EUROMXENE CONGRESS 2024

26th-28th JUNE • VALENCIA

BOOK OF ABSTRACTS

WELCOME

Welcome to the EUROMXENE Congress 2024

We are delighted to host the inaugural MXene Symposium in Europe (**EUROMXENE2024**).

The field of materials science and nanotechnology has been significantly impacted by the discovery of MXenes in 2011. Since that year, there has been a huge increase in research into the synthesis, characterization and applications of two-dimensional (2D) carbides and nitrides. The general formula for MXenes is Mn+1XnTx, where M is an early transition metal, X is carbon or nitrogen, n ranges from 1 to 4, and Tx corresponds to the surface terminating groups connected to the transition metal layer. The chemical composition as well as ordering of the metal atoms in the structure increase the possible structures to more than 100. Surface terminations expands this number by a further order of magnitude, while the potential ability to form solid solutions at M and X sites, as well as mixed terminations, results in an unlimited range of 2D materials with a plethora of unique properties.

The extraordinary versatility and exceptional properties of MXenes make them ideal for a wide range of applications including energy storage, environmental, electronics, telecommunications, gas and liquid separation and adsorption, biomedical and optoelectronics. Given its broad appeal, MXene has attracted a large number of researchers. As a result, publication trends on MXene have flourished in recent years. By 2023, MXenes have shown promise in various research areas such as electromagnetic interference shielding, nanocomposites, and hybrid materials. In addition, new applications are emerging where MXenes outperform other nanomaterials, including photocatalysis and electrocatalysis.

During this symposium, we will have the privilege of listening to the most up-to-date research on MXenes from the foremost specialists in these materials worldwide.

Join us for Europe's first conference on one of tomorrow's key materials.

Dra. **Ana Primo** and Prof. **Hermenegildo García**.

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PLENARY LECTURES

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KEYNOTE SPEAKERS

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MXENES FOR WAFER SCALE ELECTRONIC DEVICES

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The integration of MXenes in electronic devices (MXetronics) is a newly emerging field in which MXenes have shown potential. MXenes are essentially 2D metal contacts with a tunable work function, suggesting they can be used in a variety of electronic devices. Our group has been developing deposition processes, transfer techniques, interface engineering, surface functionalization, photolithographic patterning, and wet and plasma etching of MXenes to demonstrate and improve the performance of electronic devices using MXenes. In fact, MXenes have been successfully integrated with oxide semiconductors, 2D semiconductors, quantum dot semiconductors, and wide band-gap semiconductors at the wafer scale. The data so far indicates that the quality of MXene Ohmic contacts is generally inferior to those of traditional metal contacts, leading to lower device mobility. However, for devices that require Schottky contacts (e.g., HEMTs), MXenes perform much better. In this talk, the benefits and challenges of using MXenes in various electronic devices will be discussed, with a particular focus on the role of the interface. Strategies to improve the MXene/semiconductor interfaces and to improve the wafer-scale fabrication processes will be summarized. In addition, using MXene thin films as active layers in electronic devices will be discussed.

THE FUTURE OF MXENES

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MXenes are an extensive family of two-dimensional (2D) early transition metal carbides, nitrides, oxycarbides, carbonitrides, and related structures with a general formula of Mn+1XnTx, where M is a transition metal, X is carbon or nitrogen (oxygen substitution is possible), T represents the surface terminations (O, OH, halogen, chalcogen, etc.), and n = 1—4. More than 40 stoichiometric MXene compositions and dozens of solid solutions have already been reported. Still, the number of possible compositions is infinite if one considers solid solutions (more than 50 have been made in our lab) and combinations of surface terminations. MXenes have opened an era of computationally driven atomistic design of 2D materials. MXenes possess electronic, optical, mechanical, and electrochemical properties that differentiate them from other materials. MXenes can be considered 2D building blocks for the assembled materials and devices that will power future technologies.

Chemically tunable superconductivity has been demonstrated in Nb- and Mo-based MXenes. Highly nonlinear optical properties of MXenes are being explored. Several MXenes have been predicted to act as topological insulators. Many MXenes are metals but with a tunable density of states at the Fermi level, like semiconductors. Moreover, their properties are tunable by design. They can be modulated using an ionotronic approach, leading to breakthroughs in the fields ranging from optoelectronics, electromagnetic interference shielding, and communication to electrochemical energy storage, catalysis, sensing, soft robotics and healthcare. In several applications, such as electromagnetic interference shielding, MXenes have already outperformed all other materials. In this talk, I'll discuss the emerging synthesis methods and structure of MXenes, their electrochemical and optoelectronic properties, and outline prospectives for applications of MXenes in fields ranging from electronics to healthcare, thermal management, communication, and energy storage.

UNDERSTANDING MXENES FROM FIRST PRINCIPLES

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In this talk, physical and chemical properties of MXenes will be discussed on the light of appropriate models and density functional theory calculations emphasizing the scope and limitations of the presently available approaches. In particular, the nature of the electronic ground state of MXenes with M2C stoichiometry is described in detail showing that some of these bare MXene exhibit a magnetic ground state. In these cases, the magnetic order is further discussed.[1] Another important topic involves how to relate chemical bond or atomic structure features to experimentally observable properties such as core level binding energy shifts, accessible by means of X-Ray Photoelectron Spectroscopy, or the vibrational frequencies of adsorbed molecules, easily gained through Infrared Spectroscopy.[2],[3] Next, a series of examples will be discussed to illustrate how theoretical modelling provides information about details of chemical reactions occurring at MXenes surfaces that are not easily accessible to experiments, and also to show that relevant predictions can be made. These examples involve determining conditions at which active sites at the MXene surface become available for heterogeneously catalyzed reaction,[4] CO2 capture[5] and its possible subsequent utilization as in the reverse water gas shift reactions.[6] Finally, the problem of proper modelling of MXenes in electrochemical environment will be addressed.[7]

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DEVELOPMENT OF NEW MXENES FROM A THEORETICAL AND EXPERIMENTAL PERSPECTIVE

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More than a decade after the discovery of MXene, there has been a remarkable increase in research on the synthesis, characterization, and applications of the growing family of two-dimensional (2D) carbides and nitrides. Today, these materials include one, two, or more transition metals arranged in chemically ordered or disordered structures of three, five, seven, or nine atomic layers. By combining M, X, and various surface terminations, it appears that a virtually endless number of MXenes is possible. However, for the design of structures and compositions beyond current MXenes, suitable precursors and tools for accelerated materials development are needed. This lecture will provide a brief summary of the atomic-scale design and synthesis of MXenes and their parent materials, demonstrating how MAX phases and their 2D derivatives serve as a playground for materials discoveries. Theoretical methods for predicting MXene precursors and for assessing their chemical exfoliability will be discussed and correlated with experimental work. Inspired by MAX/MXenes, other 2D materials derived from selective etching will also be exemplified, such as recently developed Ru- and Au-based (goldene) laminates.

