

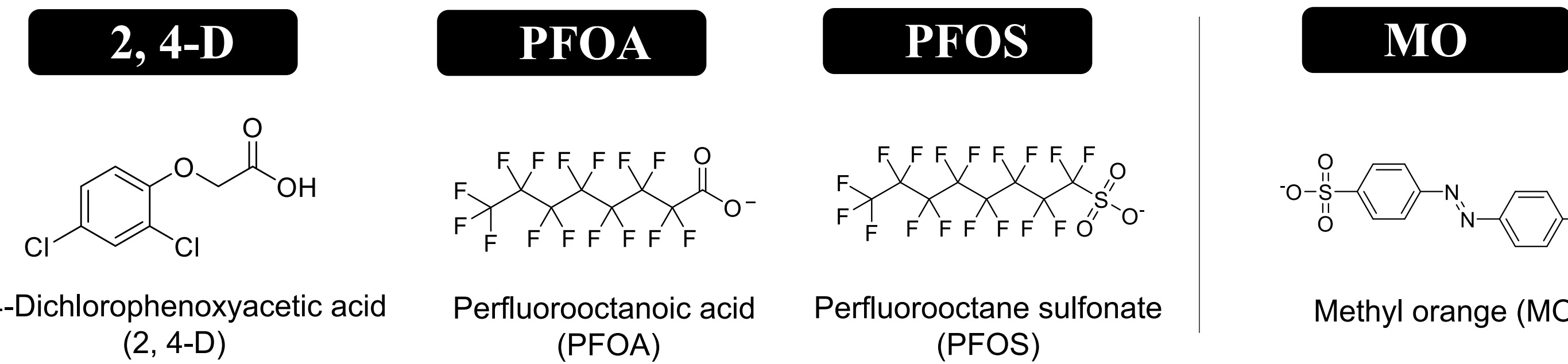
Perovskite Photocatalysts for Environmental Remediation

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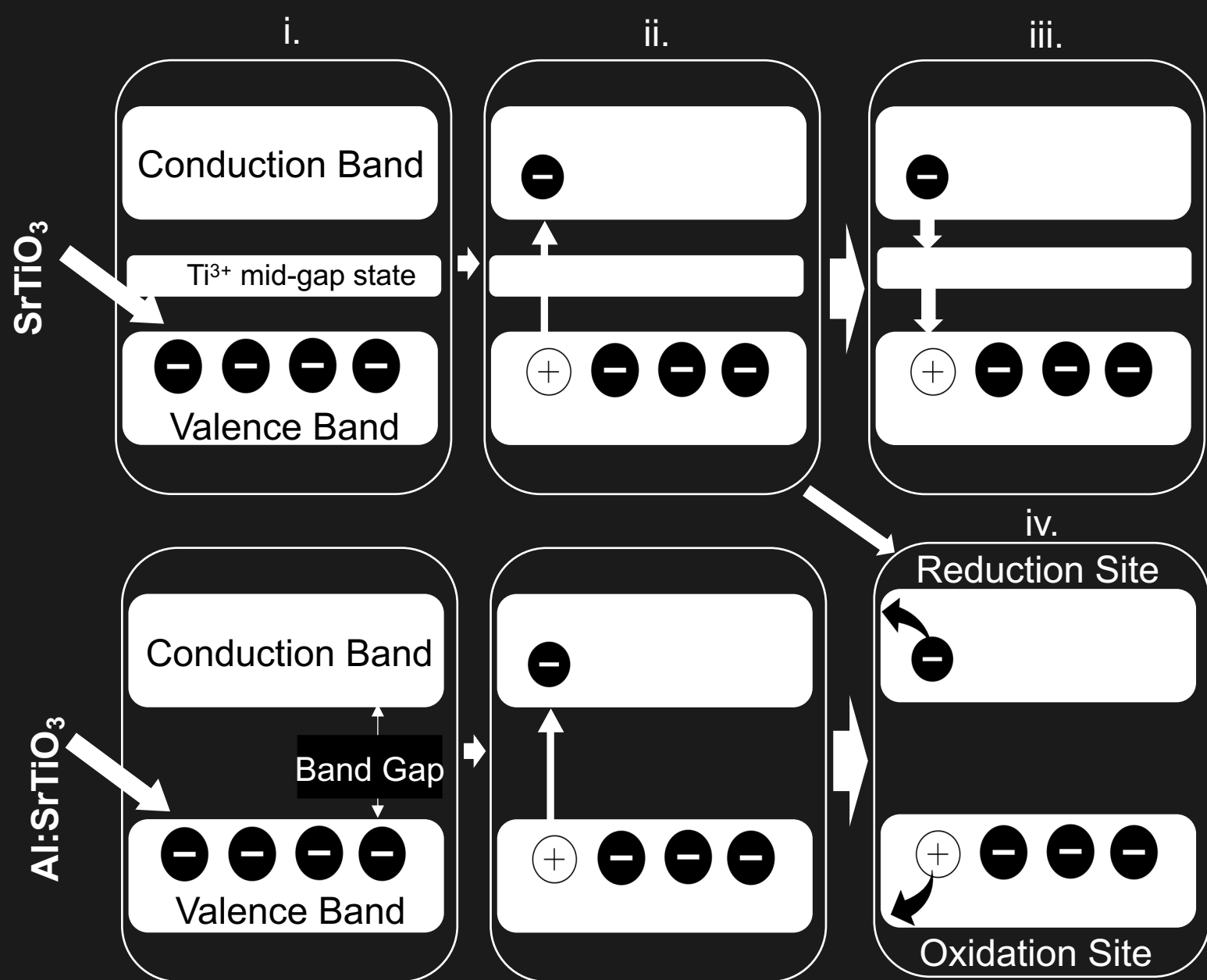
Persistent Organic Pollutants (POPs)

