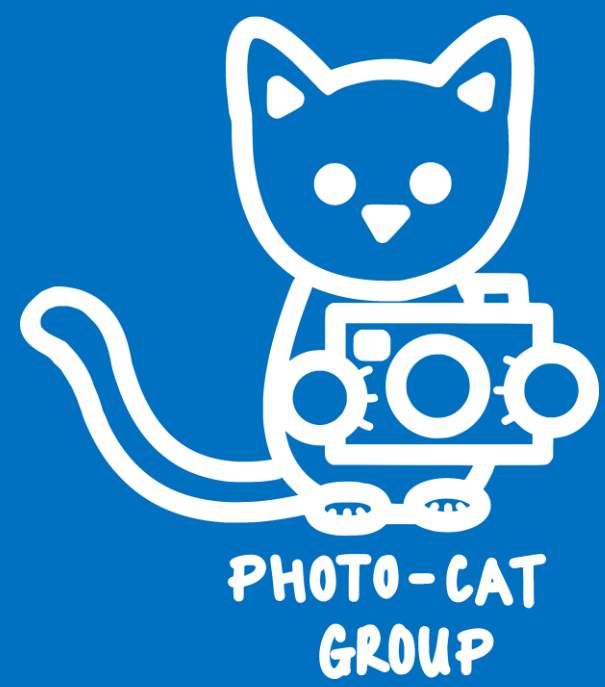
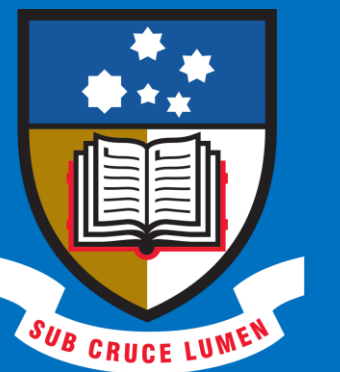




Tantalum-Based Metal Oxides for the Photocatalytic Degradation of PFAS

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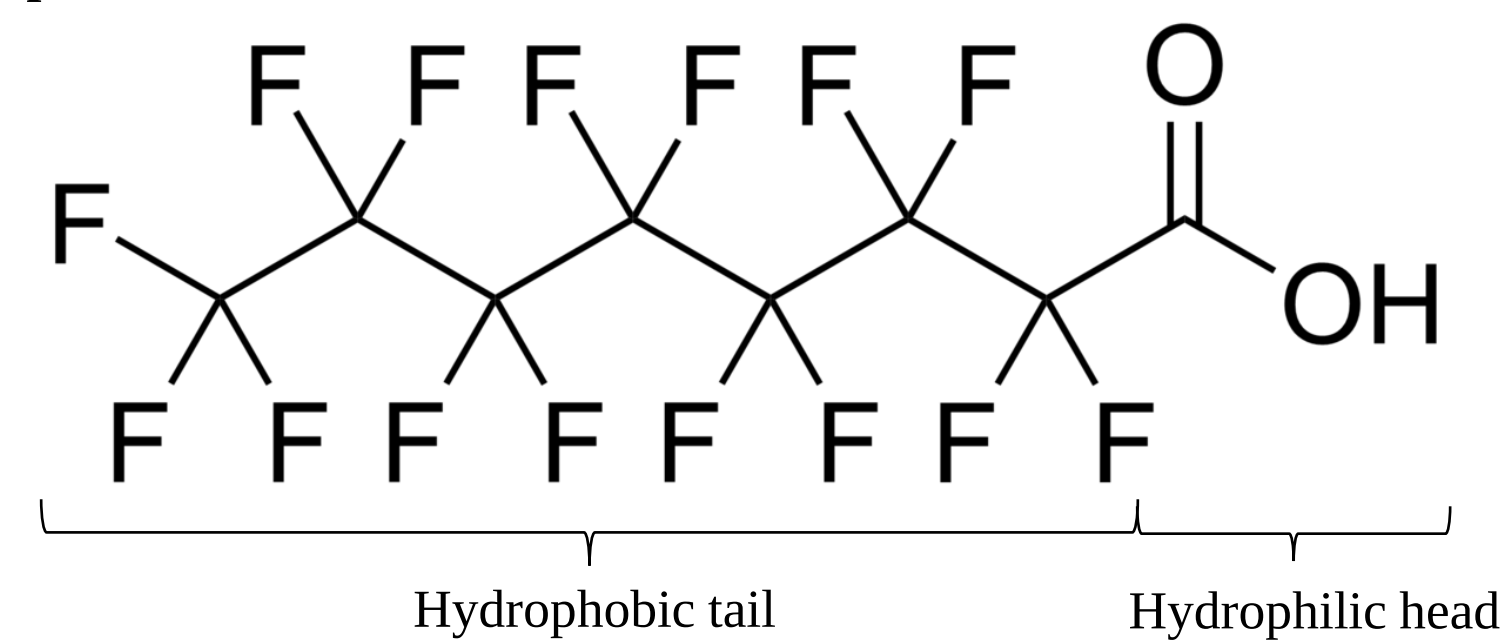


