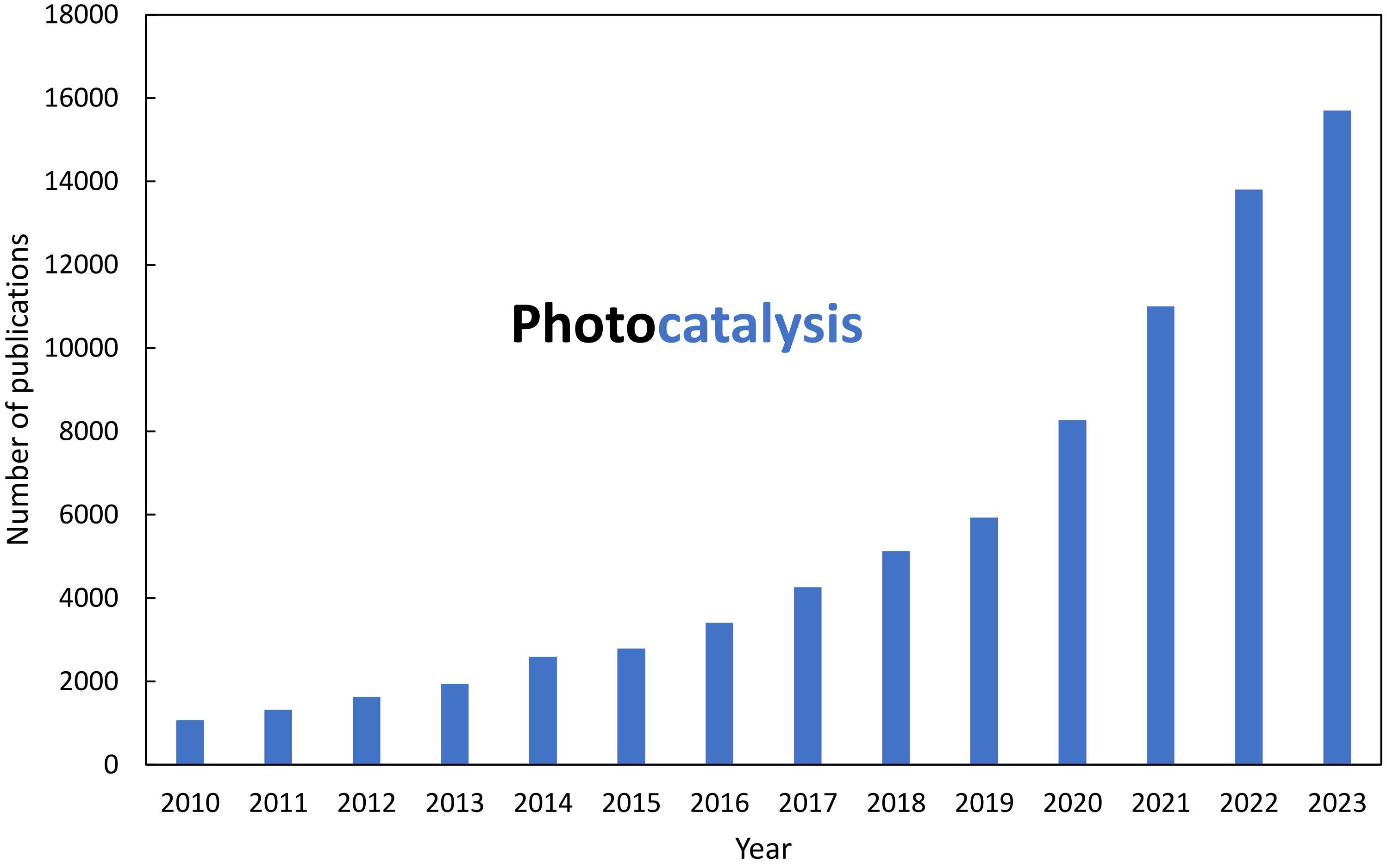

Fig. 2. Publications per year regarding photocatalysis of persistent chemicals.