MXENE COMPOSITE S-SCHEME PHOTOCATALYST FOR SOLAR FUEL PRODUCTION

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Solar-driven CO2 reduction holds great potential for addressing the emerging energy shortage and environmental crises. MXene has garnered significant attention owing to its hydrophilicity, metallic conductivity, anisotropic charge mobility, layer-dependent optics, and tailored surface chemistry. However, unitary MXene-derived photocatalyst exhibits poor performance due to the rapid recombination of photoelectrons and holes. Herein, we develop MXene-derived S-scheme heterojunction photocatalysts with efficient separation of powerful photogenerated carriers, and investigate their CO2 reduction performance, along with the mechanism of charge transportation and separation. Firstly, 2D TiO2 mesoporous nanosheets with three to four C3N4 layers grown in situ are employed to design a core-shell 2D/2D van der Waals heterojunction (TiO2/C3N4). Edge-terminated 0D Ti3C2 MXene quantum dots are subsequently integrated into the C3N4 surface via electrostatic interactions. The resulting 2D/2D/0D TiO2/C3N4/Ti3C2 heterojunction photocatalyst exhibits enhanced CO2 reduction activity for both CO and CH4 production. An S-scheme charge transfer mechanism operates for the prepared samples during CO2 reduction, as authenticated by in situ X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance analysis. Secondly, unique ZnO/Nb2O5/Nb2C S-scheme heterojunctions are fabricated via the electrostatic self-assembly of ZnO quantum dots and Nb2O5/Nb2C MXene. Such heterostructures demonstrate exceptional CO2 photoreduction activities with high selectivity for CH4 without the assistance of any molecular catalyst or scavenger, resulting from the S-scheme mechanism-induced efficient separation of powerful photoexcited charge carriers. Density functional theory calculations, in situ irradiation XPS, along with ultrafast transient absorption spectroscopy, corroborate the driving force, separation mechanism, and microscopic dynamics of photoexcited charge carriers within the heterojunctions in detail.

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KEYNOTE SPEAKERS

CHEMICAL SCISSOR-MEDIATED STRUCTURAL EDITING OF LAYERED TRANSITION METAL CARBIDES

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Intercalated layered materials are usually produced by inserting guest species into the van der Waals (vdW) gaps of inherently layered materials such as graphite, hexagonal boron nitride (hBN), and transition metal dichalcogenides. The guest-host interaction alters the electronic structure and enables property tailoring for energy storage, catalysis, electronic, optical, and magnetic properties. Intercalation in non-van der Waals (non-vdW) nanolaminated materials and their two- dimensional (2D) derivatives is, however, rare and lacks understanding of the chemistry and structural tunability involved. Here, we show a structural editing protocol for non-vdW layered ternary carbides and nitrides (known as MAX phases) and their vdW multilayer derivatives (MXenes). Gap-opening and species-intercalating stages are separately mediated by chemical scissors and guest intercalants, respectively. A large family of 3D MAX phases with unconventional components and structures as well as 2D MXenes with versatile termination species, is accomplished. Moreover, a reverse transformation from 2D MXenes to 3D MAX phases is realized through knockout of surface termination species by metal scissors and stitching of ceramic slabs by zero-valence metal atoms. This scissor-mediated structural editing would enable structural and chemical tailoring in a broad class of layered ceramics.

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SYNTHESIS, PROPERTIES AND APPLICATIONS OF TWO-DIMENSIONAL TRANSITION METAL CARBO-CHALCOGENIDES

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Two-dimensional transition metal carbo-chalcogenides (TMCCs) can be described as a convergence between 2D MXenes and 2D transition metal dichalcogenides, incorporating the carbide core of MXenes with the chalcogenide surface of TMDCs.

These materials resemble MXenes with a chalcogen surface, achieved through a simplified solid-state synthesis that avoids the complexities of MAX phases synthesis and etching. This approach allows for the straightforward synthesis of tens of grams in laboratory settings without the need for hazardous acids. We have pioneered the synthesis of the first members of the TMCC family, Nb2S2C and Ta2S2C, using liquid exfoliation facilitated by electrochemical lithium intercalation. In this presentation, we will delve into the recent developments in the synthesis of multilayer TMCCs and their exfoliation into 2D sheets. Furthermore, the impact of various transition metals on the properties of TMCCs will be explored, alongside their performance in diverse applications, including their potential as electrodes for energy storage and conversion.

PROCESSING AND APPLICATIONS OF 2D MXENE INKS

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Direct printing of functional inks is critical for applications in diverse areas including electrochemical energy storage, smart electronics and healthcare. However, the available printable ink formulations are far from ideal. Either surfactants/additives are typically involved or the ink concentration is low, which add complexity to the manufacturing and compromises the printing resolution. Here, we demonstrate two types of two-dimensional titanium carbide ($Ti_3C_2T_x$) MXene inks, aqueous and organic in the absence of any additive or binary-solvent systems, for extrusion printing and inkjet printing, respectively. We show examples of all-MXene-printed structures, such as micro-supercapacitors, conductive tracks and ohmic resistors on untreated plastic and paper substrates, with high printing resolution and spatial uniformity. The volumetric capacitance and energy density of the all-MXene-printed micro-supercapacitors are orders of magnitude greater than existing inkjet/extrusion-printed active materials. The versatile direct-ink-printing technique highlights the promise of additive-free MXene inks for scalable fabrication of easy-to-integrate components of printable electronics.

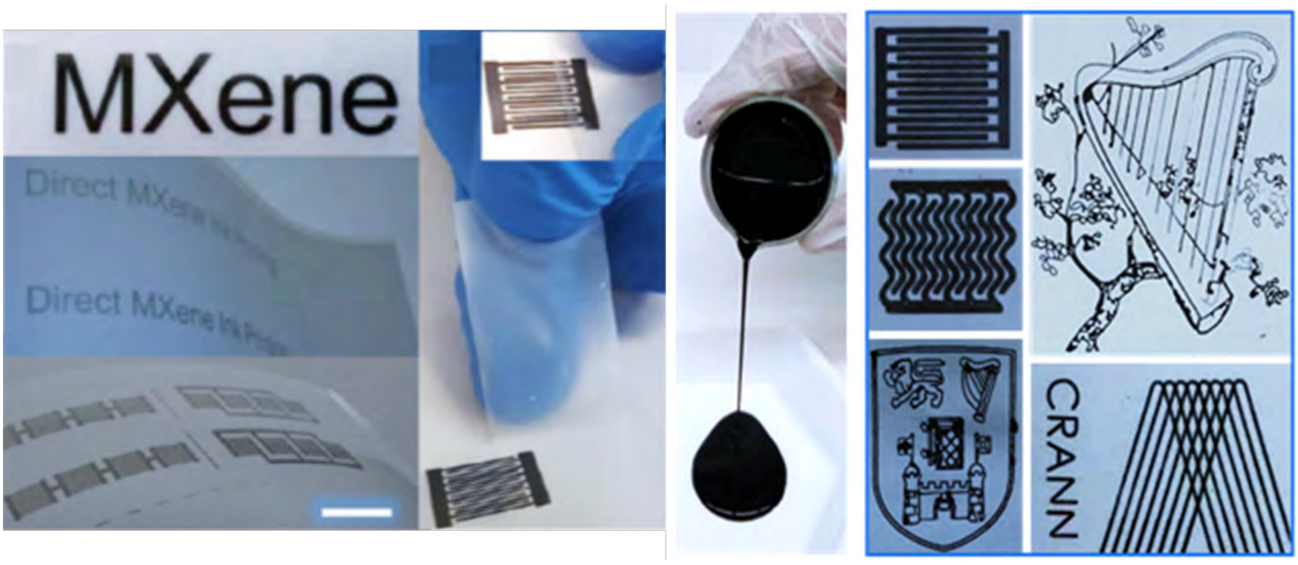

Figure 1: Printed devices based on MXenes inks

IN SITU INSIGHTS INTO THE REACTIVITY IN MOLTEN SALTS OF MAX, MXENES AND RELATED MATERIALS

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Inorganic molten salts are non-volatile liquids stable at high temperatures, often up to 1000 °C and beyond. Thanks to thermal stability in this wide temperature range, to specific solvation and redox properties, these liquids provide the ability to trigger chemical reactions that either pertain to traditional solid-state syntheses, or differ from existing reaction pathways. This enables syntheses of unprecedented materials and nanomaterials, especially for strongly covalent materials.[1] Such opportunities have been demonstrated for MXenes in the last years. Indeed, the adequate choice of molten salts enables selective etching of A elements (A=Al, Si, Ga) in MAX phases, thus delivering carbide and nitride MXenes [2-5] with new terminations. The involved reactions remain however poorly understood. Especially their kinetics and their wide range applicability to MAX compounds and other families of layered materials, like borides, are still to be assessed.