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Per- or Polyfluoroalkyl Substances (PFAS)

PFAS are a large group of synthetic chemicals known widely for their beneficial applications in industry, such as in non-stick coatings of cookware, waterproof goods, greaseproof packaging and firefighting foams.

These beneficial properties can be attributed to their unique chemical structure which contains both hydrophobic and hydrophilic areas.



The presence of many C-F single bonds renders PFAS recalcitrant to biodegradation and other chemical destruction techniques.

PFAS are ubiquitous, toxic, and their overuse in industry has resulted in widespread contamination across the globe.

Some current destruction techniques can achieve high PFAS conversion, however the products of degradation are short chain PFAS and fluorocarbon greenhouse gases, both of which are toxic and persistent.

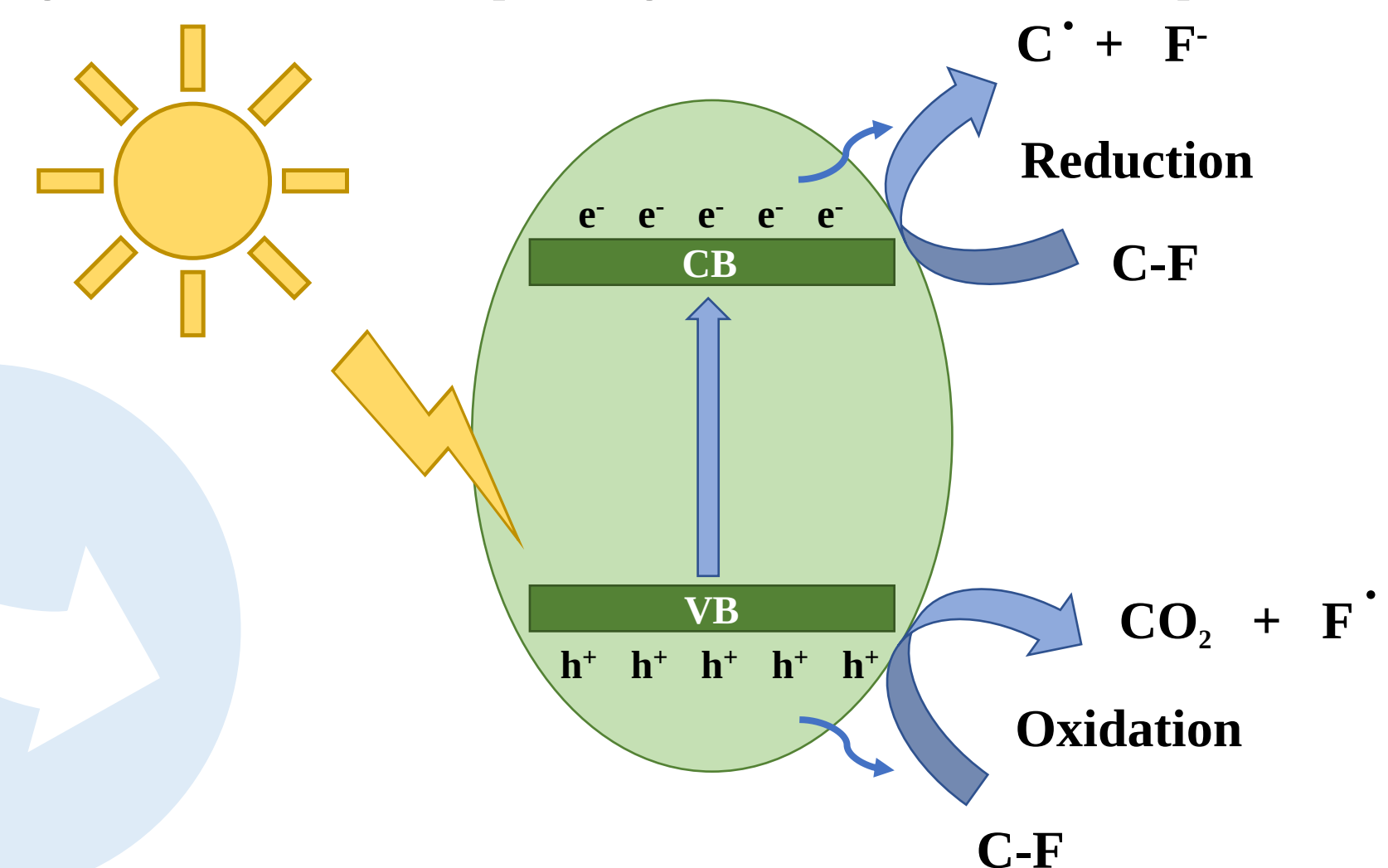
There is an imminent need to develop alternative degradation techniques that are effective at mineralising PFAS into its most non-toxic products, CO₂ and F⁻.