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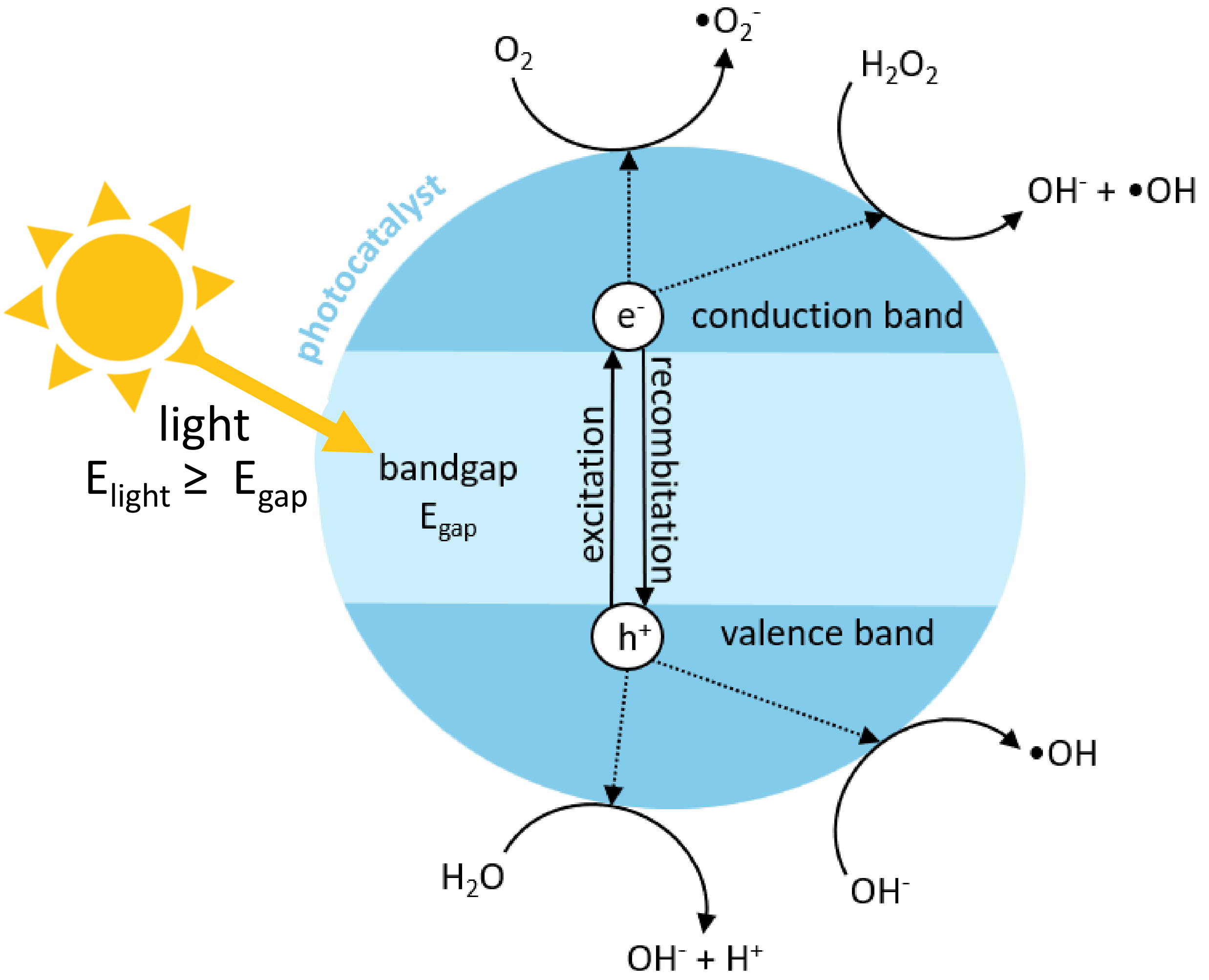
Photocatalysis

1. **direct:** specific target degradation
   - Target needs physical contact to catalyst surface
   - e-/h+ transfer to target is possible

2. **indirect:** ROS attack target
   - More effective for degradation of organic pollutants*



https://doi.org/10.1016/B978-0-323-99866-6.00009-X

Synthesis of the TiO_2-supported NP photocatalysts

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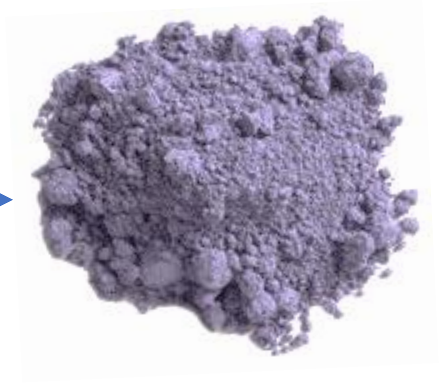
TiO_2 (P25)

→ **wetness impregnation**
Y/K/Na
2/5/10 %

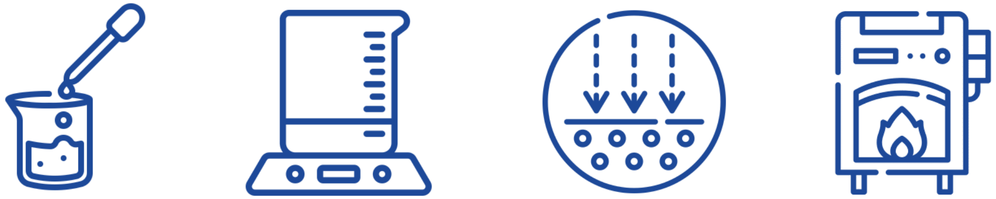
→ **direct anionic exchange**
2 % gold
NH_3 assisted

→



Au2/Y5/P25

2 % Au | 5 % Y | Base P25



Dissolve Precursor | create TiO_2 suspension | Filtration | Drying & calcination

• **confirmed:** rutile & anatase phase

Au-presence

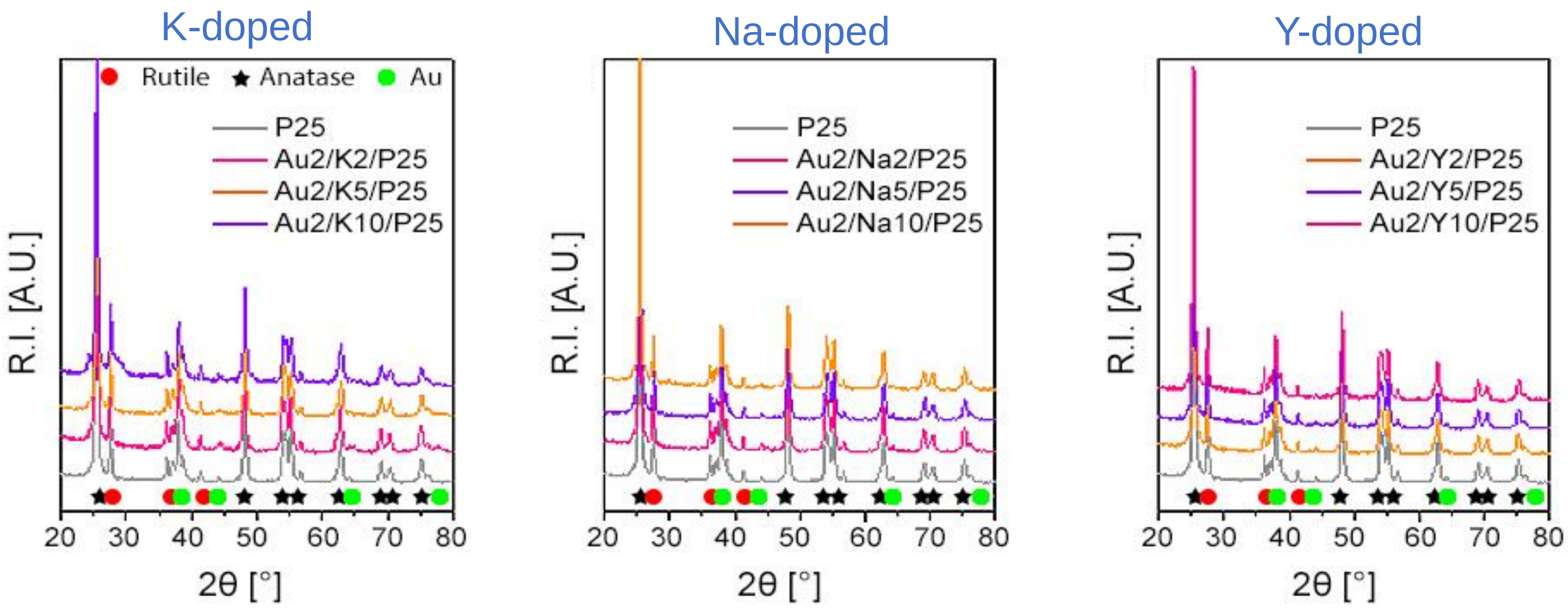
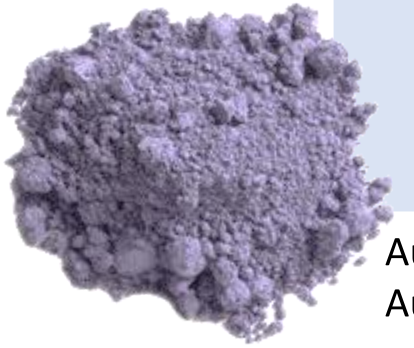