In this talk, we will discuss the reactivity of layered materials into molten salts by studying in situ their synthesis and the etching mechanisms. We will first introduce the sample environment we have developed to performed synchrotron-based in situ X-ray diffraction and X-ray absorption spectroscopy experiments. We will then discuss how galvanic replacement and delamination reactions occur in MAX phases depending on the composition of the MAX phase and of the molten salts.[6] Finally, we will present the synthesis and reactivity of layered metal borides (so-called 'MAB' phases[7]) phases in molten salts.

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FUNCTIONALIZATION OF MXENE FOR ENERGY STORAGE AND CATALYSIS

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The field of MXene chemistry is rapidly advancing, characterized by the emergence of novel terminations and surface functionalization strategies. MXenes can be transformed into a diverse array of related compounds through controlled reactions with chalcogens and various other reagents. By converting titanium-based MXenes and other variants to chalcogenides, composite materials can be generated while preserving the original morphology. These materials demonstrate enhanced properties suitable for a wide range of applications such as energy storage and photocatalysis. Through specific chemical processes, MXenes based on vanadium, niobium, and molybdenum can be converted into chalcogenides or vanadates/niobates, offering opportunities for the development of high-performance materials for applications in photocatalysis, supercapacitors, and batteries. Additionally, covalent functionalization strategies can be employed to stabilize the surface of MXenes and tailor their properties, thereby enhancing charge storage capacity for high- energy-density supercapacitors. The presentation will also showcase the use of various zwitterionic molecules for functionalization to achieve increased capacitance.

ORAL PRESENTATIONS

V2C MXENES AS HETEROGENEOUS CATALYSTS FOR THE AEROBIC OXIDATION OF BENZYLIC HYDROCARBON

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MXenes are 2D nanomaterials having alternating sheets of one atom-thick early transition metal layer and one atom-thick of carbon or nitrogen layer.[1,2] The external surface contains termination groups, whose nature depends on the etching agent employed in the preparation of the MAX phase.[3] In this presentation, the possibility of employing the metal-surface termination groups in MXenes as heterogeneous catalysts for benzylic hydrocarbon will be presented. This proposal derives from the consideration that early transition metal atoms bonded to hydroxyl and oxo groups are a general type of active sites in heterogeneous catalysis and it is believed that similar catalytic centers can also be present in the MXene structure. This work illustrates the use of V_2C Mxene to illustrate its catalytic activity and to show how the catalytic performance is altered upon modifying the surface groups. As test reaction we selected the aerobic oxidation of indane to the corresponding indanol/indanone mixture using molecular oxygen as terminal oxidizing reagent (Scheme 1). Two previously reported procedures to modify the surface groups, namely surface dehydroxylation by thermal treatment under diluted hydrogen flow and surface oxidation with ammonium monoperoxy sulfate to convert some surface groups into oxo groups were used, observing in both cases a decrease in the catalytic activity of V_2C. Based on this, $V^{III}/^{IV}$-OH are proposed as catalytic centers in this aerobic oxidation. Overall, this presentation will show the merits of MXenes in heterogeneous catalysis, based on their chemical composition and surface functionality. The catalyst was also used in three cycles with no significant decay in its performance, suggesting the catalyst stability under these conditions.

Scheme 1. Aerobic oxidation of indane using V_2C as a heterogeneous catalyst.

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LOW DIMENSIONAL SNSE – TI3C2 MXENE COMPOSITE AS BINDER-FREE ANODE FOR ENERGY STORAGE APPLICATIONS

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Two-dimensional (2D) materials exhibit unique structural and electronic properties such as reduced thickness, high conductivity, packing density and tuneable band gap.[1] These properties present compelling opportunities for their applications in sustainable battery technologies.[1] Sodium-ion batteries (SIBs) are attracting great interest as an alternative to lithium-ion batteries due to their material abundance, lower cost, and environmental sustainability. However, the quest for a high-performance anode for SIBs remains challenging owing to the severe volume expansion caused by the intercalation of the large Na-ion.

Tin (II) selenide (SnSe), a layered 2D material, demonstrates very high theoretical capacity as an anode for both sodium and lithium-ion battery systems. Nevertheless, its instability primarily attributed to the substantial pulverization of active materials during cycling poses a challenge.[2] To address this, we investigated a novel 2D composite material comprising SnSe nanoparticles and MXene (Ti3C2Tx) nanosheets (Figure 1) to be used as an anode in batteries. Due to the exceptional conductivity and viscosity of MXene [3], it can act as a conductive binder in this composite eliminating the need for traditional non-conductive binders like PVDF and CMC. This reduces the dead volume in the electrode and enhances its specific capacity. Additionally, the MXene layers with terminating fluorine functionals promote the growth of stable solid-electrolyte interfaces (SEI) which in turn improves the overall coulombic efficiency of the battery.[4] Further optimization studies were done with VC and FEC electrolyte additives. Characterization techniques including XPS, SEM, EDX, XRD and AFM were performed on the composite nanomaterial to study its morphology, as well as compositional and structural changes upon processing. The electrode material showed a high initial discharge capacity of 700 mAh/g and 98% coulombic efficiency for 100 cycles in lithium-ion batteries. This shows promise in overcoming instability issues of SnSe, thereby improving the performance and longevity of SIBs for sustainable energy storage solutions.

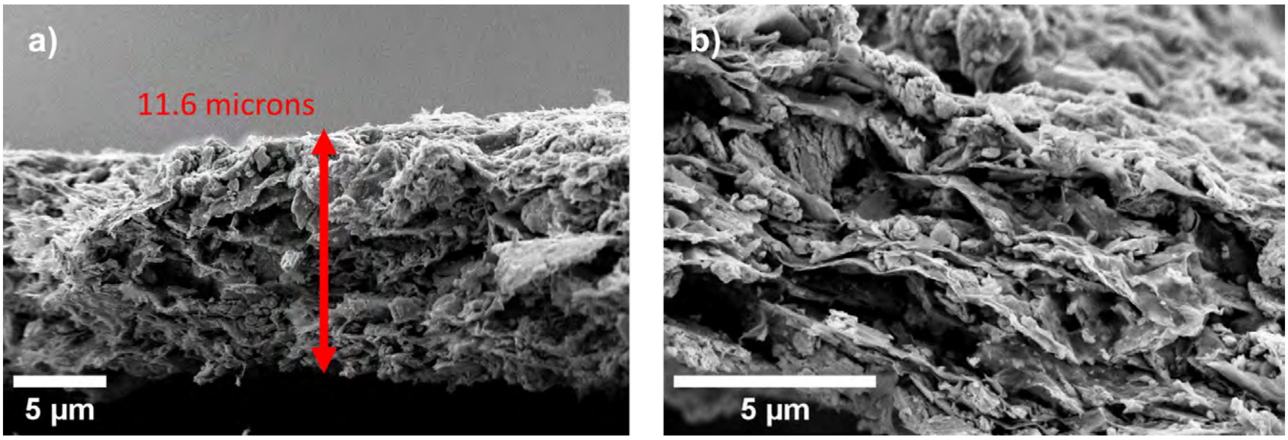

Figure 1: SEM images of the cross-section of the SnSe-MXene composite slurry casted electrodes. a) shows the thickness of the slurry casted electrode to be 11.6 microns and b) shows the SnSe nanoparticles between the MXene nanosheets.

