Intrinsic hazard properties characterisation

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Innovating with Purpose: A Hands-on Journey into Functional, Safe & Sustainable **Advanced Materials**

Why AdMa?

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Opinion

From small to clever: What does the future hold for the safety and sustainability of advanced materials?

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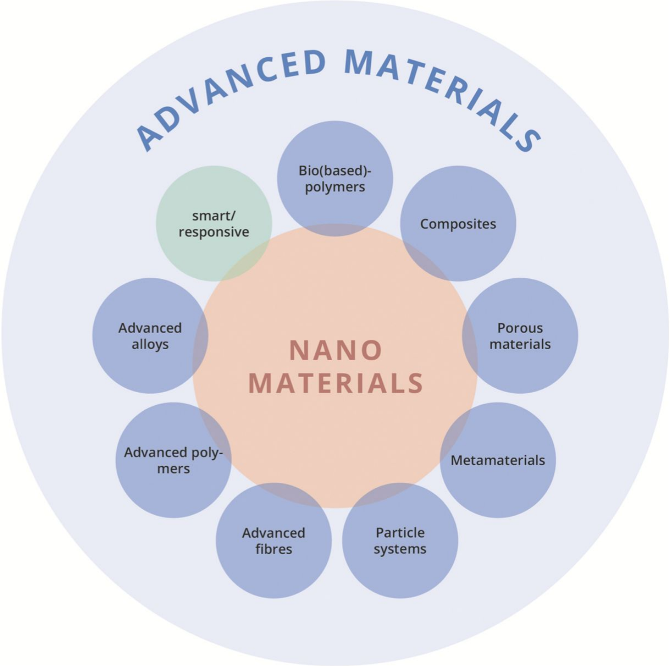
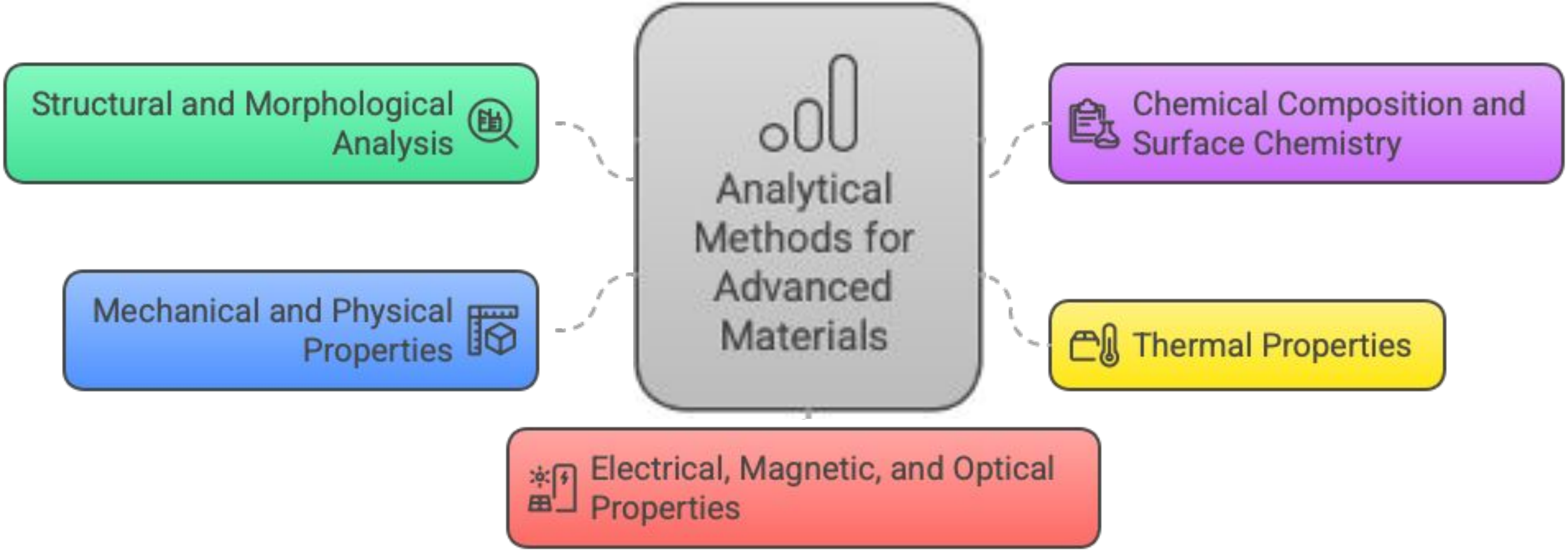
ABSTRACT

The world expects solutions to a multitude of technological challenges, from curing disease to mitigating climate change, from increasingly more "clever" or "advanced" materials. But how do we address the safety of ever more novel substances and what have we learned from the last 15 years of nanosafety research? In this opinion letter, we[1] share our views on how to develop a framework for these new families of materials, that capitalizes on the nanosafety progress achieved to date, and how to ensure the wider nanoscience community could play a part in this new challenge.