Persistent organic pollutants (POPs) are a class of organic compounds recognized by the Stockholm Convention as posing a significant threat to the health of humans, organisms, and ecosystems. POPs contain strong C-Cl and C-F bonds making them impervious to environmental degradation including metabolic and bacterial breakdown, hydrolysis, and photolysis (example POPs shown below (left)).



There is an imperative need to develop an effective method of degradation for these compounds to mitigate their emerging health and environmental impacts. Photocatalysts can break these C-Cl and C-F bonds. Methyl orange (MO) (shown on the right) is used as a model pollutant to monitor photocatalytic efficiency.

Photocatalysis



i. Illumination- Light incident on the photocatalyst with greater energy than the band gap of the semiconductor.

ii. Excitation- Absorption of this light produces an excited electron in the conduction band and leaves a positively charged hole in the valence band.

iii. Recombination- Relaxation of the excited electron to the valence band.

iv. Migration and Reduction/ Oxidation - Excited electrons and holes migrate to semiconductor surface with the ability to reduce and oxidise species, such as pollutants, into benign by-products.

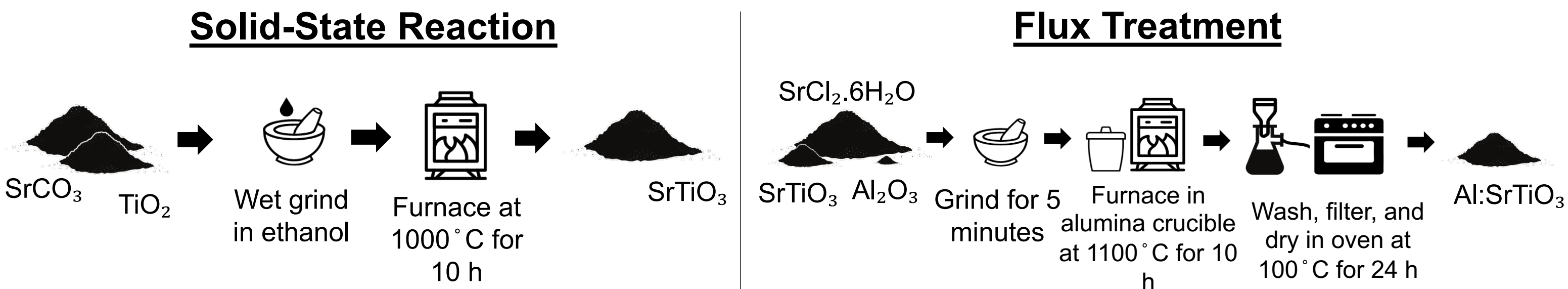
Advances in water splitting have utilised SrTiO_3 , however, it is not yet known if these photocatalysts are transferable for use in pollutant degradation.