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TI3C2TX//RUO2 ASYMMETRIC SUPERCAPACITOR DEVICE WITH HIGH ENERGY DENSITY

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Titanium carbide ($Ti_3C_2T_x$) is a member of the two dimensional transition metal carbides/nitrides family called MXenes and is characterized by high conductivity, surface area and good hydrophilicity imparted by surface terminating functional groups [1]. Delaminated $Ti_3C_2T_x$ exhibit redox activity in aqueous electrolyte like H_2SO_4, wherein the hydronium ions interact with the transition metal to cause a change in its oxidation state [2]. However, the process of delamination is quite tedious and also lacks scalability [3]. The present work provides a solution to this issue, through in situ modification using NaOH, which improves the redox behavior of the multilayer MXene, without additional delamination steps, maintaining the scalability of the reaction. The present modification also enhances the quality of MXene formed, as by adjusting the concentration of metal cation, MXene devoid of any MAX phase could be obtained. The conventional LiF/HCl etching technique always has, unetched MAX phase in the system due to mild nature of the etching. In the present study, sodium hydroxide was introduced in the in-situ HF forming synthesis technique, at the late etching stage. Sodium hydroxide assisted hydrothermal synthesis is reported to have higher concentration of alkali and the higher temperatures result in the formation of TiO_2, even though it gave 92wt% purity MXene [4]. Moreover delamination via intercalation of dimethyl sulphoxide(DMSO) was necessary to obtain typical pseudocapacitve behaviour. In the proposed work however, a full removal of unetched MAX phase was obtained at room temperature itself through the alkali assisted in situ etching technique. The optimization of concentration of sodium hydroxide resulted in formation of MXene, devoid of unetched MAX phase or TiO_2, with inherent delamination. The optimized MXene was used in the fabrication of an asymmetric supercapacitor. Due to the presence of negative surface terminations, MXene act as a negative electrode. The work is extended to the development of a suitable positive electrode, RuO_2 for the fabrication of an asymmetric supercapacitor. RuO_2 is a compatible choice due to its redox behavior in H_2SO_4, similar to MXene. The asymmetric system in the present study can overcome the thermodynamic potential for hydrogen evolution encountered in symmetric supercapacitors working in aqueous electrolytes. Each electrode being working in a different window, makes it possible to extend the voltage window of the device beyond 1 V. Moreover, since energy density vary as square of potential, an extended window also enhances the energy density of the device. The developed asymmetric supercapacitor has a specific capacitance of 73 F/g, energy density of 23 Wh/kg and power density of 796 W/kg.

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TAILORING MXENE SYNTHESIS AND ASSEMBLY FOR ENHANCED PERFORMANCE IN ENERGY STORAGE APPLICATIONS

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Tailoring MXene Synthesis and Assembly for Enhanced Performance in Energy Storage Applications

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Recent advances in two-dimensional (2D) MXenes have opened new avenues in materials science due to their unique physical, chemical, and electrochemical properties. This presentation will delve into our group's comprehensive research focused on optimizing the synthesis process and assembly techniques to maximize the performance of MXenes in various applications. MXenes, characterized by their exceptional electrical conductivity and electrochemical properties, have shown great potential as electrode materials for energy storage devices. Our findings indicate that the synthesis conditions crucially affect MXenes' morphology, defect concentrations, and surface chemistry, which in turn impact their electrical, electrochemical, and mechanical performance. Particularly, this talk will emphasize how the introduction of defects during synthesis can be manipulated to enhance the mechanical properties and the capacitive performance of MXene electrodes. We have explored how these defects influence the ultrafast intercalation of ions and enable fast and reversible redox reactions, critical for high-performance energy storage applications. Moreover, the assembly of MXene flakes into heterostructures is shown to significantly improve their capacitive and mechanical robustness. Our recent studies suggest that standardized synthesis protocols are essential to achieve consistent MXene properties and facilitate reliable performance reporting across different applications. The presentation will also discuss the development of new strategies for MXene synthesis and assembly that are aimed at enhancing the performance of MXene-based devices. These strategies include innovative techniques for controlling the synthesis process to fine-tune the electrochemical properties and mechanical stability of MXenes. Finally, the talk will outline the current gaps in the knowledge surrounding MXenes and propose future research directions aimed at further understanding and exploiting the potential of MXene materials in advanced technological applications. The talk will conclude with insights into the chemical and electrochemical stability of defected and heterostructured MXenes.

OPTIMIZATION OF MXENES PROPERTIES FOR USING AS ELECTRODES FOR HIGH POWER METAL ION ENERGY DEVICES

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MXenes are new 2D materials that have a wide range of application due to their unique structural, moprhological, electrical and other properties. It has been demonstrated that they are useful in a wide range of electrochemical energy sources, including batteries and supercapacitors, aqueous and non-aqueous. It should be noted that this type of material is the best choice when using it to make electrodes. Their primary advantage is their high conductivity and large surface area, which provide a good contact with the electrolyte and facilitate rapid charge transfer. It is also important to note that one of the most important advantages of these materials is the ability ability to remain in the form of single flakes for a long time, particularly in aqueous solutions, allowing electrodes of small thickness to be formed by using a variety putting methods to current collectors. Due to this, a large portion of the mass of the material is able to be used in fast electrochemical reactions, which means that such devices have high power and high capacity.

Our study was designed to investigate the electrochemical behavior in high current conditions of materials with a uniform distribution of Max phase particles synthesized using the traditional high temperature method and due to the use of a vacuum cup for ball milling. For grinding, a stainless steel cup of 50 ml was used with a special lid, which comes with a pump that makes it possible to squeeze out air from the cup's volume. Our results show that after successful etching and delamination of the samples, we are able to obtain an emulsion that can be used to create very thin electrodes, which can then be tested in different electrolytes under conditions of different currents. on the basis of a complex of electrochemical studies (CVA, galvanostatic charge-discharge, impedance spectroscopy) of the electrodes, it can be concluded that the materials synthesized by us are able to work in high currents conditions (up to 10C), providing at the same time a high value of specific capacity and power during long cycling.

WHAT POTENTIAL DOES (RU-)MO2CTX MXENE HAVE FOR THE THERMAL SYNTHESIS OF AMMONIA? FROM HABER-BOSCH (HB) TO CHEMICAL LOOPING PROCESSES

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Since their first appearance in 2011,[1] MXenes have gained increasing attention in a wide range of application fields owing to the combination of their 2D layered structure and excellent physico–chemical properties.[2] However, while numerous works have investigated the performances of MXenes in electro- and photocatalysis, very few have been carried out on the thermocatalytic properties of MXenes.[3] In particular, to our knowledge, no work has been undertaken on the thermocatalytic synthesis of ammonia on MXene, despite the growing interest of NH3 as a decarbonized energy carrier due to its chemical hydrogen storage properties. However, recent theoretical studies point the potential of MXene, such as Mo2C, to produce ammonia with less energy-consuming conditions via the Haber-Bosh (HB) process (N_2 + 3H2 $/rightleftharpoons$ $2NH_3$).[4,5]

Consequently, this pioneering work aims at determine the experimental potential of Mo_2CT_x MXene as catalyst for the HB ammonia synthesis in the 400-500 °C temperature range at atmospheric pressure and until 5 bar. The behaviour of this MXene toward N_2 and NH_3 is also examined in terms of nitride formation and the reactivity of the resulting material toward H_2 is also investigated. Finally, nitriding/hydrogenation cycles to mimic a chemical looping process, an alternative route to the HB process to reduce energy demanding conditions, is studied. This promising process is divided in two sub-reactions in which N_2 and H_2 reactants are fed separately with (i) the feeding N_2 (charge step) and (ii) the H_2 phase (discharge step, ammonia production).

The influence of the impregnation of ruthenium on the MXene for the HB process as well as the nitriding process is also explored. The promising results highlight new aspects that should be explored in future works to extend the use of Mo_2CT_x MXene for the thermal production of ammonia.