Fig. 3. XRD diffractograms obtained for the Au catalyst series.

Characterisation of NPs: UV-VIS

- **Au:** 550 nm peak → purple appearance
- **K & Y:** increase of absorption

Depends on dopant amount!



Au2/K2/P25
Au2/K10/P25

Au2/Y2/P25
Au2/Y5/P25

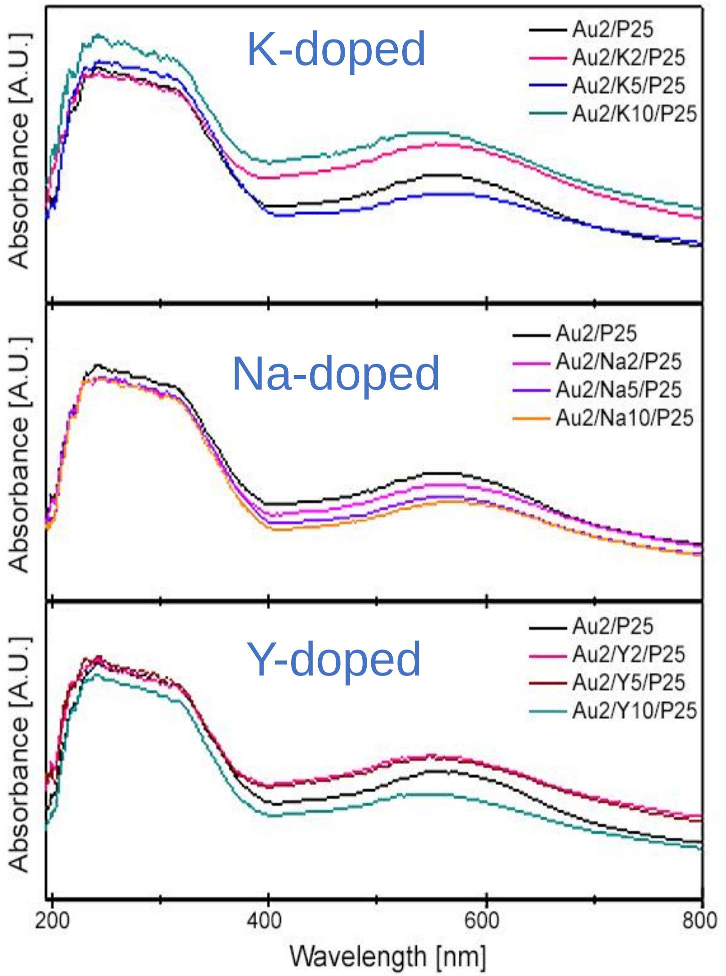


Fig. 4. UV-Vis spectra obtained for the Au catalysts series.