Photocatalysis for PFAS Degradation

Photocatalysis is a process where materials that absorb light can be used to drive chemical reactions.

Semiconductors are typically used due to the small gap between their occupied valence band and unoccupied conduction band that allows for the excitation of electrons when provided with energy.

This can drive oxidation/reduction processes including the degradation of PFAS depending on the material's redox potential.



Basic photocatalytic process for PFAS degradation.

Transition metal doping has proven to improve photocatalytic activity by reducing the electron-hole recombination.

Studies using TiO₂ under UV irradiation have reported 100 % PFAS conversion, but only 34.8 % mineralisation.¹

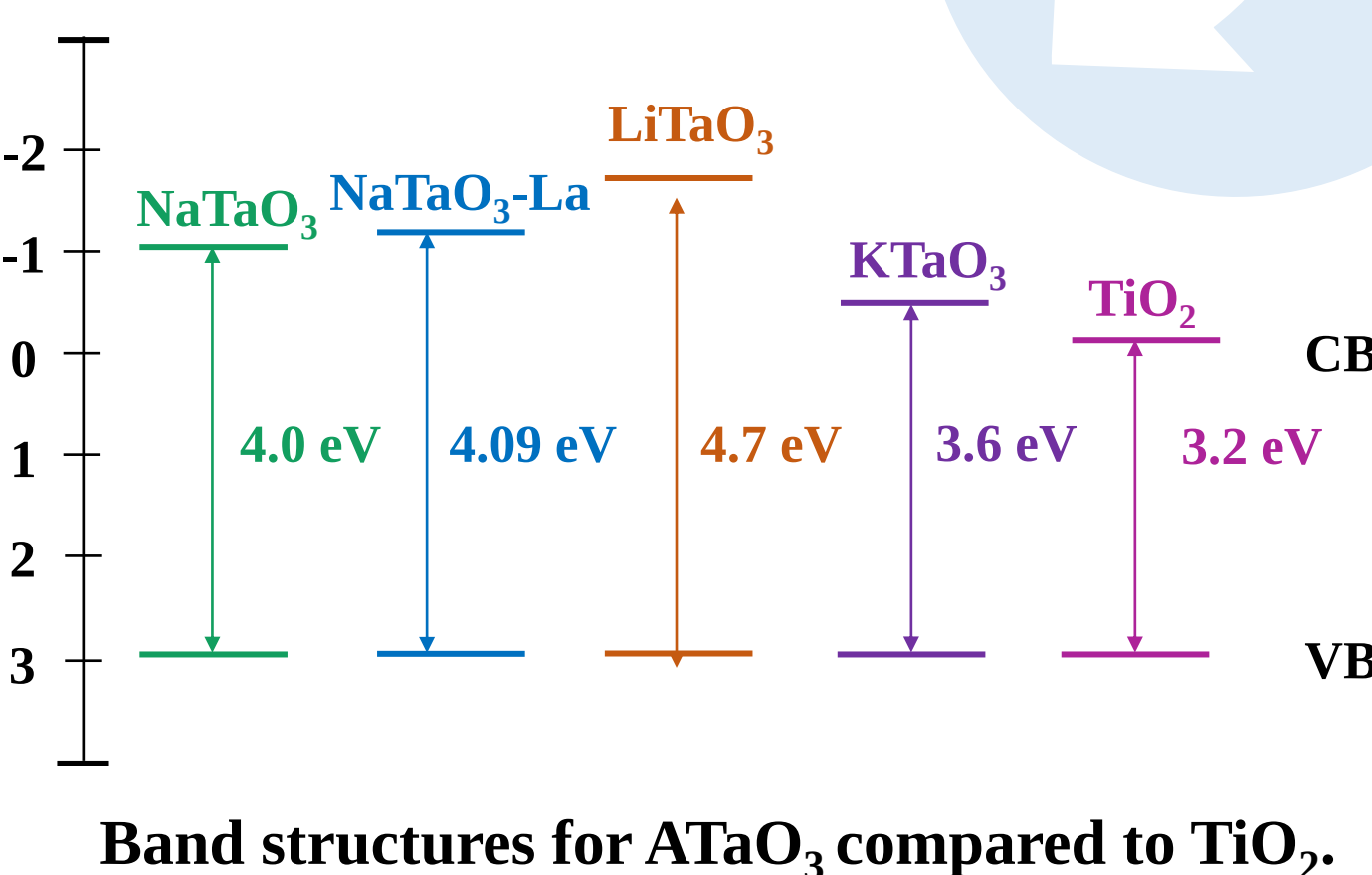
As complete mineralisation is still difficult, other semiconductors with greater redox potentials need to be explored.

Tantalum-Based Metal Oxides

Tantalum-based metal oxides have been widely researched for the application of water splitting and are among the most efficient photocatalysts for this purpose to date.²

They have wide band gaps (> 3.5 eV) which allow for greater redox potentials, and La doping has found to improve photocatalytic activity by modifying the surface of the photocatalyst.²

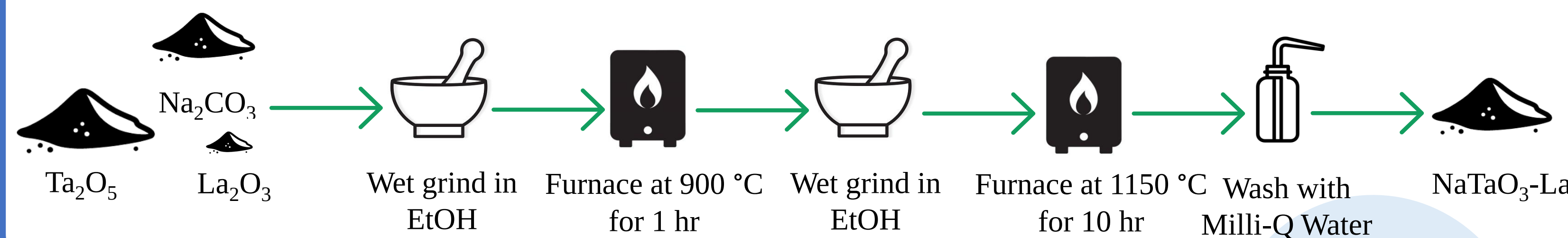
UV irradiation is required to initiate photocatalytic reactions which renders their use uneconomical for most applications, however they have not yet been considered for PFAS degradation.