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PHOTOTHERMAL TARGETED CANCER CELL ABLATION USING MXENES-ANTIBODY COMPLEX

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Despite the relatively low prevalence of melanoma (only about 1% of skin cancers), it is considered as one of the fastest-growing forms of cancer. Early diagnosis accompanied by surgical excision remains the main approach to treating localized melanomas. Personalized treatment plans based on individual genetic profiles are emerging as a promising alternative to the limitations of traditional therapeutic approaches. However, with tumor resistance rapidly evolving, exploring different avenues, such as photothermal therapy, is critical to expanding treatment options to a broader range of patients.

Photothermal therapy (PTT) is a targeted cancer treatment modality that utilizes photothermal agents, such as nanoparticles or dyes, capable of converting absorbed light into heat. These agents preferentially accumulate in tumor tissues upon administration due to tumor vasculature's enhanced permeability and retention effect. Subsequent irradiation with near- infrared (NIR) laser, typically within 1st or 2nd biological transparency windows (700-1100 nm), ensures deep tissue penetration with minimal absorption by surrounding healthy tissues.

Upon NIR light exposure, the photothermal agents–photosensitizers undergo electronic excitations that lead to non-radiative relaxation processes, effectively converting the light energy into localized thermal energy. This rapid localized heating induces temperatures sufficient to denature proteins and disrupt cellular structures, leading to targeted tumor cell apoptosis or necrosis without harming adjacent normal tissues. The specificity of PTT is further enhanced by the design of the different photothermal agents, which can be conjugated with targeting molecules such as antibodies or peptides to increase their affinity for cancer cells. Due to its active surface and high photothermal effect, one of the most promising photosensitizers is the new class of 2D materials – MXenes.

Our **study aimed** to create the MXenes-antibody (Ab) complex and to provide an assessment of the targeted photothermal effect on an in-vitro culture of melanoma cells using an NIR-I laser.

Ti3C2Tx MXenes were modified by with polydopamine (PDA) with different thicknesses followed by anti-CEACAM1 antibodies immobilization. The cytotoxicity of the elaborated complex, their apoptotic potential, affinity, and selective photothermal ablation were studied.

Our results demonstrated the appropriate biocompatibility of Ti3C2Tx, Ti3C2Tx-PDA and Ti3C2Tx-PDA-Ab complexes with various cell types (HDF, HACaT and B16F10) after 4 and 24 hours of co-cultivation. It has been proven that increasing the PDA layer does not provide any advantages for modified MXenes, in particularly in biocompatibility and photo-thermal conversion. Laser irradiation modes were experimentally selected for effective impact on the complex and safety of CEACAM-negative cells. Highly selective ablation of tumor cells using near-infrared (NIR) irradiation observer in CEACAM1- positive melanoma cells loader with Ti3C2Tx-PDA-Ab complexes. At the same time, CEACAM1-negative cells, after whasing the Ti3C2Tx-PDA-Ab complexes, did not demonstrate a reduction of their viability.

Conclusion

The findings underscore the promising role of Ti3C2Tx MXenes in the field of oncology, particularly for photothermal therapy in treating skin cancer. Enhancements to this approach, such as MXene surfacer modification with the polydopamine and conjugating with specific antibodies, could broaden the applicability to various cancer types. The selective photothermal eradication of tumor cells utilizing MXenes shows great promise as an effective and targeted alternative in the arsenal of cancer treatment strategies.

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CHEMICAL CHARACTERIZATION OF DEFECTS IN TI3C2TX MXENES BY SYNCHROTRON BASED-SOFT XRAY SPECTROSCOPY

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MXenes offer a wide spectrum of properties with numerous fields of application.[1,2] The structure-property correlation can be strongly affected by the surface chemistry and defects.[3-5] A detailed understanding of the structure and the defects is thus required but grasping the chemical nature of these defects is challenging. In this work, soft X-ray Absorption Spectroscopy (XAS) and high-resolution Xray Photoelectron Spectroscopy (HR-XPS), performed at the BESSY II synchrotron in Berlin, Germany, as well as density functional theory (DFT) are used to investigate the surface chemistry, the chemical nature of defects, and the structure of Ti3C2Tx MXenes.

Ti3C2Tx MXenes were synthesized using mixed-acid methods to create structural defects with a systematic study of the etching time and the HF concentration. XA spectra at the Ti L- and C K-edges provide insights into the MXene core structure and defects while O K- and F K-edges are highly sensitive to the surface chemistry.[6] The correlation with DFT calculations of the simulated O K-, F K-, and C Kedges brings insight into the structure, surface chemistry, and defects such as atomic vacancies in the MXenes.[7] Additionally, HR-XPS measured with variable X-ray energies allowed by the use of a synchrotron light source, was used to gain insight into the surface terminations and the location of the defects using a depth profiling model.

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BIOMEDICAL APPLICATION OF MXENE FOR CARDIAC TISSUE REGENERATION

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The cardiovascular system disease rate is a crucial element of national well-being and plays a vital role in the sustainable development of society. Despite progress in treatment strategies, including pharmaceutical and surgery, none of them have yet been proven effective in preventing the progression of heart failure. Thus, the increase in morbidity and mortality from cardiovascular diseases around the world and the inability of standard treatment methods to restore heart function forces us to explore alternative solutions, particularly in tissue engineering of cardiac tissues.

Strategies for guiding cardiac tissue regeneration include various methodologies, including cell-based interventions, gene therapy, direct transformation of non-cardiac cells, acellular biologics, and innovative tissue engineering methods to restore damaged hearts [1]. Electrically conductive 3D scaffolds are one of the innovative tissue engineering methods that possess promising results. Among various polymers, polycaprolactone (PCL) demonstrated significant interest due to its remarkable physicochemical properties, biodegradability, and biocompatibility [2].

Taking into account the hydrophobic nature of PCL, we aimed to produce electrospun PCL mats with oxygen plasma posttreatment and elaborate the PCL-MXene composite for cardiac tissue regeneration. Previous studies have demonstrated the potential of MXenes (a large new family of two-dimensional nanomaterials) to develop conductive scaffolds for regenerative medicine. However, a new deposition technology is still required to achieve optimal structural and functional properties of the scaffold [3]. Pre-treatment by oxygen plasma allows us to use the “deep coating” method for immobilizing Ti3C2Tx MXene onto a tissue-engineered structure.

In this research, we provided an investigation of the structural and chemical properties of PCL-MXene electrospun mats with an assessment of their biological properties.

We produced PLC electrospun mats with fiber diameters up to 2 μm and porous area fractions ranging from ≤0.5 to 2 m2 followed by MXene coating. MXene deposition slightly alters the structure of PCL membranes but did not provide significant changes in pore area and fiber diameter. The addition of MXenes to PCL mats made the electroconductive with conductivity ranges from 5.22 mS/m to 326.33 mS/m. The biological study demonstrated that PCL-MXene composites are non-toxic, promote cell proliferation, and provide a significant active surface area for interaction with myocytes.

To summarize, a novel approach of PCL-MXene composite development demonstrated a promising solution for the elaboration of a new class of tissue engineering constructions for heart regeneration.

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INSIGHTS ON THE NATURE OF THE CHEMICAL BOND OF COMPOSITES MADE OF TIO2 CLUSTERS SUPPORTED ON TI2C FROM DENSITY FUNCTIONAL THEORY

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To overcome the catalytic limitations of titania (TiO_2) arising from an exceedingly large energy gap,[1] and short lifetime of the photogenerated charge carriers,[2,3] hybrid composites involving titania nanostructures supported over low dimensional carbides/nitride MXenes have been proposed. Indeed, it has been shown that these composite systems facilitate an efficient separation of charge carriers.[4-6] However, the nature of the chemical bond and electronic structure of these hybrid systems is almost unknown.