Characterisation of NPs: TEM

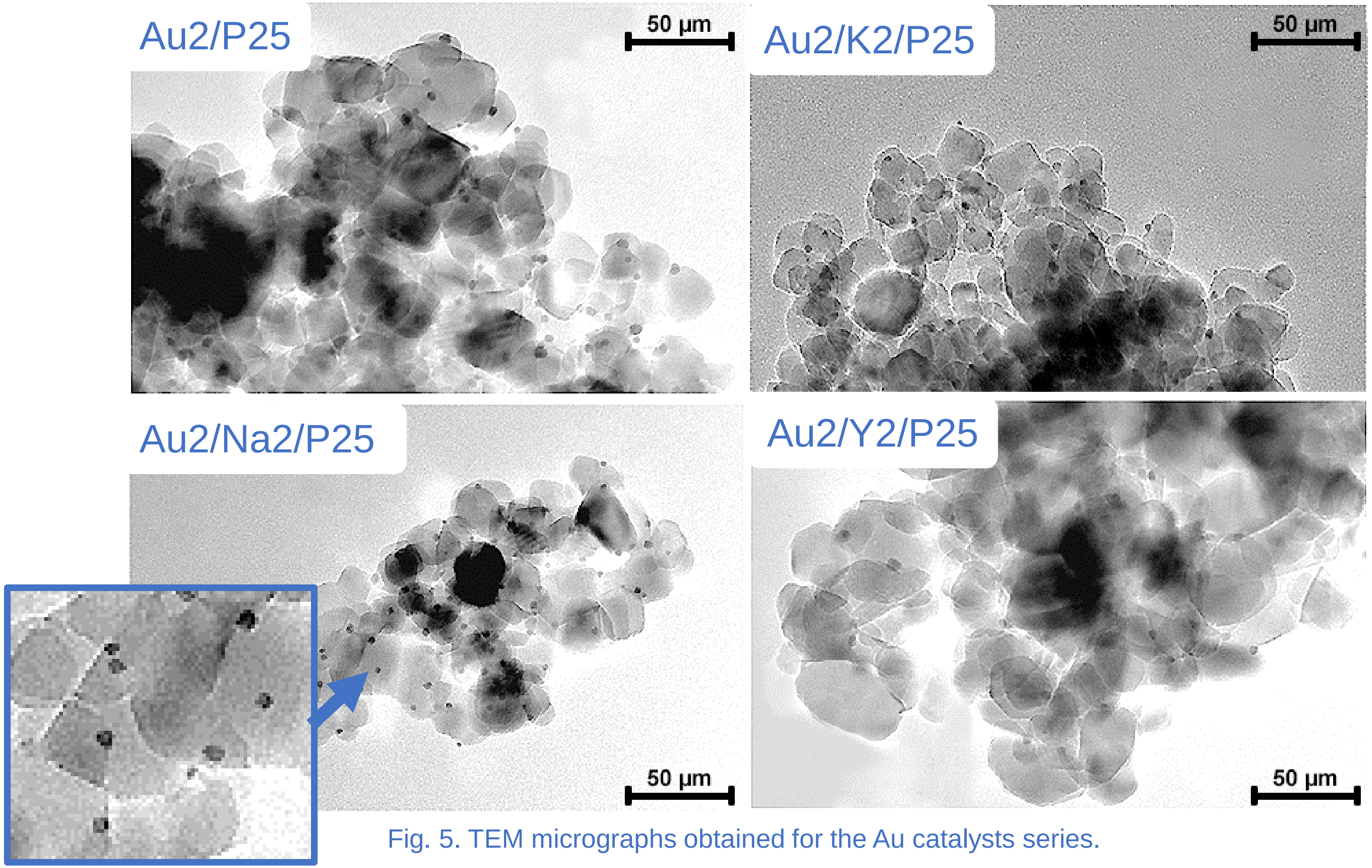


Fig. 5. TEM micrographs obtained for the Au catalysts series.

- spherical anatase
- angular rutile
- round small gold NPs

Characterisation of NPs: Particle size

- **Y-doping:** smallest particles
- **Na-doping:** biggest particles

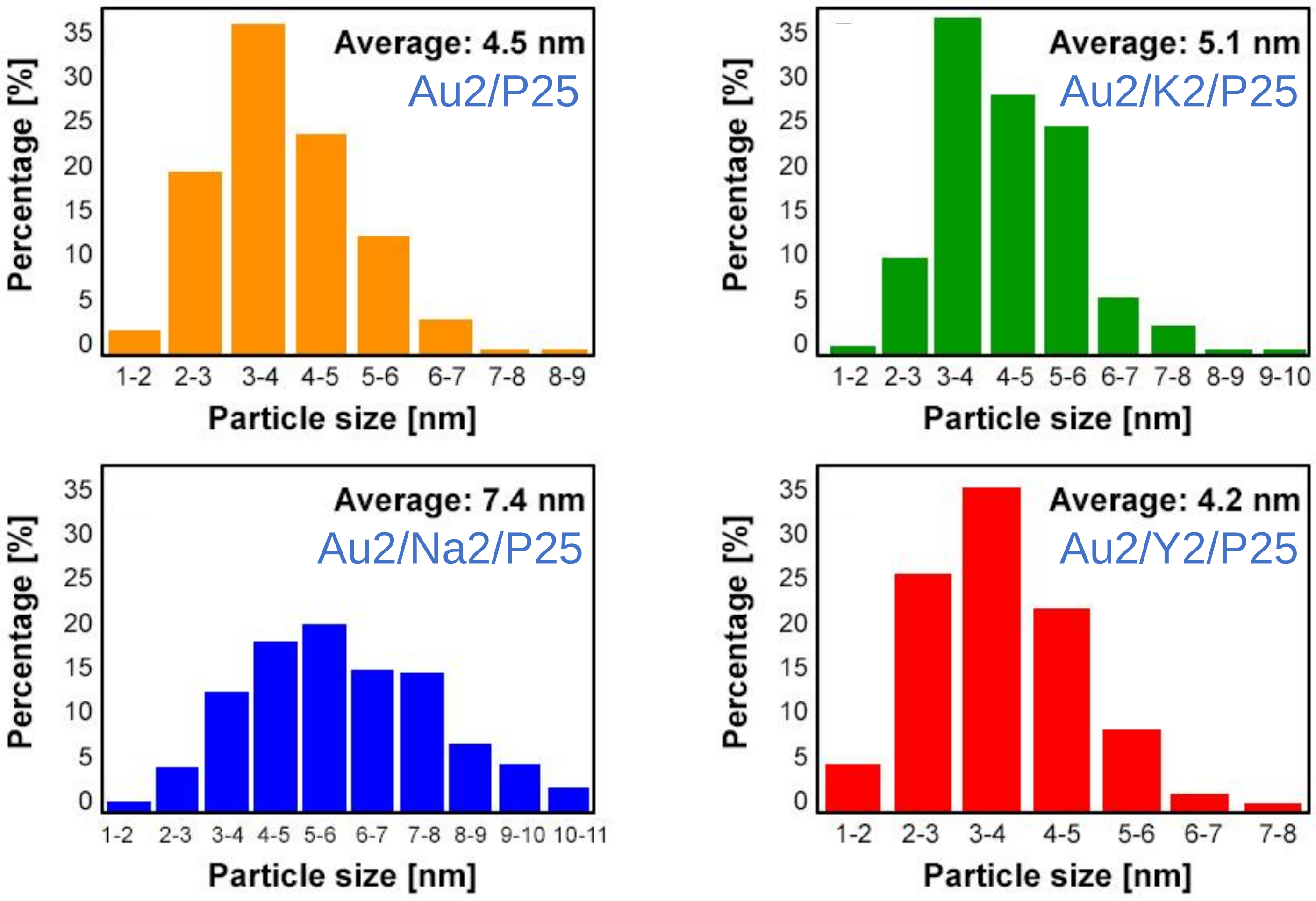


Fig. 6. Histograms of particle size distribution for the Au catalysts series.