Research Aims

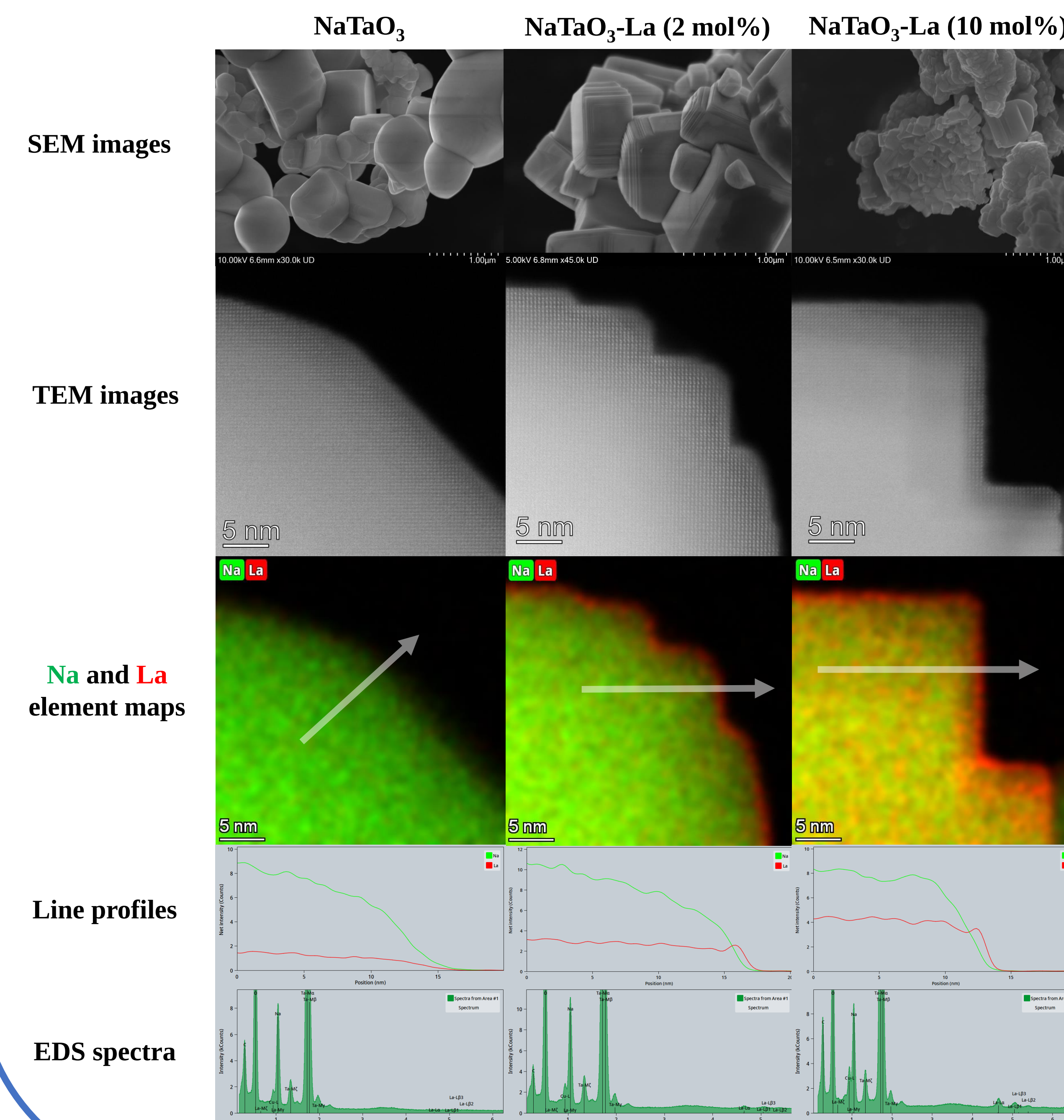
1. Explore the effect of varying the La mol % doping in NaTaO₃ on photocatalytic activity.
2. Determine the products of PFOA degradation via photocatalysis with La-doped NaTaO₃ using and liquid chromatography-high resolution mass spectrometry (LC-HRMS).
3. Monitor F⁻ production using an ion selective electrode (ISE) to determine % mineralisation.