Here, to gain insights into the structural, electronic, and bonding properties of these semiconductor/MXene composites, density functional theory (DFT) based calculations, with the GGA type PBE functional, are carried out for systems involving small titania clusters $(TiO_2)_n$ (n=5 and 10) supported on the pristine Ti_2C (0001) MXene surface. Our findings indicate a strong exothermic interaction accompanied by significant charge transfer from the MXene substrate to the adsorbed titania clusters, leading to notable deformation of the titania clusters. The analysis of the density of states (DOS), carried out using the more accurate PBEx hybrid functional,[7] reveals a metallic character with titania-related states intersecting the Fermi level. The calculation of the C(1s) and O(1s) core level binding energy shifts, measurable by means of X-Ray Photoelectron Spectroscopy (XPS), evidence a complex origin beyond the broadly accepted charge transfer mechanisms. It is expected that the calculated results provide useful information to experimentalists working in the design and synthesis of this type of systems, with potential applications in catalysis.[8]

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SYNTHESIS AND PHOTOCATALYTIC ACTIVITY STUDY OF LAYERED TINα NANOSHEETS AS EMERGING MATERIALS TOWARDS GREENER N2 FIXATION TO AMMONIA

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MXenes are a novel family of two-dimensional (2D) transition metal carbides, carbonitrides and nitrides, directly prepared from selective etching of the A-site element in MAX phase precursors. Their general chemical formula Mn+1XnTx describes comprising n+1 layers (n=1–4) of early transition metals ('M'), interleaved by n layers of carbon and/or nitrogen atoms ('X'), with Tx representing surface terminations bonded to the outer M layers (i.e. –F, –O, –OH). Thus, their unique morphology and functionalities, together with a fascinating integration of mechanical, electronic, chemical, and optical properties makes them promising materials for advanced applications [1]. Owing to their consolidated role in the field of photocatalysis [2] and along with the increasing demand for high-performance renewable energy sources for chemicals production.

In this presentation, we will focus on the application of titanium nitride-derived Mxenes in the nitrogen fixation reaction by discussing whether these materials act as photothermal or thermal catalysts and delve into how the synthesis and purification parameters impact the overall catalytic performance.

Mxenes were obtained from two different MAX phases (Ti3AlN and Ti2AlN) and required the etching of Al layers that was carried out through Lewis acid molten salt method under Argon atmosphere and high excess of CuCl2 [3]. As a fundamental synthetic parameter, the increasing etching temperature (from 600 to 950) effect has been evaluated first.

Subsequently, a purification step is needed to remove deposited metallic copper over the raw Mxene. Parameters such as purification temperature, persulfate oxidating agent-nature (i.e. ammonium, potassium and sodium persulphate) and its concentration (i.e. 0,1-0,4 M) led to several multi-layered Ti3N2 and Ti2N. All these variables are proved to directly affect the formation of equilibrium phases as well as their final morpho-structural properties. Extensive physical and chemical characterization of the material were performed to get a comprehensive structural and electronic properties of each Mxene.

Each as-synthetized MXene has been tested in batch reaction under irradiation or dark trying to answer if the reaction undergoes by photothermal or thermal mechanism. Confirmation of nitrogen source of this reaction originates from reactive gas source was confirmed though 15N2 isotope labelling experiment. Additionally, optimization of reaction conditions was carried out also considering different external conditions of light intensity, pressure and temperature.

Finally, in this work we discuss the suitability of ammonia quantification methods by means of both indophenol blue method and 1H NMR

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CHARGE DELOCALIZATION IN MXENE FLAKES: FUNDAMENTAL UNDERSTANDING AND APPLICATION TO ELECTROCATALYST DESIGN

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Thanks to their unique properties, MXenes have found applications in many different fields such as energy conversion, electronics, and sensing. However, they tend to oxidize rather quickly when exposed to water or humid air, which hinders their commercialization. In the case of $Ti_3C_2T_x$, oxidation has been shown to lead to the formation of TiO_2 and therefore to a complete loss of its targeted properties.[1] While many studies have focused on understanding this oxidation process at the atomic scale and on how to prevent it or recover the initial properties of oxidized MXene films,[2] very few have investigated the spatial dynamics of this process at the single flake level. Relying on transmission electron microscopy (TEM), some researchers were able to track the formation of TiO_2 nanoparticles on individual $Ti_3C_2T_x$ flakes, but the electrons' origin remained unclear. Even if most TiO_2 nanoparticles were spotted on the flakes' edges,[1] the electrons might have travelled from farther away given the high conductivity of $Ti_3C_2T_x$.

Recently, some of us showed by using nanoscale electrochemical probes that even if only a small region of the flake is addressed electrochemically, the response corresponds to that of the entire flake, meaning that ions and electrons can be involved even if they are located microns away from the contact point.[3] To verify this charge delocalization, we correlated these nanoscale electrochemical measurements with scanning transmission X-ray microscopy (STXM). The advantage of this technique compared to TEM is that it can directly map the oxidation state of Ti at a very high spatial resolution (≈25 nm) and therefore tell where exactly the electrons were withdrawn from.[4]

In oxidative conditions, the oxidation state of Ti was found to increase several microns away from the contact point, proving a certain degree of charge delocalization within individual flakes. Interestingly, the clear border between the oxidized and pristine regions indicates that in given conditions, a fixed amount of charge can be extracted from the contact point.

From the materials design point of view, this means that the local oxidation of MXene flakes by noble metal ions in solution should yield homogeneously distributed metal nanoparticles both spatially and in size, as every nanoparticle would draw the same amount of charge from the flake and deplete it, preventing the nucleation of other nanoparticles in its vicinity. After optimizing the synthesis procedure,[5] we were indeed able to obtain such composites with an Au precursor. Notably, these materials show excellent performances as electrocatalysts for the hydrogen evolution reaction, better than each of the components separately, hinting at a strong metal-support interaction between the MXene flakes and the metal nanoparticles. Investigating this interaction, we establish new design principles for MXene-based electrocatalysts.

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HIGHLY SELECTIVE H2S GAS SENSORS BASED ON MXENE-ORGANIC COMPOSITE

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Environmental monitoring is vital for safety and thus gas sensors are gaining an immense interest in society and research community. Among different analytes, detecting hydrogen sulfide (H_2S) is crucial as H_2S is a toxic and flammable gas, largely found in petroleum and mining industries, as well as our daily life, e.g., putridity of foods and bacterial breakdown of human and animal wastes. Exposure to H_2S for humans has the risk of causing severe health problems such as eye and throat injury, dizziness, and loss of sense of reasoning at low concentration, and it can even lead to death at a very high concentration (above 1000 ppm). Most of the available H_2S gas sensors, however, are expensive and suffering from various problems such as high cost and power consumption, the high limit of detection (LOD), low selectivity, and inflexibility.

Therefore, developing a readily available and low-cost gas sensor with better selectivity and LOD toward H_2S is necessary for human health and environmental monitoring.

Recently, two-dimensional (2D) materials (e.g., graphene,[1] MoS2,[2] and black phosphorus (BP)[3] and MXene[4]) have attracted intensive research interest due to their unique physical and chemical properties such as large surface area, versatile surface chemistry, and room-temperature gas sensing capability.[5] Especially MXenes, consisting of 2D transition metal carbides and nitrides, have shown promise for gas sensors due to outstanding metallic conductivity (10^3–10^4 S cm^{-1}), high mechanical stability, high hydrophilicity, and the presence of abundant surface functional groups that provide active sites for gas adsorption.[5] Lee et al. and Kim et al. were among the first to investigate gas-sensing performance of pristine MXenes,[6,7] followed by a rapidly increasing number of studies. Sensing of different analytes, including NO, NH_3, CO and etc., have been investigated. However to the best of our knowledge, only very few H_2S gas sensor based on the $Ti_3C_2T_x$-related materials has been reported thus far.[8] Moreover, the intriguing role of intrinsic surface functional groups on the gas sensing performance has not been evaluated extensively even with theoretical calculations, which impairs understanding of the sensing mechanism.