Analytical Methods for Advanced Material Characterisation



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Analytical Methods for Advanced Material Characterisation

Analytical Methods for Advanced Materials

🔬 Structure/Morphology

SEM – Surface morphology, microstructure
TEM – Nanoscale structure, crystallinity
AFM – Surface roughness, topography
XRD – Phase ID, lattice structure
SAXS – Nanostructure, porosity
DLS/NTA – Particle size distribution

⚗️ Chemical composition

EDS/EDX – Elemental analysis
XPS – Surface chemistry, oxidation states
FTIR – Functional groups
Raman – Molecular structure
ICP-OES/MS – Bulk/Trace element quantification
NMR – Molecular structure (polymers, organics)

🔥 Thermal properties

TGA – Thermal stability, decomposition
DSC – Phase transitions, melting points
Thermal Conductivity – Heat transfer

🧲 Mechanical properties

Nanoindentation – Hardness, modulus
UTM – Strength (tensile, flexural)
Rheometry – Viscosity, viscoelasticity

⚡ Electrical, magnetic, optical

UV-Vis – Optical absorption, bandgap
PL – Photoluminescence - Emission characteristics
Conductivity/Impedance – Electrical behaviour
SQUID – Magnetic properties

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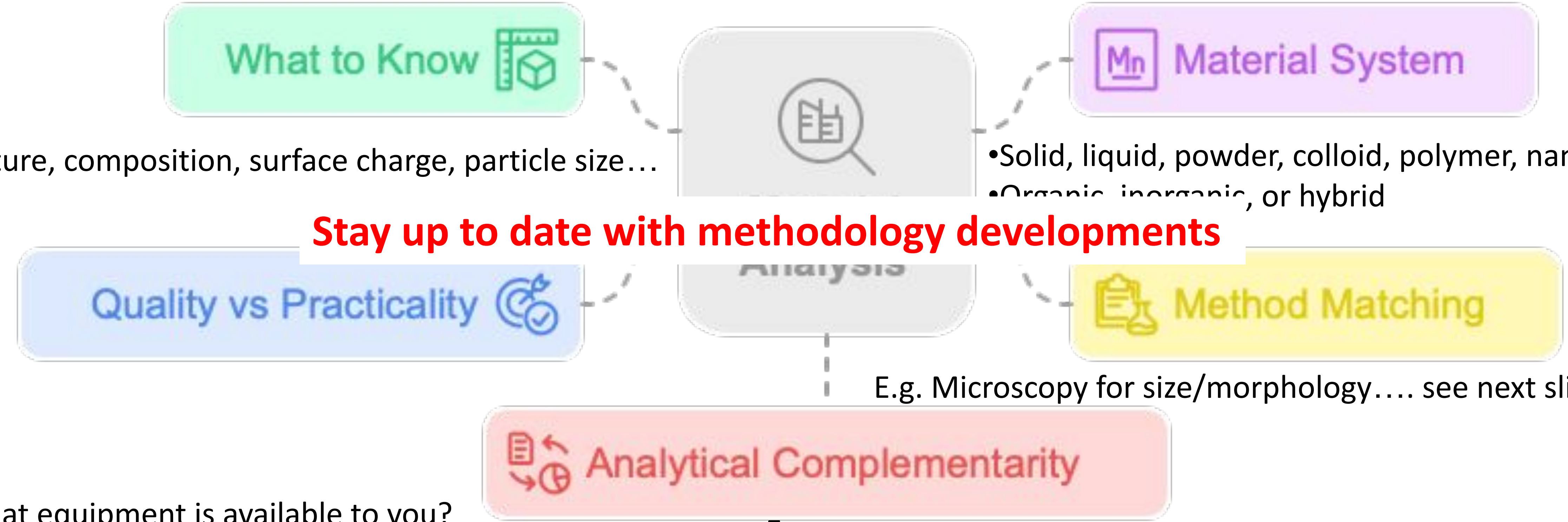
Selecting/Prioritising Characterisation Method(s)



E.g. structure, composition, surface charge, particle size…

- Solid, liquid, powder, colloid, polymer, nano
- Organic, inorganic, or hybrid

Stay up to date with methodology developments

E.g. Microscopy for size/morphology…. see next slide

- **Access**: What equipment is available to you?
- **Sample needs**: Quantity, prep, destructive vs non-destructive?
- **Resolution vs speed**: TEM gives atomic detail, but SEM is faster.
- **Budget & time**: Some methods are high-cost or require expert operators.

E.g.

- **TEM + DLS** → nanoparticle size and dispersion
- **XPS + FTIR** → surface composition and functional groups

✨

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Method matching

Characterisation need	Primary Method(s)	Secondary/Complementary
Elemental composition	ICP-OES/MS, EDX/EDS, XPS	XRF, CHNS analyser
Particle size (nm–µm)	DLS, TEM, SEM	SAXS, AFM
Surface chemistry	XPS, FTIR, Raman	NMR, ToF-SIMS
Crystallinity/phase ID	XRD, TEM	Raman, DSC
Thermal stability	TGA, DSC	MS–TGA (if gas analysis needed)
Mechanical properties	Nanoindentation, UTM	AFM (force mapping)
Optical properties	UV-Vis, PL, Ellipsometry	FTIR, Raman
Magnetic/electronic	SQUID, EIS	Cyclic Voltammetry
Porosity/surface area	BET (N_2 adsorption), SAXS	Mercury intrusion, gas pycnometry
Morphology/surface	SEM, TEM, AFM	Optical microscopy, profilometry

Method hyphenation

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Selecting/Prioritising Characterisation Method(s)

ACEnano

A Method Tool Box

The ACEnano knowledge infrastructure: https://acenano.douglasconnect.com

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Techniques and endpoints

List of protocol techniques and endpoints covered by the ACEnano project.