Pre-screening photocatalysis experiments

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- **lowest performance:** acidic pH
- **best performance:** pH 7
  - Au2/Y2/P25
  - Au2/Y5/P25
  - Au2/K2/P25
  - Au2/K10/P25

  pH 10
  - Na-doped

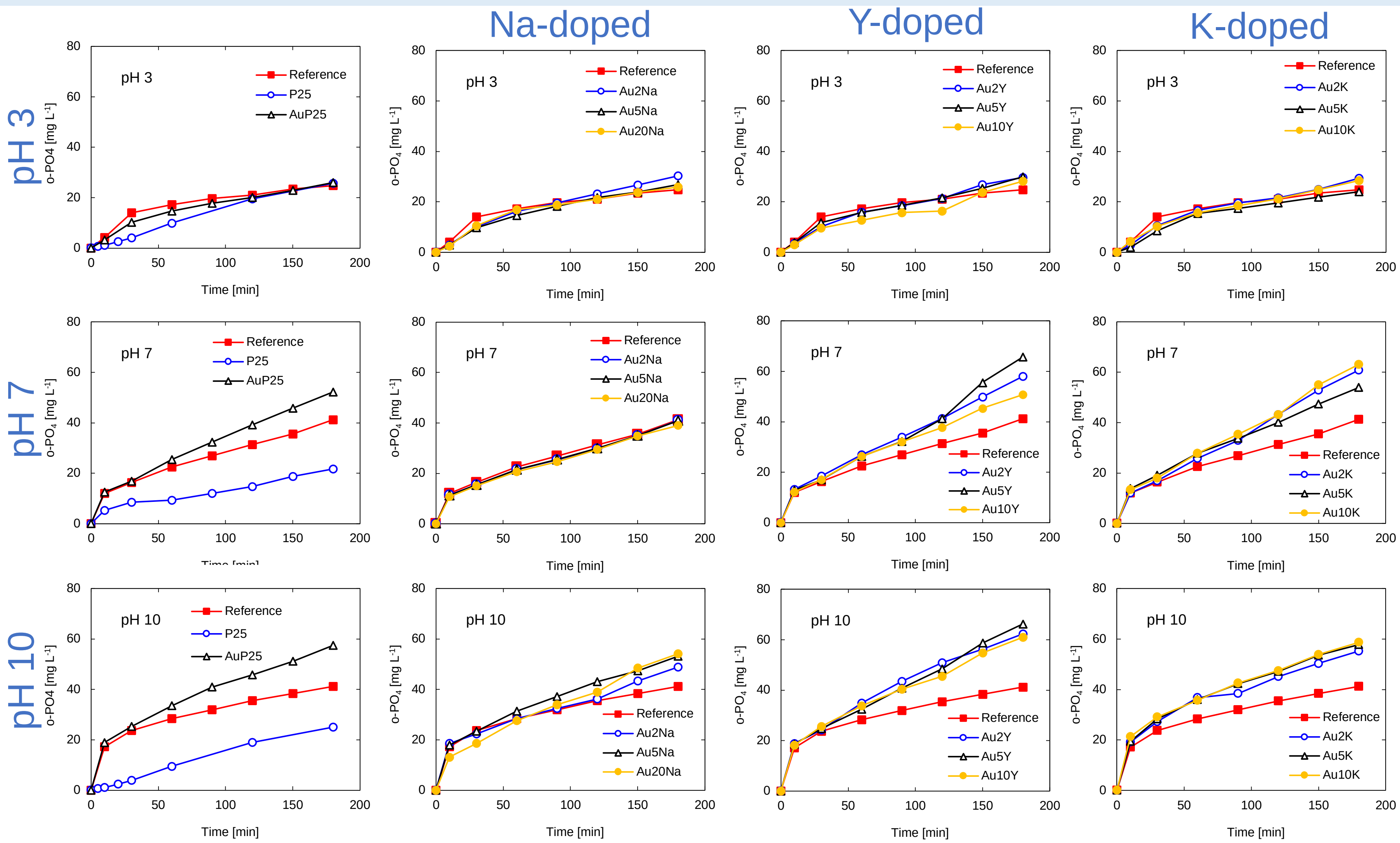

Fig. 7. o-$PO4^{3-}$ Release of pre-screening photocatalysis (100 mg L^{-1} EDTMP, pH 3;7;10).