In this talk, I will present the gas sensing performance of pristine $Ti_3C_2T_x$ and its nanocomposites with poly [3,6-Diamino-10-methylacridinium chloride-co-3,6-diaminoacridine-squaraine] (PDS-Cl). While we observe clear H_2S selectivity (negative response) already on the pristine thin film of $Ti_3C_2T_x$ sensors, the composites of PDS-Cl polymer and $Ti_3C_2T_x$ (Ti3C2Tx /PDS-Cl) retain excellent selectivity toward H_2S and provide higher surface to volume ratio for MXene flakes, that consequently enhances the sensing response (~ 30 times higher compared to pristine MXene at 1 ppm H_2S) with low detection limit (0.5 ppm), and good repeatability. To gain detailed insight into the interaction between gas molecules and $Ti_3C_2T_x$, we carried out density-functional theory calculations, where we accounted for the fact that MXene surfaces contain a mixture of =O, -OH, and -F functional groups. We show that this has a dramatic effect on the gas adsorption (charge transfer and binding energy) and is necessary for reproducing the experimental observations. Based on these, we finally propose a sensing mechanism.

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EXOTIC PHOTOTHERMAL PROPERTIES IN TI-BASED MXENES FOR OPTOELECTRONICS

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Transition metal carbides and/or nitrides (also known as MXenes) represent the latest and largest discovered family of two-dimensional materials1, showing an exponentially increasing number of publications over the last five years and, thus, exerting a great influence on the current materials science research2. They show unique and versatile physicochemical properties, thereby offering the chance to access the best of many worlds and achieve state-of-the-art performance and technological breakthroughs3. In recent years, MXenes have gained ever-growing attention for their efficient light-to-heat conversion, approaching 100%4, thus making them prime candidates in related conversion systems, such as solar-powered water evaporations, photothermal actuators and so on5. Nevertheless, thermal and photothermal characteristics of MXenes represent the less investigated class of properties, highlighting a fundamental lack of knowledge in the field that is crucial to further advance the MXene research and expand their range of investigation for groundbreaking discoveries.

In our work, we delve into the analysis of photothermal and thermal properties of Ti-based MXenes, namely Ti3C2Tx and Ti2CTx, as well as their potential use for optoelectronic applications. As illustrated in Figure 1a, we compare their electrical response upon laser irradiation (λ = 450 nm, Power = 10 mW, Intensity = 2.5 W/cm2, Device area = 2x1 mm2) along with their photothermal behavior by changing the environmental conditions, pressure and/or temperature (T). Figures 1b and 1c display the current response recorded at room T and ambient pressure (Air) for a single laser pulse (OFF-ON-OFF cycle).

From the comparison of the two Ti-based MXenes, we observe clearly distinct behaviors: Ti3C2Tx shows a negative (photo) response upon laser irradiation (i.e., current decreases), while Ti2CTx exhibits a positive (photo)response (i.e., current increases). This is due to the different Resistance (R) vs. T trend recorded for the two systems, with Ti3C2Tx showing dR/dT > 0, unlike Ti2CTx with dR/dT < 0. Moreover, the overall different kinetics of the process have been observed for the two MXenes: while Ti3C2Tx exhibits a symmetric and fast current rise and decay (≈ 10 s), Ti2CTx presents a striking asymmetric and much slower kinetics during the current rise (≈ 30 s) and decay (≈ 104 s). By using Newton's and Fourier's laws, we are able to estimate the ratio of the thermal conductivity for the two MXenes, with Ti3C2Tx showing a larger value by a factor ≈10. The latter characteristic paves the way to the use of Ti2CTx in applications taking advantage of multiple photo-levels, such as memory devices. Moreover, such exotic photothermal kinetics is strongly affected by the operating conditions and can be fine-tuned by exposing the devices to different atmospheres (Air vs. Ultra-High Vacuum) and T (from 100 K to 350 K), as displayed in Figures 1d and 1e. In conclusion, our work highlights the dramatic effect of structure and composition in Ti-based MXenes on their optoelectronic properties, with particular emphasis on their photothermal and thermal characteristics. Particularly, the exotic photothermal kinetics recorded for Ti2CTx might pave the way for its use in multi-stimuli memory and neuromorphic devices.

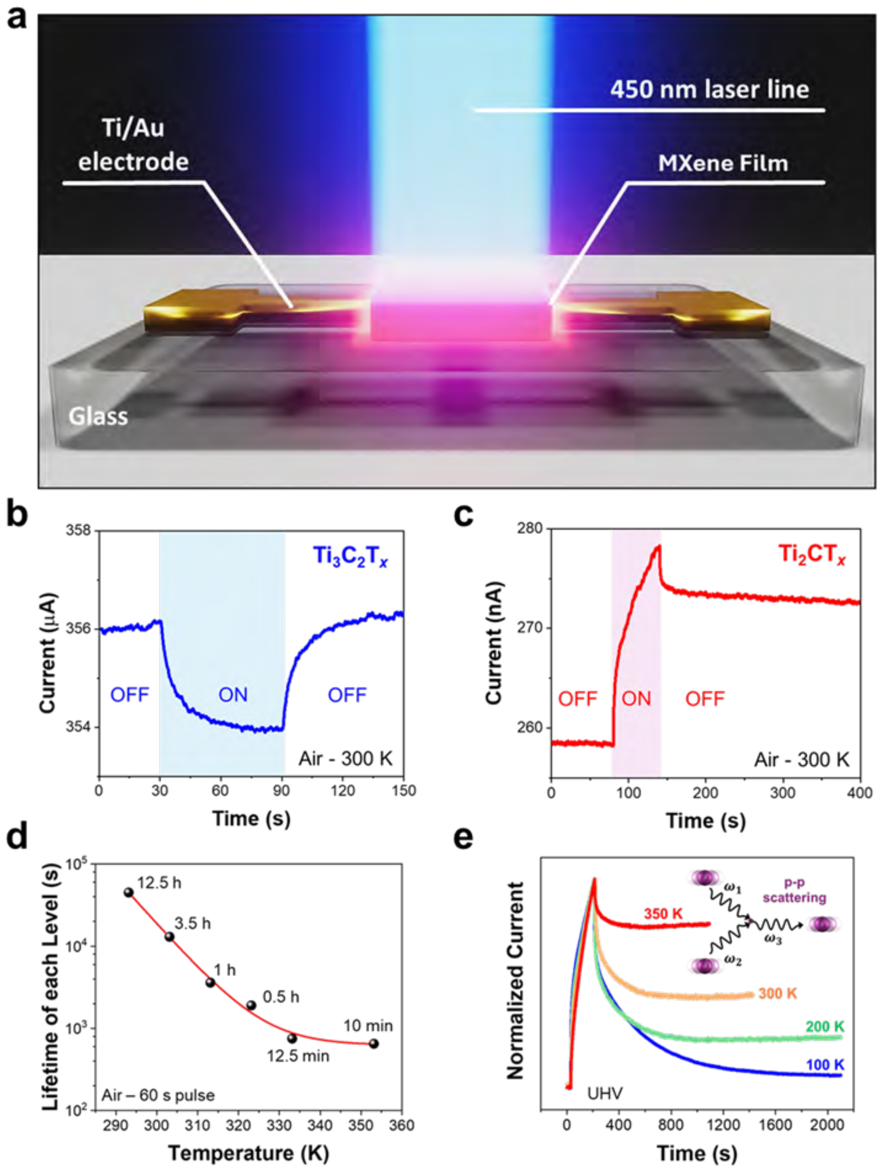

Figure 1: a, Illustration of the experimental measurement setup for MXene devices. Photothermal response in the air at 300K for b, Ti3C2Tx and c, Ti2CTx spray-coated thin films. d, Lifetime of photocurrent level, achieved after 60 s laser pulse (λ = 450 nm), as a function of temperature for Ti2CTx in air. e, Normalized current response after 180 s laser irradiation (λ = 450 nm) for Ti2CTx at different temperatures under UHV conditions.