Technique	Endpoints
	All Filter
Assay-on-a-chip (Assay-on-a-chip)	Hydrophobicity NP-cell interaction Solubility/dissolution
Asymmetrical Flow Field-Flow Fractionation (AF4) Asymmetrical flow field-flow fractionation (AF4) separates (nano)materials in suspension according to their different diffusion coefficient, respectively hydrodynamic particle diameter, based on the Stokes-Einstein-relationship.	Particle Size Distribution
Atomic Force Microscopy (AFM)	Particle shape Particle Size Distribution
Brunauer–Emmett–Teller analysis (BET)	Volume Specific Surface Area (VSSA) / porosity
Capillary Electrophoresis (CE)	Functional coating Homoaggregation rate Particle Size Distribution
Capillary Electrophoresis-Mass Spectrometry (CE-MS)	Corona characterisation

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ACEnano Knowledge Infrastructure

This platform is the Knowledge Infrastructure of the ACEnano Project - Analytical and Characterisatio Excellence in nanomaterial risk assessment: a tiered approach. ACEnano aim to introduce confidence adaptability and clarity into nanomaterial risk assessment by developing a widely implementable and robust tiered approach to nanomaterials physicochemical characterisation that will simplify and facilitate contextual (hazard or exposure) description and its transcription into a reliable nanomaterial grouping framework.

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Selecting/Prioritising Characterisation Method(s)

ACEnano

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Brunauer–Emmett–Teller analysis

The BET measures the surface area of a powder by physical adsorption of gas molecules onto the surface of the solid, determining the specific surface area and porosity, as all porous structures adsorb the small gas molecules.

Endpoints
Volume Specific Surface Area (VSSA) / porosity

Benefits
BET serves as the basis for the measurement of the surface areas, providing valuable characteristics for the microporous material.

Technology readiness level
TRL 8 - system complete and qualified

Targeted market/sector
Commercial and research laboratories, Nanomaterials producers or suppliers, Nanomaterials users

Targeted activity
Academia, Industrial, Research

Measurement protocols | Sample preparation protocols | Datasets | Providers

Protocol	Submitted by	Access
Sample Analysis by BET - v1_b Endpoint: Volume Specific Surface Area (VSSA) / porosity This protocol describes the measuring of the amount of physically adsorbed gas according to the Brunauer, Emmett and Teller (BET) method.	Universitat Wien	Open access

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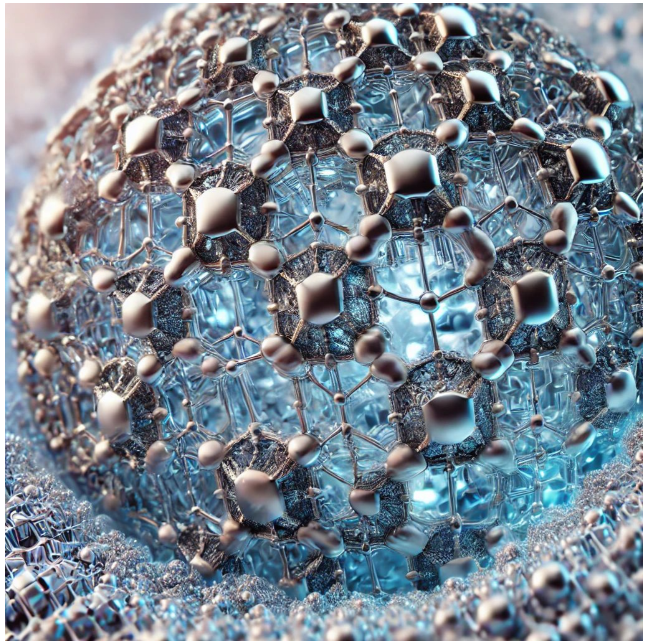
Case study: MXenes



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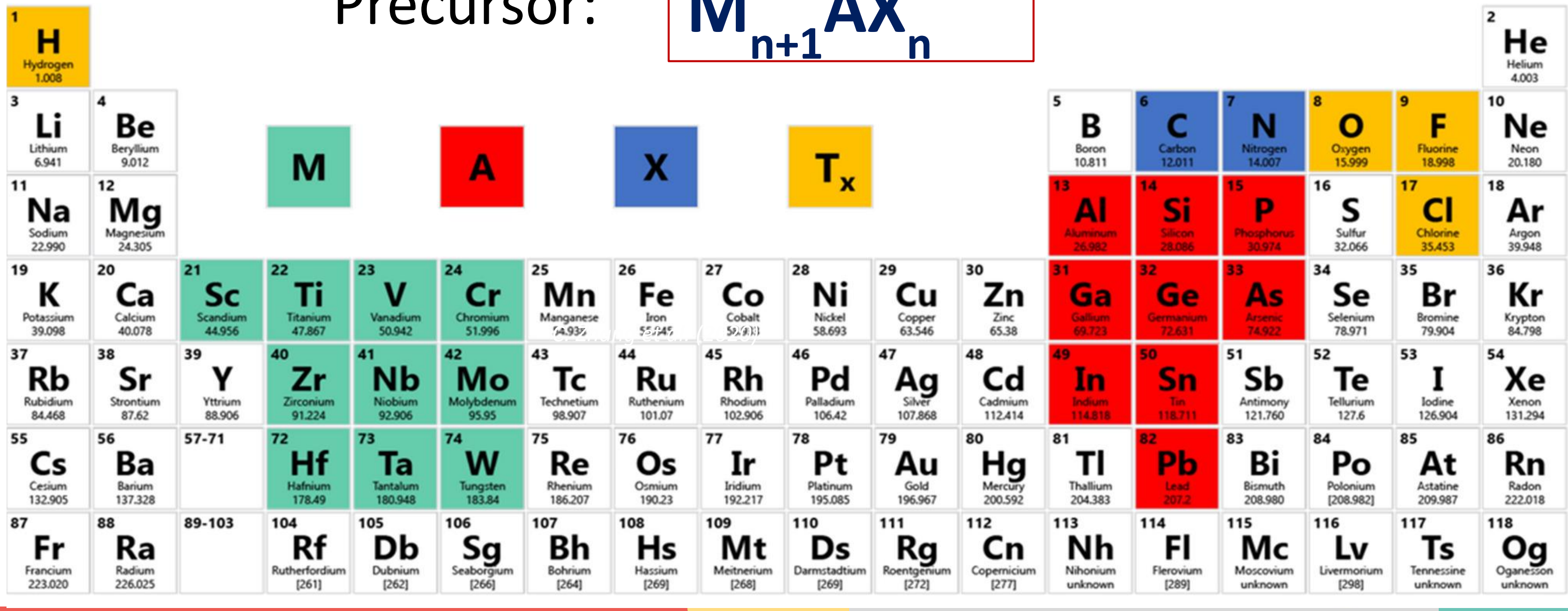
What are they?