Photocatalysts, by nature, are reusable and have been shown to break the strong C-Cl and C-F bonds present in all POPs.

Relaxation of the excited electron to the valence band (recombination) limits photocatalytic efficiency. Aliovalent doping of perovskite lattices can help reduce recombination rates.

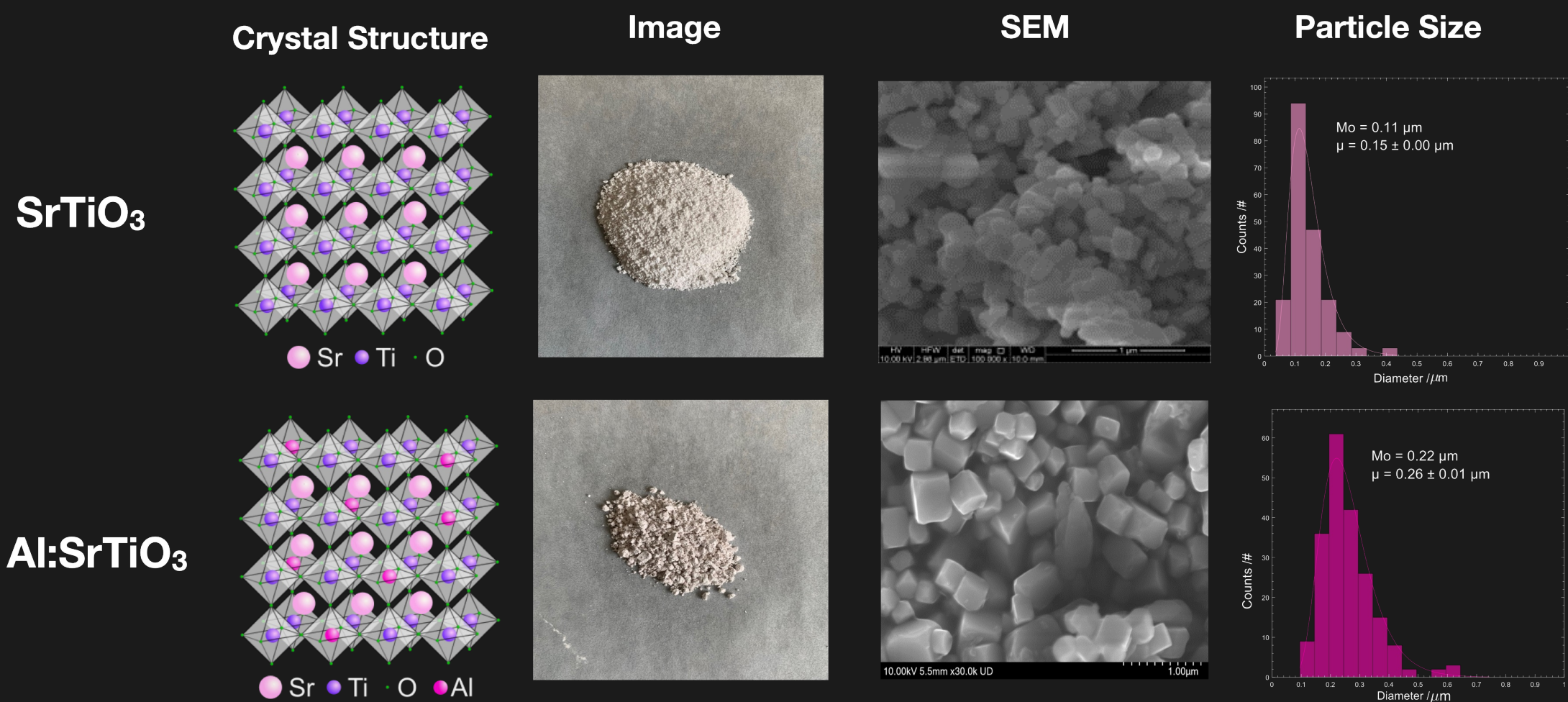
Photocatalysis is a catalysis process whereby, upon illumination, reactive species are formed on the particle surface. These reactive species can drive reduction/ oxidation reactions such as water splitting or POP mineralisation.