Solid-State Synthesis of NaTaO₃-La

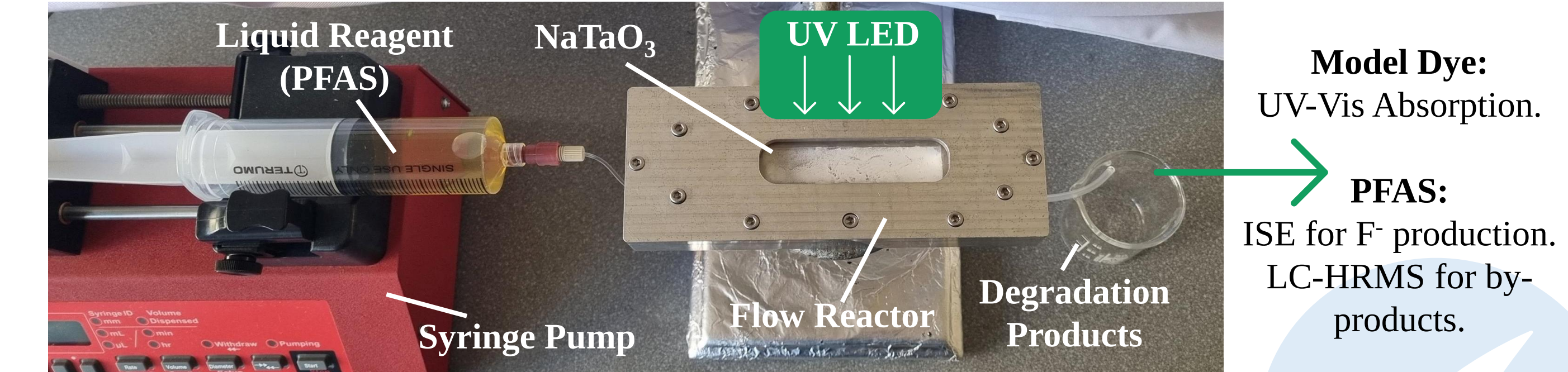


NaTaO₃-La Characterisation

Scanning electron microscopy (SEM) revealed terrace-like features on the nanoparticles that increases with La mol % doping. High resolution transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS) confirmed increasing La content and identified La to be incorporated at the surface.