- MXenes are 2-D materials, carbides/nitrides of early transition metals
- Representative formula: $M_{n+1}X_nT_x$ → $Ti_3C_2T_x$
- T_x = surface terminations (=O, OH^-, F^- or Cl^-)

Precursor: $M_{n+1}AX_n$



At least 100 stoichiometric MXene compositions and a limitless number of solid solutions offer not only unique combinations of properties but also a way to tune them by varying ratios of M or X elements.

The Rise of MXenes, Gogotsi & Anasori (2019)

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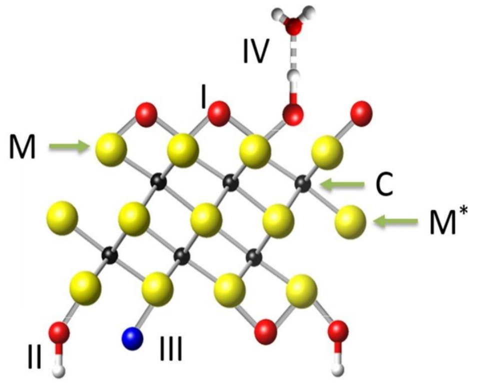
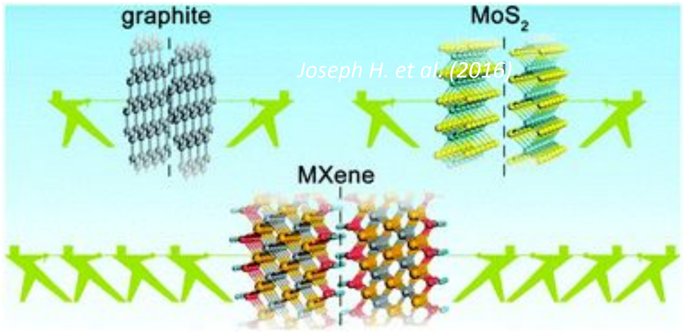
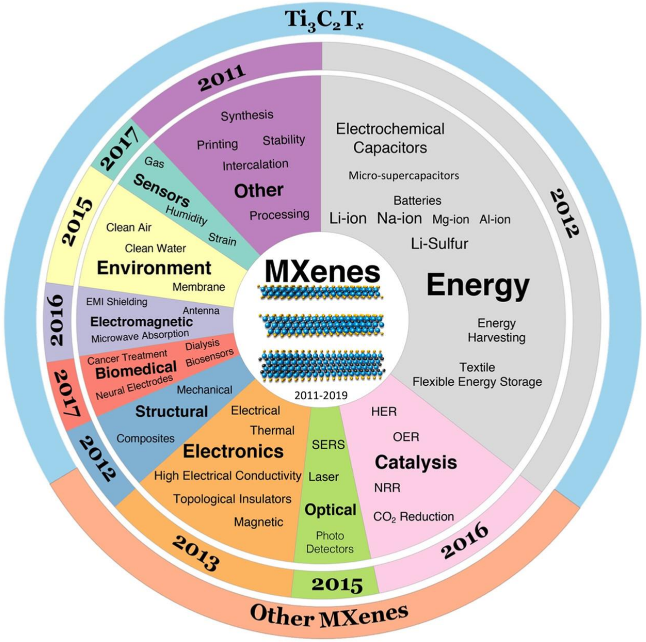
MXene properties





- Nanosheet layers are held strongly by H-bond 2–6x stronger than graphite and MoS_2 sheets
- Hydrophilic, disperse readily in water
- High metallic conductivity
- Biocompatibility
- Tuneable surface properties



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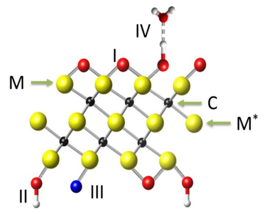

Challenges for MXene applications

From the Energy sector to the Environment

- ❑ Synthesis cost: MAX phase precursors requires
  - pure elements
  - considerable amount of energy

- ❑ Health and safety concerns as related
  - the use of HF and
  - flammability of pure metal elements (e.g. Ti)

- ❑ As adsorbent, the surface area is still poor

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Towards safe & sustainable MXenes

- Lower cost synthesis routes by using cheaper precursors and at a reduced temperature
- MXene $Ti_3C_2T_x$ as an adsorbent to treat BTEX in water
- Alternative carbon forms to improve properties

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Experimental MAX synthesis

Step 1: optimize synthesis T

- ❑ TiO_2-Al-C system: graphite and activated carbon (AC) used as C.