Synthesis



Al³⁺ Doping to Improve Photocatalysis

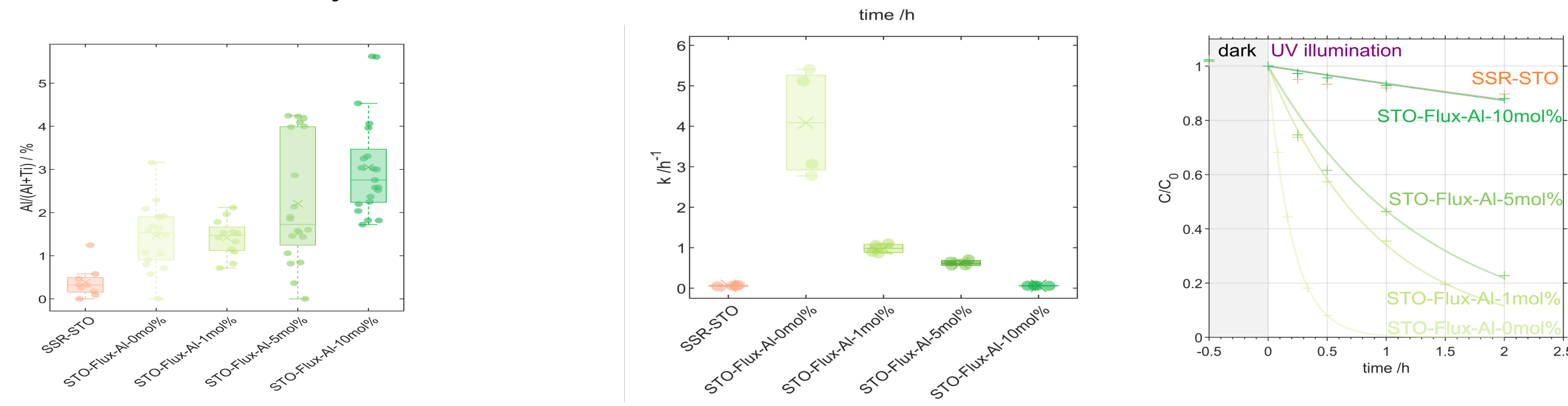
The molten flux synthesis facilitates the aliovalent doping of Al^{3+} into the SrTiO_3 lattice ($\text{Al}:\text{SrTiO}_3$). This process also causes a change in particle morphology (shown in SEM images), resulting in photocatalysts with improved crystallinity (confirmed by reduced peak width in XRD).



Effect of Doping

At these high temperatures, the molten $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ salt partially solubilises the Al_2O_3 and alumina crucible, enabling Al^{3+} ions to replace Ti cations. The incorporation of Al^{3+} into the lattice is confirmed by EDS.