Performance of selected NPs

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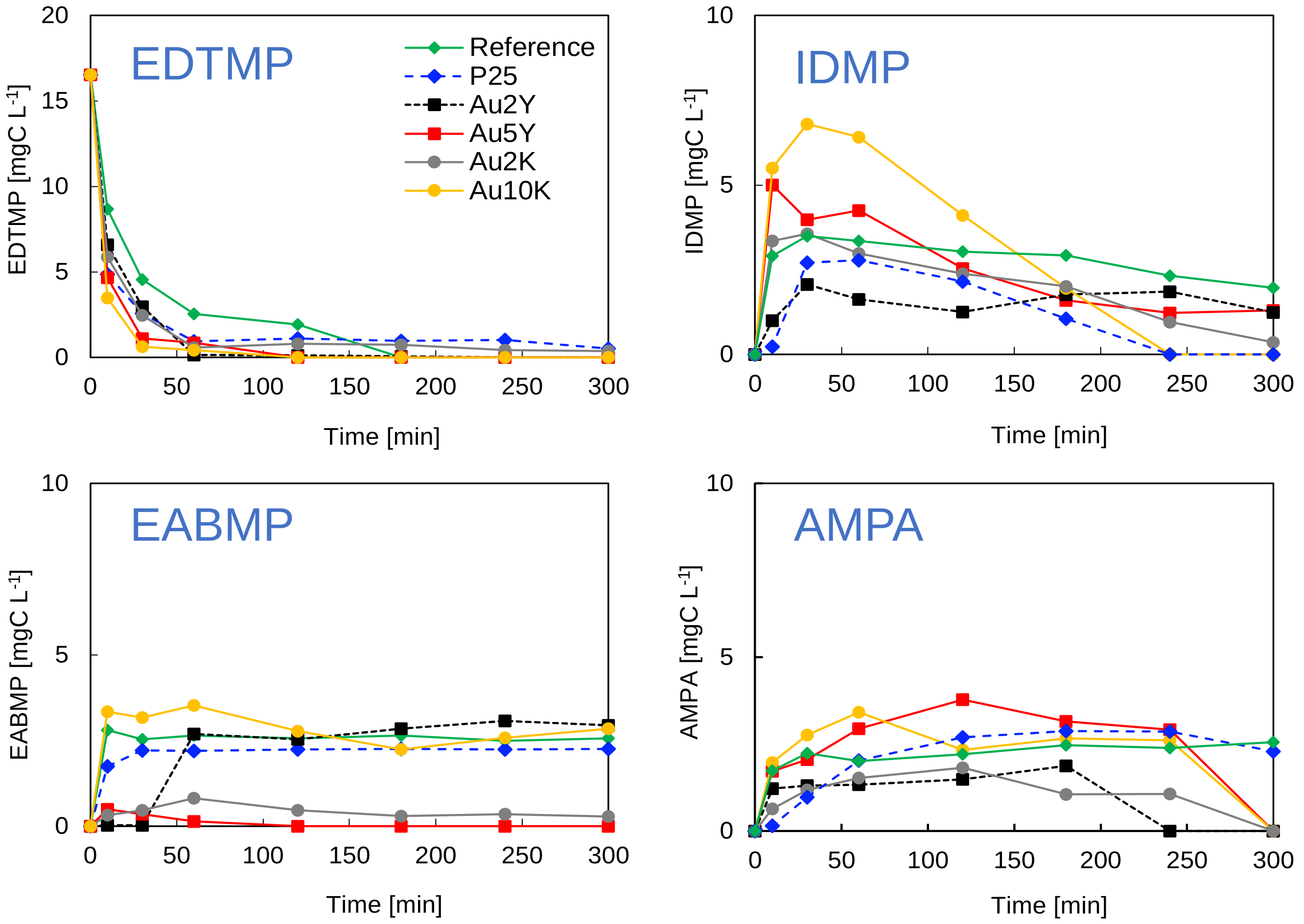

LC-MS

Fig. 8. Long-term photocatalysis (100 mg L^{-1} EDTMP, pH 7).

Tab. 1. $o\text{-}PO_4^{3-}$ release and mass balance.

[%]	$o\text{-}PO_4^{3-}$ release	P gap [%]	C gap [%]	N gap [%]
Reference	47	0	54	21
Au2/Y2/P25	88	0	74	75
Au2/Y5/P25	92	0	92	88
Au2/K2/P25	79	15	96	95
Au2/K10/P25	88	0	82	87
P25	65	0	69	45

- rapid degradation of EDTMP in 60 min
- doubled $o\text{-}PO_4^{3-}$ release Au2/Y5/P25

Influence of selected NPs on the kinetics

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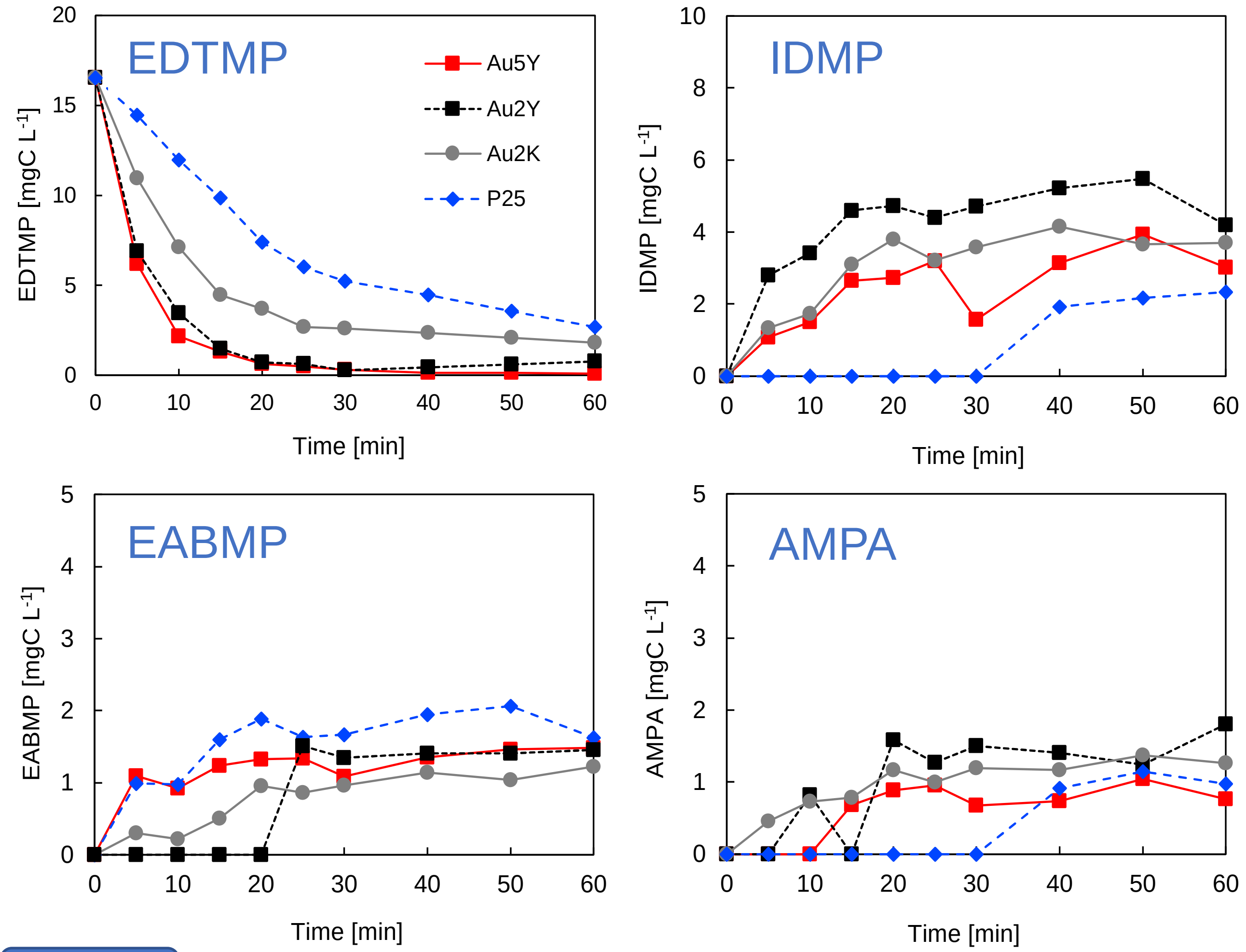