- ❑ Adopted MS3 approach (KCl+NaCl as molten salt solution)
- ❑ Conditions: Temp 1000°C, under high purity argon, 2h
- ❑ Recover, characterize and store

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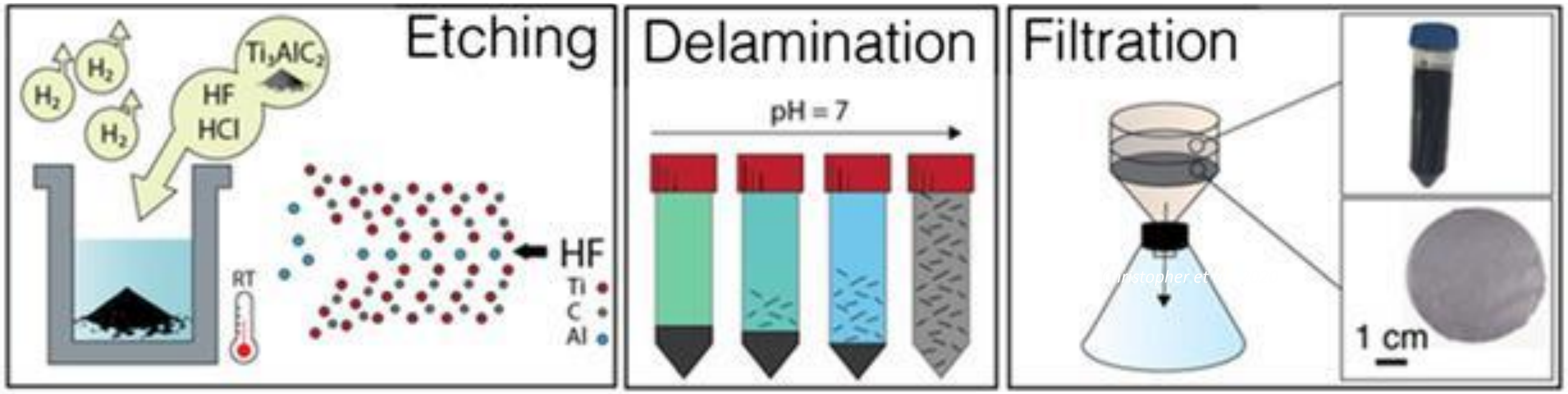
MXene synthesis

Step 2: optimize materials/chemicals



- Safety precautions
- 20% HF + HCl + 0.5g MAX
- Stir continuously for 24h at 35ºC.
- Centrifuge and wash until pH is approx. neutral
- Intercalation: stir in 2.5% TMAOH overnight.
- Wash, sonicate and vacuum-dry

KEY ADAPTATIONS

Safety
Sustainability
Functionality

- **Characterization: TGA, XRD, FTIR, FESEM, XPS**

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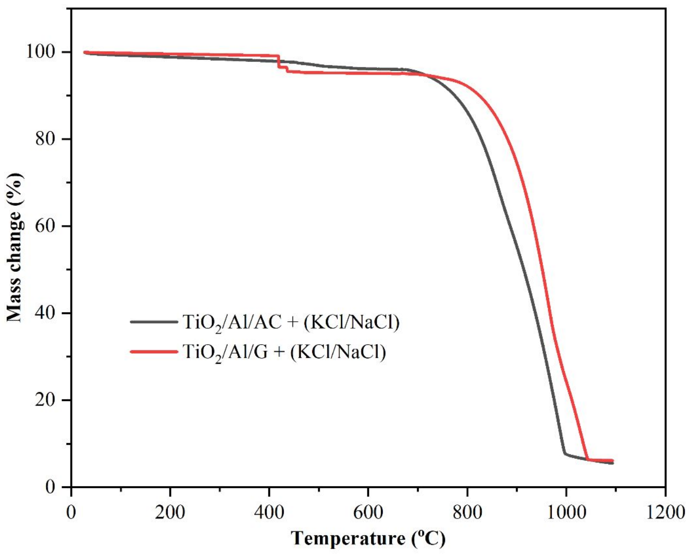
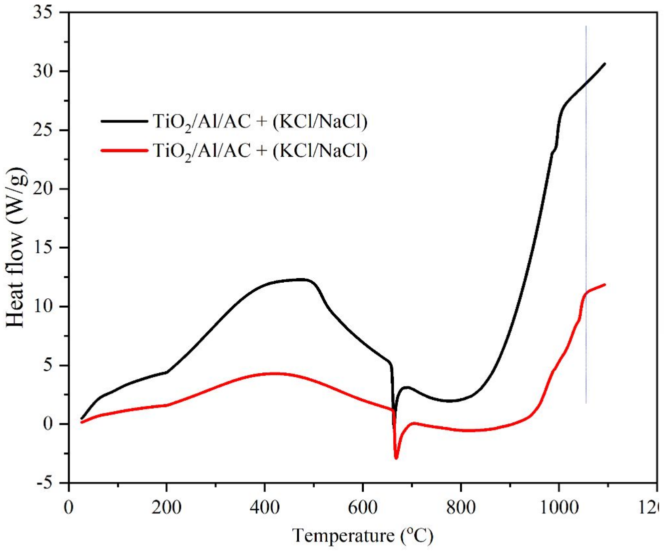
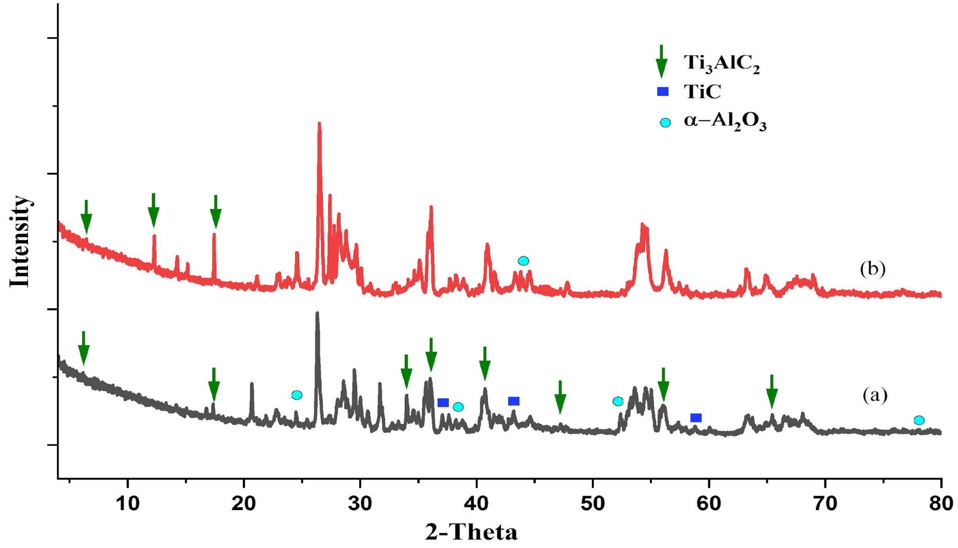
Comparisons between graphite and activated carbon MXenes