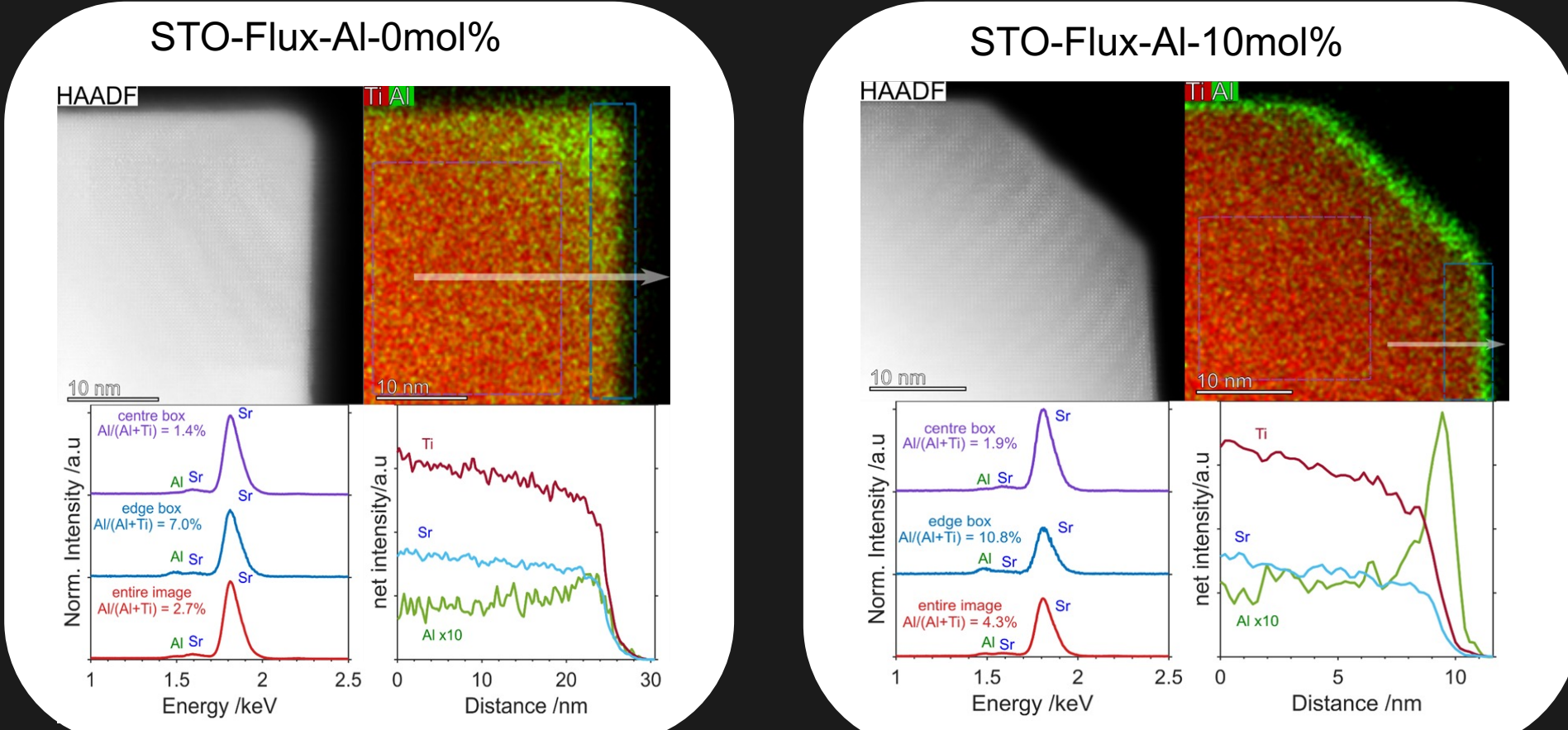
Oxygen vacancies in the perovskite lattice cause the self-reduction of Ti^{4+} to Ti^{3+} . The formed Ti^{3+} empty electronic band is situated within the band gap of SrTiO_3 , thus, facilitating recombination and reducing photocatalytic efficiency. Doping SrTiO_3 with Al^{3+} prevents the formation of the Ti^{3+} mid-gap state, thereby improving photocatalytic efficiency. Al doping was shown to improve photocatalytic efficiency by 100-fold!



BUT WHY DOESN'T EFFICIENCY CONTINUE TO INCREASE WITH Al DOPING?