LC-MS

Fig. 9. 60-min-photocatalysis (100 mg L^{-1} EDTMP, pH 7).

Tab. 2. Degradation rate constants and half-life of EDTMP.

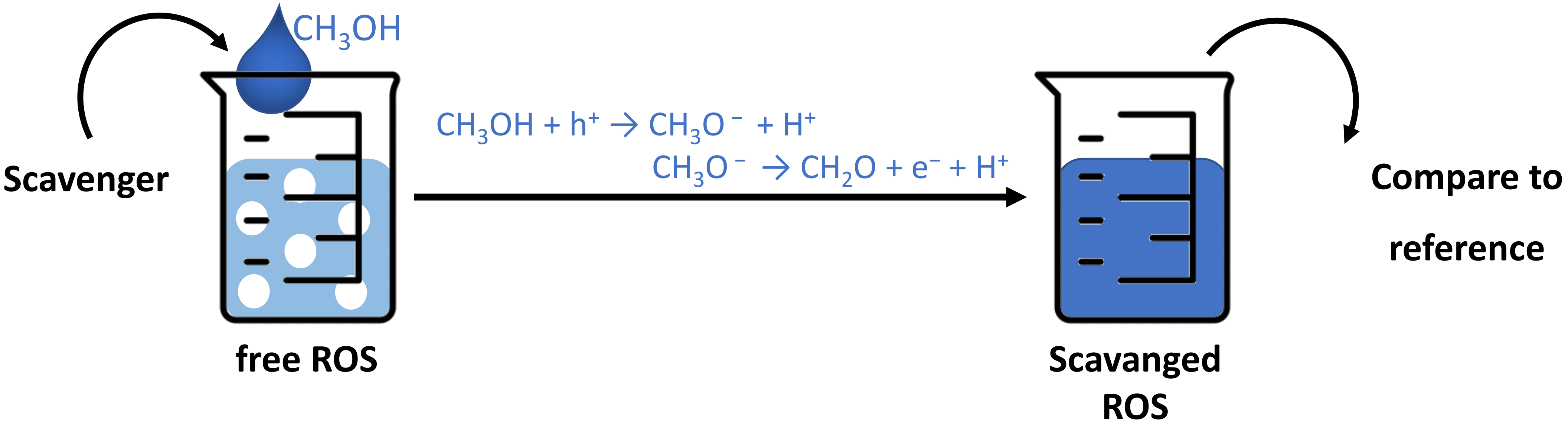
Catalyst	k_{uv} [s^{-1}]	Half-life [min]	RSS*
Au2/Y2/P25	2.9 E^{-3}	3.9	8.4
Au2/Y5/P25	3.9 E^{-3}	2.9	54.4
Au2/K2/P25	1.9 E^{-3}	6.0	60.7
P25	9.8 E^{-4}	11.7	54.1

- highest k_{UV} & lowest $t_{1/2}$: Au2/Y5/P25

*RSS: Residual sum of squares

Scavengers

- **aim:** investigate reactive species responsible for target degradation
- **method:**