Continuous Flow Photocatalysis Reactions



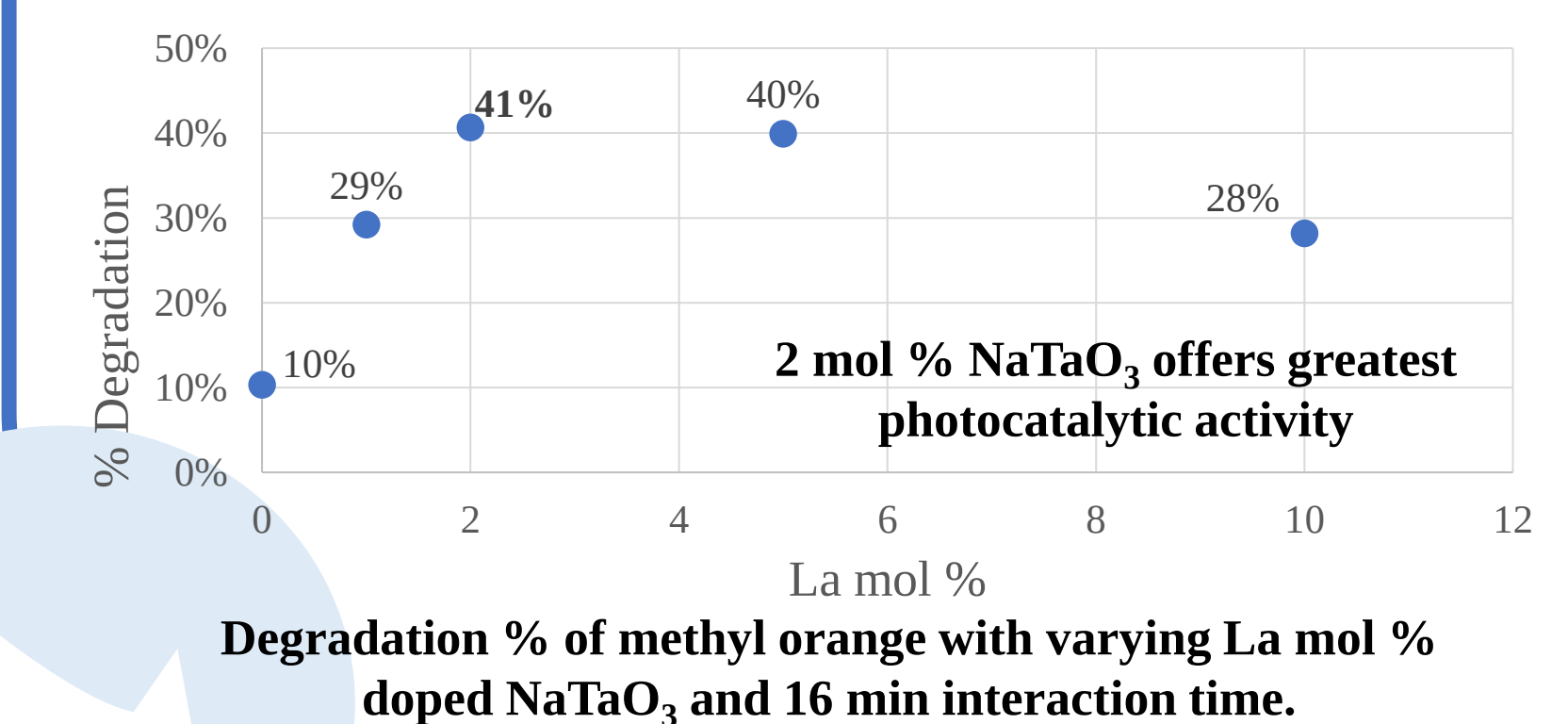
Methyl Orange Model Dye

Methyl orange is a model textile dye that can be used to predict photocatalytic activity.³

PFAS and methyl orange are both anionic, and perfluorooctanesulfonic acid (PFOS) shares the same head group (SO₃⁻).

Model dye photocatalysis reactions found La doping to improve the photocatalytic activity of NaTaO₃.