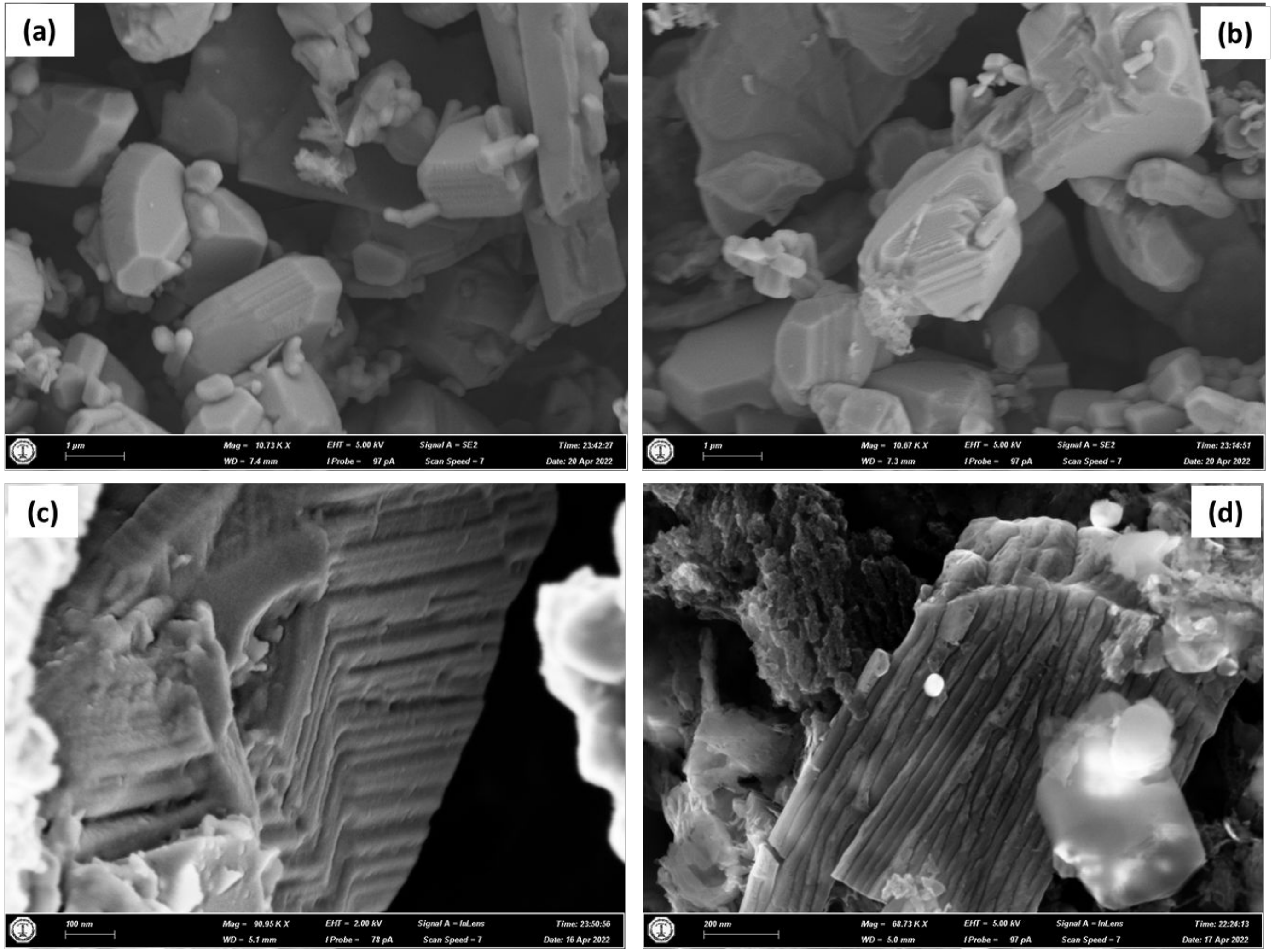




Results: TGA & XRD



Results: SEM



- (a) MAX-G
- (b) MAX-AC
- (c) MXene-G
- (d) MXene- AC

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Results: BET

MXene type	BET surface area (m^2/g)	Source
MXene-G	1.99	*Current study*
MXene-AC	**24.1**	***Current study***
$Ti_3C_2T_x$-50%HF/DMSO	10.0	Xia et al.(2017)
V_2CT_x	9.0	Wang et al. (2018)