https://doi.org/10.1016/j.xcrp.2022.100889

Determination of ROS by scavengers

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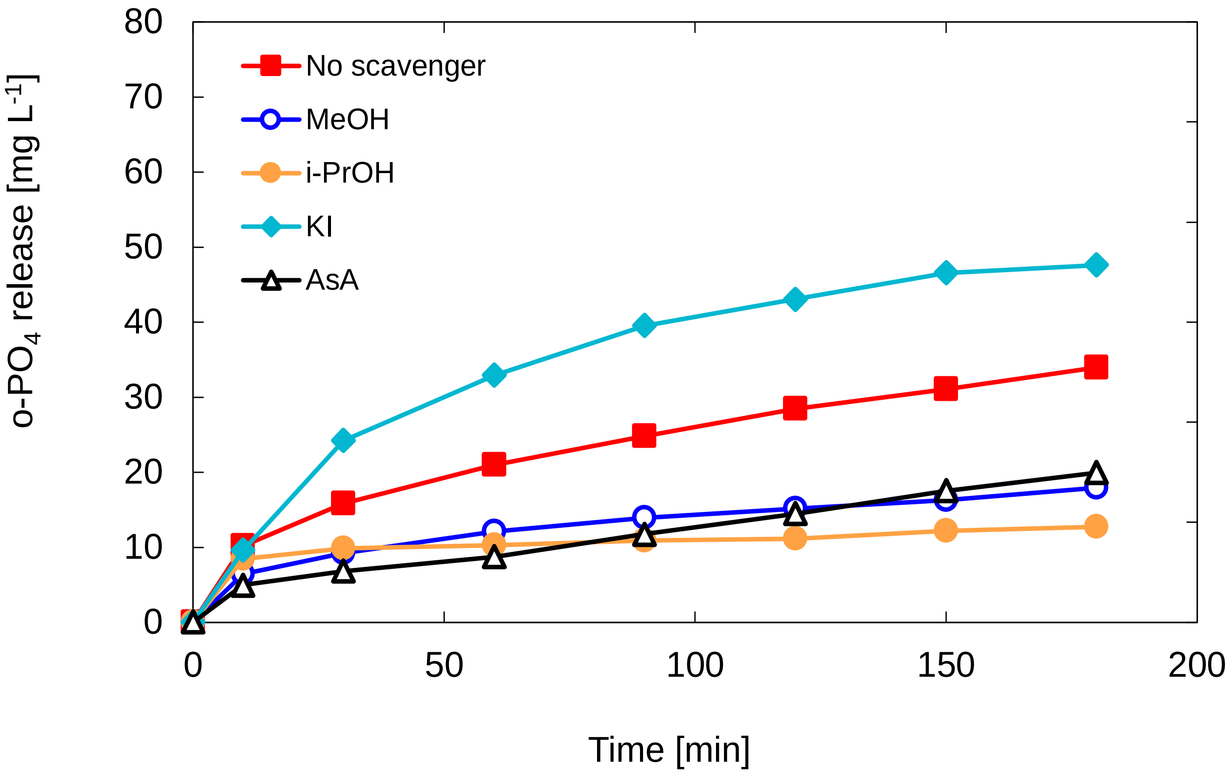

Fig. 10. Scavenger tests with 100 mg L-1 EDTMP and 100 mg L^{-1} Au2/Y5/P25, pH 7.

Tab. 2. P release of EDTMP during photocatalysis (Au2/Y5/P25, pH 7, scavenger).

Condition	Scavenged ROS	Scavenged medium	P release	
			$o\text{-}PO_4^{3-}$ [mg L^{-1}]	$o\text{-}PO_4^{3-}$ [%]
Without	-	-	33	38
MeOH	h^+ & •OH	Bulk and surface	19	21
i-PrOH	•OH	Bulk	12	14
KI	•OH & h^+	Surface	47	54
AsA	$•O_2^-$	Bulk	14	17

- **primary ROS:** •OH (bulk) & h^+ (surface)

Influence of the dopants

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Au: Inhibit e^-/h^+ recom-bining

Anatase > rutile

TiO_2

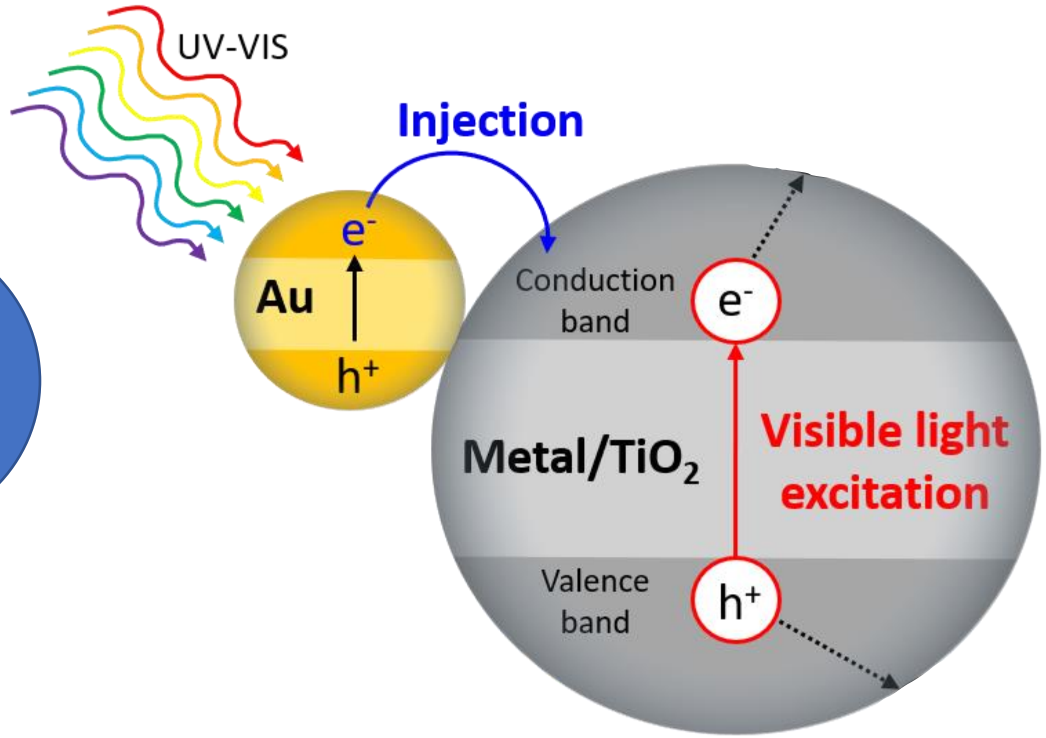
K: VLA but poor binding

2 % K $t_{1/2}$ 6 min

Na: poor binding

Y: small d_p & VLA & good binding

5 % Y $t_{1/2}$ 3 min



VLA: Visible light absorption

Mechanism of photocatalytic EDTMP degradation

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- degradation mechanism similar to photochemical processes
- 4 fold enhanced kinetics