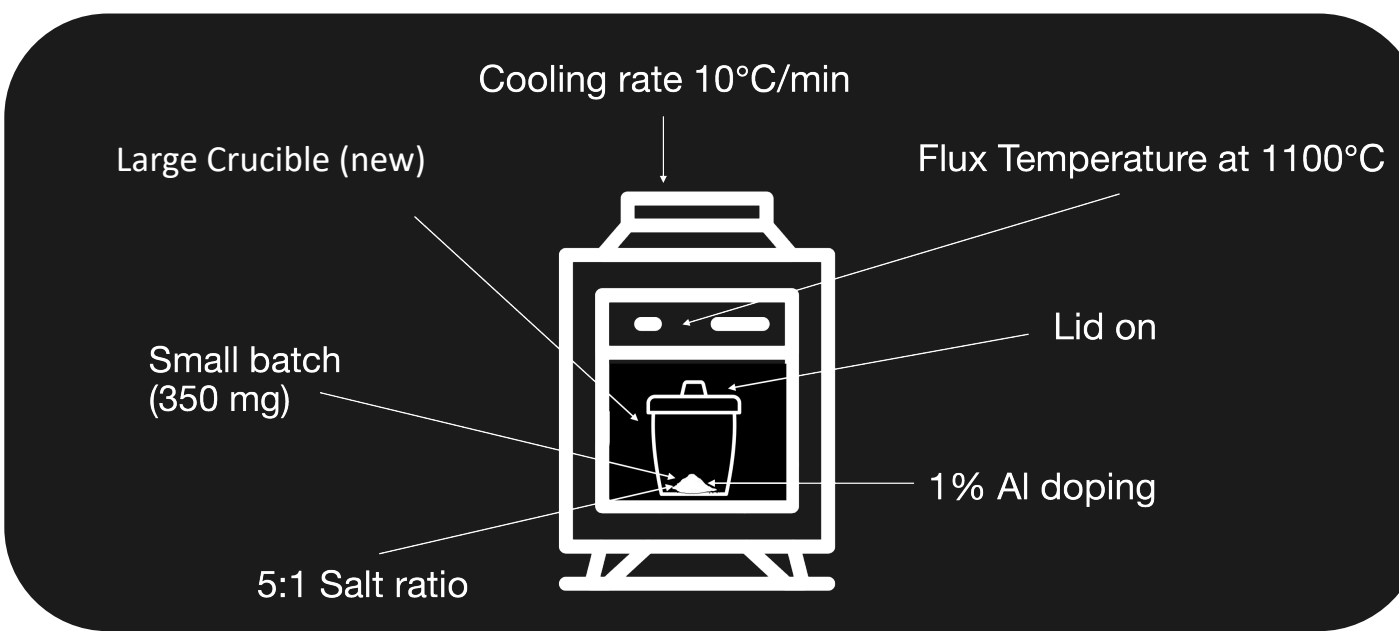
TEM Analysis

High resolution transition electron microscopy (TEM) with elemental mapping identifies a thin (1-2 nm) layer of enriched Al doping at the particle surface. This Al shell likely inhibits interactions between the photocatalyst and model pollutant. Therefore, high Al doping % reduces photocatalytic efficiency due to the formation of the Al shell.