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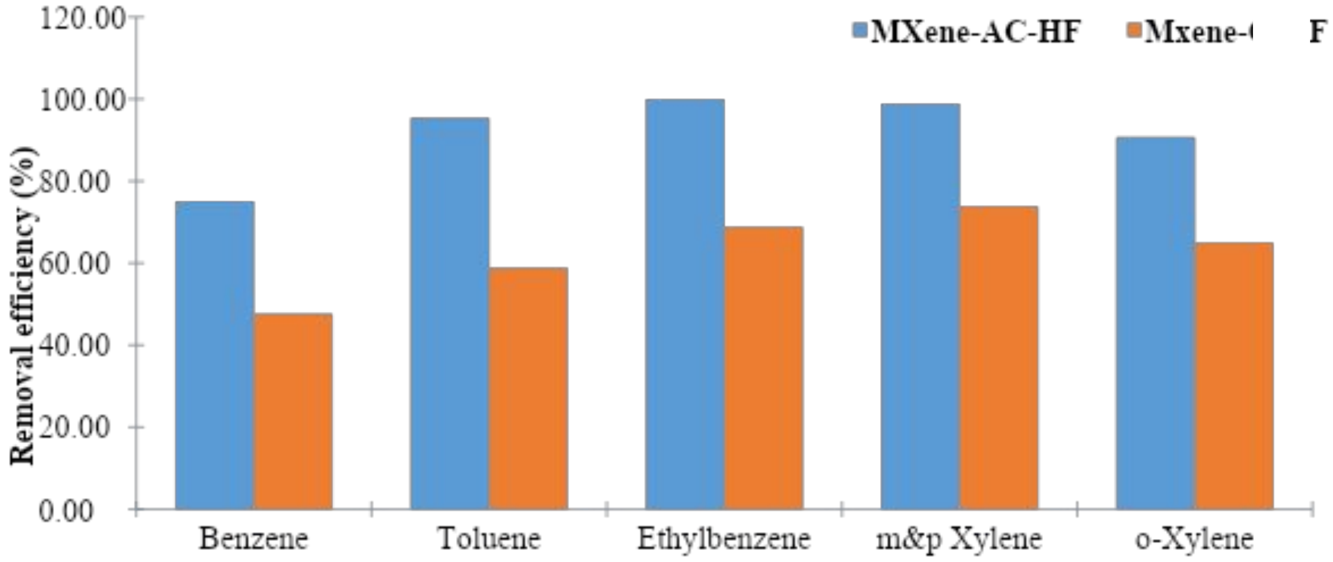
Results: Sorption



Activated Carbon (blue) vs Graphite (orange)

Experimental conditions: 5g/L adsorbent dose; 150rpm agitation; time, 30min.
Concentrations: B = 2.5ppm, T = 2.1ppm, E = 0.35ppm, m&p X = 1.1ppm, o-X = 0.3ppm

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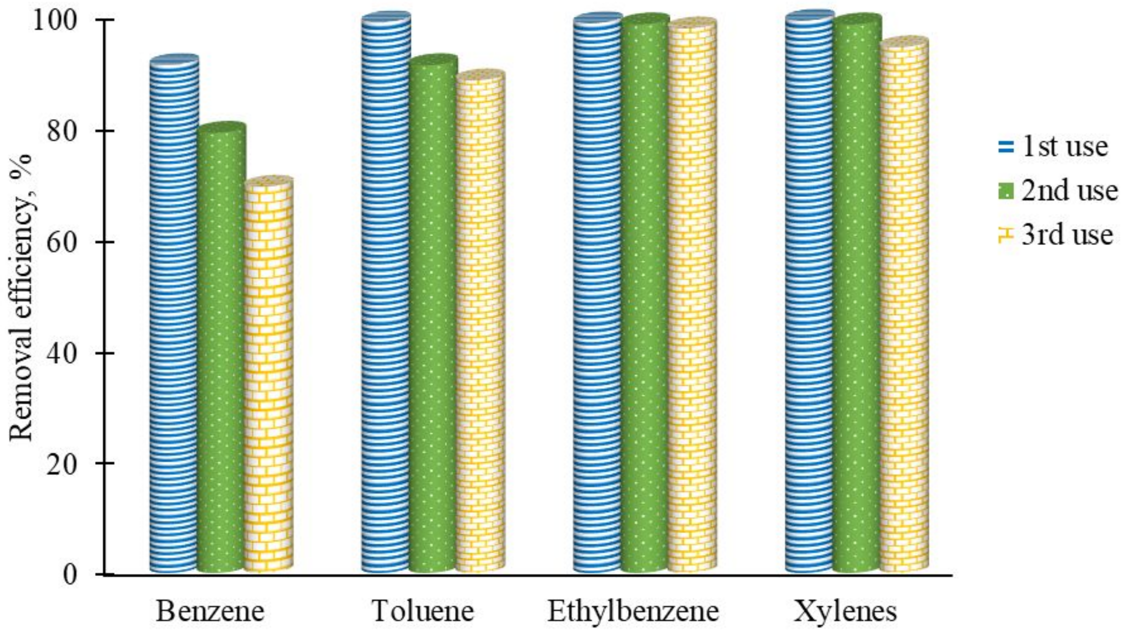
Results: Adsorbent re-use