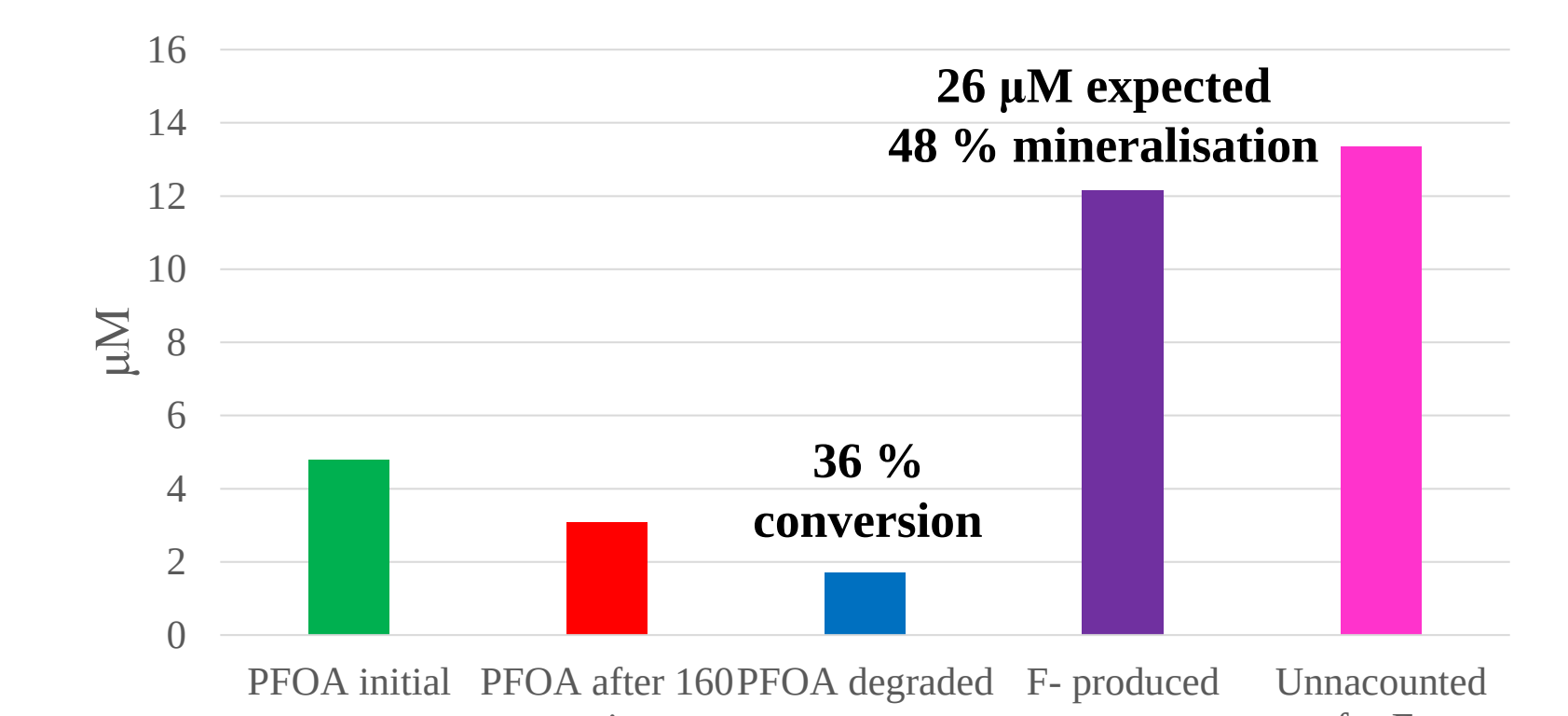
2 mol % La was found to be optimal, with higher La % still active due to similar La-rich shells observed in TEM.



PFOA

Perfluorooctanoic acid (PFOA) is the 8 carbon, carboxylic acid PFAS and is one of the most common PFAS contributing to global contamination.

PFOA photocatalysis reactions with NaTaO₃-La (2 mol%) showed successful degradation after 160 min interaction time.



PFOA degradation products after 160 min interaction time. 48 % mineralisation is relatively high compared to the 4 % mineralisation achieved with TiO₂ under the same conditions.

Analysis via LC-HRMS revealed no obvious conversion to short chain PFAS molecules.

Future experiments will investigate longer interaction times to potentially increase the PFOA conversion %.

Conclusions & Future Work

Doping with La was found to improve the photocatalytic activity of NaTaO₃ nanoparticles, with 2 mol % La offering the greatest photocatalytic activity in photocatalysis reactions with a model dye (41 %).

Photocatalysis reactions with PFOA and the 2 mol % La-doped NaTaO₃ photocatalyst showed successful degradation, with 36 % PFOA conversion and 48 % mineralisation achieved. No obvious conversion to short chain PFAS molecules was observed via LC-HRMS analysis, leaving 52 % of F⁻ unaccounted for.

Future work will investigate longer interaction times to hopefully increase the PFOA conversion % and further increase mineralisation. The photocatalytic activity of LiTaO₃ and KTaO₃ for PFAS degradation will further be explored & compared.

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