Optimising Conditions

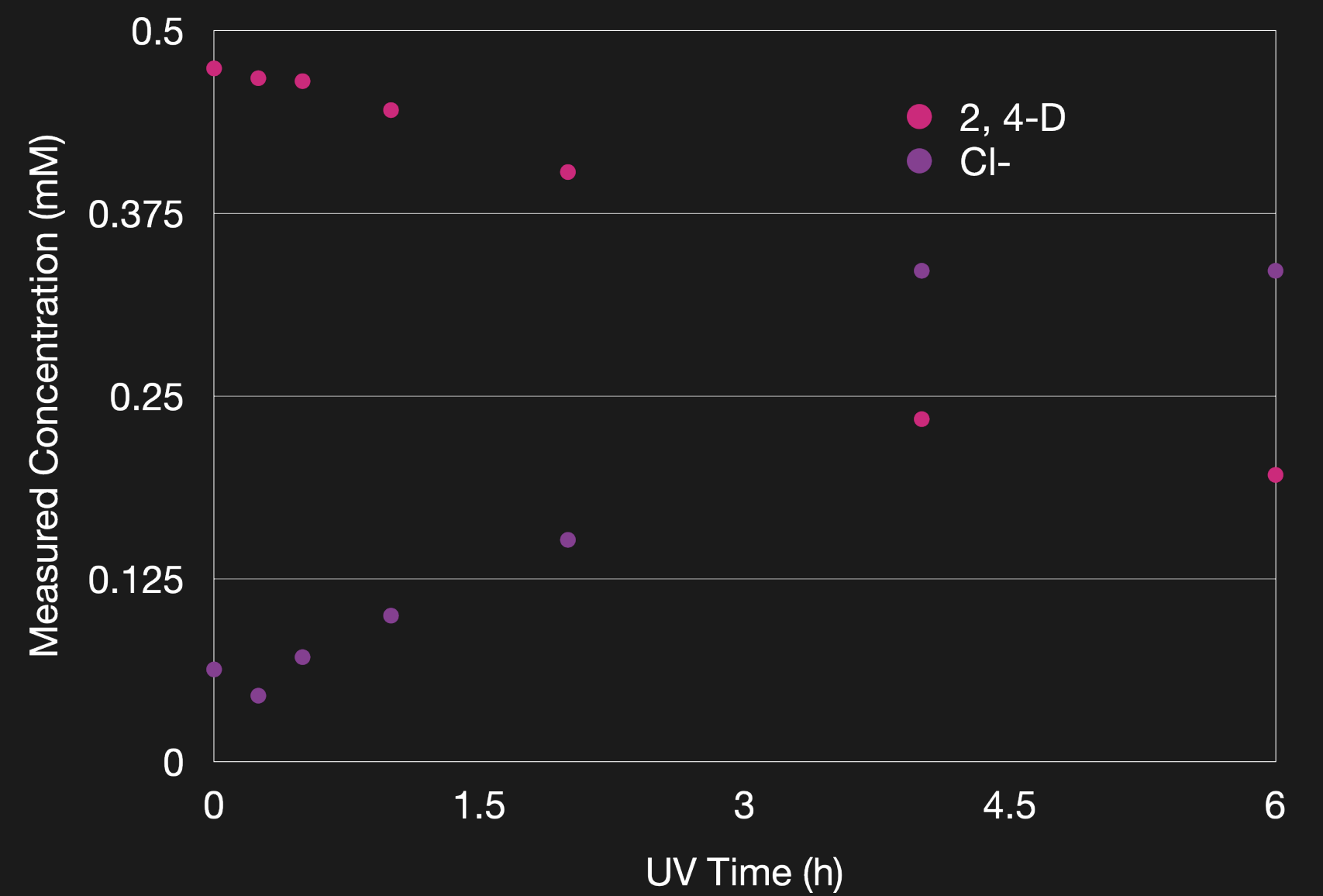
Early results showed high variability between syntheses. Aimed to alter synthesis conditions to optimise performance and reproducibility.



Experiments determined synthesis conditions (depicted on the left) to be ideal for producing and active and reproducible photocatalyst.

2, 4-D Degradation

2,4-Dichlorophenoxyacetic acid (2, 4-D) is a chlorinated pesticide that is commonly used to target broadleaf weeds. The degradation of 2, 4-D (right) was achieved via a photocatalysis reaction using $\text{Al}:\text{SrTiO}_3$ photocatalysts under 365 nm LED lights. Degradation products were monitored using UV-Vis spectroscopy and an ion-selective electrode. The decrease in 2, 4-D concentration corresponds with an increase in Cl^- concentration. This suggests that the photocatalysis reaction is successfully breaking the strong C-Cl bonds present in all POPs, liberating Cl^- ions.



Conclusions

Al doping SrTiO_3 improves photocatalytic efficiency.

Too much Al forms a shell and inhibits photocatalysis.

$\text{Al}:\text{SrTiO}_3$ can break C-Cl bonds present in 2, 4-D.

Other factors can influence photocatalytic efficiency.