MXene-AC

Conclusions

- Ti-based MXenes were successfully synthesized using safer (TiO_2 vs Ti) and lower cost (temperature) processes to synthesise MAX precursors.

- The synthesized MXenes were efficient in removal of BTEX from contaminated water.

- The form of constituent carbon in MAX/MXenes plays a role in tuning the resulting MXenes.

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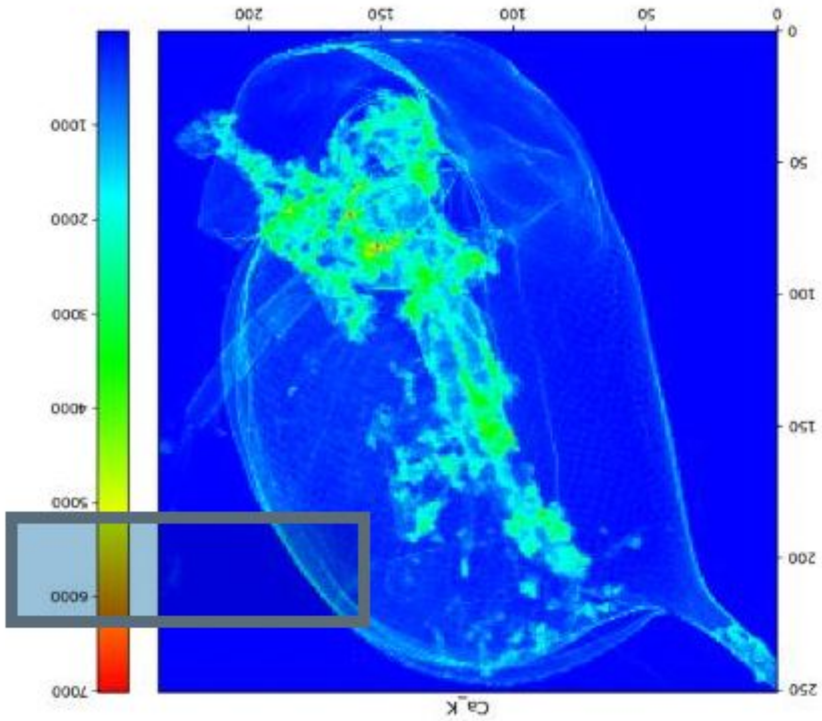
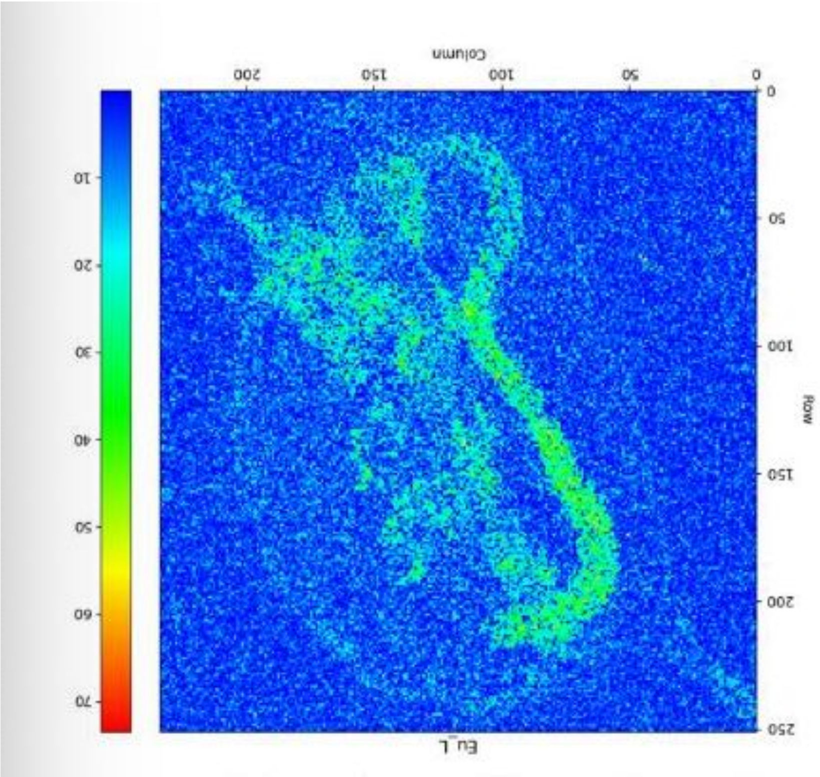
When sky is the limit……





Uptake of Eu-labelled nanoplastics by *Daphnia magna*

Thank you and....

Come and talk to us!

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