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BIO-SYNTHESIZED GOLD NANOPARTICLES/V2C MXENE FOR AN ULTRAFAST AND COMPLETE SEPARATION OF AZO DYE POLLUTANTS

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Herein, we report the preparation of V_2C MXene membranes modified with gold nanoparticles synthesized using *C. aurantium* peel extract. The extract does not only reduce $HAuCl_4$ but also surrounds and stabilizes the gold nanoparticles.

Moreover, their incorporation into the interlayer galleries of V_2C MXene, leading into the ultrafast (>1000 L m^{-2} h^{-1}) water flux with a near complete rejection (>97%) for a series of azo dye pollutants, such as congo red, methylene blue, and reactive yellow. These remarkable performances are owing to the unique two-dimensional structure of V_2C MXene and the presenceof green gold nanoparticles, which widen the interlayer galleries while guarding and trapping the azo dye molecules. Our findings could be further developed to realize MXene-based membranes for the effective separation of azo dyes-polluted water environment.

EXCITONIC EFFECTS IN MXENES

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We review here our achievements in the field of excitons in MXenes in the last several years. Electron-electron and electron-hole (exciton) effects are specifically pronounced in MXenes and other two-dimensional (2D) materials because of weak dielectric screening from the environment. We recently showed strong effects of excitons on optical absorption in selected Ti-, Sc-, Cr-, Mn-, Mo-, Zr-, and Hf- based MXenes resulting in high monolayer absorptance.[1-5] Moreover, oxygen-terminated Ti2C and several Zr- based carbides undergo semiconductor-to-metal transition by the creation of a single Ti-vacancy[6] and by strain.[4] Finally, we discover MXene candidates to unusual exciton insulator character.[5]

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ASSEMBLY OF SBA-15 TEMPLATED MESOPOROUS NIFE2O4 AND TI3C2 MXENE AS AN ANODE FOR LITHIUM-ION BATTERY

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This study reports on the concise fabrication and assembly of mesoporous NiFe2O4 and Ti3C2 MXene and its application as an alternative anode material for Lithium-ion battery. Here, the mesoporous feature of NiFe2O4 was fabricated via nanocasting method using SBA-15 as hard template. Mewahile Ti3C2 MXene was prepared using etching and exfoliating process. Based on the result, the integration of the two materials via hydrothermal method was found to demonstrate a synergistic effect in facilitating the migration of Li ions which resulted in a significant increase on the overall battery's specific capacity (1383 mAh/g) and Columbic efficiency of 98%. Such enhancement was believed to be originated not only from the high surface area of m-NiFe2O4 (168.3 m2/g) which mainly due to its mesoporosity feature, but also the unique physicochemical properties and conductivity of Ti3C2 MXene. Besides, theoretical calculation using Density Functional Theory (DFT) also revealed that the adsorption energy of lithium atom was found to be more negative at the composite's surface than that of individual materials. This suggests that the synergy between the two materials provide a more favorable environment for lithium to be intercalated at the anode which ultimately led to an increase in battery performance.

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ORDERED DOUBLE TRANSITION METAL MAX PHASES AND THEIR ETCHING INTO MXENES- SYNTHESIS AND ELECTROCHEMICAL STUDIES

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The very few reports published on the electrochemical properties of Double Transition Metal MXenes (DTMs) suggests that they perform much better than their mono metal counterparts. This is true for both ordered and solid solution DTMs[1][2][3]. Despite the theoretical predictions on the stability of a number of double transition metal MAX phases, only a few have been synthesized and etched into their corresponding MXenes. In attempt to scale up the synthesis and processing of DTMs, we present the synthesis and structural studies of ordered Cr2TiAlC2, Cr2Ti2AlC3 and solid solution Ti2NbAlC2 MAX phases and their etching into corresponding MXenes. In-situ high temperature XRD data collected on the admix of activated metal powders was used to optimize and model the MAX phase synthesis in high temperature tube furnace. Electrochemical studies such as CV, EIS and CCD of the DTMs compared with Ti3C2Tx will be presented and discussed.

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THE TRANSFORMATIVE POWER OF MXENES: FROM HARVESTING GREEN ENERGY TO ENGINEERING SYNTHETIC NANO/MICRO ROBOTS

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Herein, we present a dual-phase exploration of MXenes, showcasing their transformative applications from green energy harvesting to the engineering of synthetic nano/micro robots (NMBOTs). In the realm of green energy, we have innovatively integrated polyoxometalates (POMs) with MXenes, employing them as electrocatalysts. For hydrogen generation, Cobalt and Tungsten-based POMs were incorporated, demonstrating low overpotential and high stability, particularly with Cobalt-based POMs. In electrochemical CO_2 reduction, the integration of Copper-based POMs led to the successful production of C_2 products.

The second phase delves into the environmental application of MXenes, focusing on their use in nano/microrobotics. We developed light-driven MXene-based microrobots (Bi/Fe/MXeBOTs), fabricated using V_2C MXene as a scaffold and grafted with bismuth nanoparticles (Bi NPs) as active sites, while Fe_2O_3 nanoparticles provided magnetic control. These microrobots exhibited remarkable performance in the mineralization of Bisphenol A (BPA) to CO_2 and H_2O, demonstrating an ability to remove/degrade about 60% of BPA within just 10 minutes and achieving nearly complete removal/degradation within an hour. The photocatalytic degradation of BPA using Bi/Fe/MXeBOTs not only signifies a significant advantage in the mineralization process but also underscores the potential of MXenes in environmental remediation, as these robots use water as a non-toxic fuel and light as a renewable energy source.

These researches position MXenes as a versatile material capable of addressing critical needs in both renewable energy generation and environmental sustainability, marking a significant stride in technological innovation.

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COMPOSITIONAL MAPPING OF 2D MXENES AT THE NEAR-ATOMIC-SCALE BY ATOM PROBE TOMOGRAPHY

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Due to their 2D nature and unique set of properties, MXenes have the potential to replace commercial materials in surface-active applications such as energy storage or catalysis. Two steps are important for the top-down synthesis of MXenes: the harsh selective etching of the precursor material, and the subsequent exfoliation into nanosheets by intercalation of cations or molecules. Various combinations of chemicals are used for this purpose, which, in conjunction with the detailed synthesis route, determine the surface chemistry of the MXenes, i.e. functional groups or absorbed cations or molecules on the surface. The detailed determination of the chemical composition of such nanomaterials is therefore crucial to understand and establish the relationship between composition and functional properties [1].

Such questions can in principle be addressed by using atom probe tomography (APT). APT relies on the field evaporation of atomic or molecular ions from the apex of a needle-shaped specimen. The ions are projected onto a position-sensitive detector, that records time-of-flight and impact coordinates. By combining both information, a 3D compositional map of the field evaporated volume is reconstructed with sub-nanometer precision. APT is sensitive to both light and heavy elements, and is therefore very useful for studying, for example, the resulting surface chemistry of MXenes following wet chemical synthesis. However, specimen preparation has proven to be particularly challenging for nanomaterials, as APT requires a dense specimen with an end-diameter of about 100 nm, and established protocols using a dual beam scanning electron microscope / focused ion beam instrument are often not readily usable.

Examples of APT analyses of pristine and oxidized $Ti_3C_2T_x$ MXenes stored in colloidal solutions are summarized in Figure 1. We show the concentration of alkali elements originating from wet chemical synthesis retained in the nanostructures even during oxidation [2]. Their high concentration in the resulting TiO_2 nanowires raises the question to what extent they contribute to the oxidation mechanism and kinetics, as they appear to stabilize the oxide to the detriment of MXene. In this contribution, we discuss how APT can help to understand the detailed composition of MXenes, in order to guide their synthesis for optimized functional properties. The underlying specimen preparation workflows for single to few layer nanosheets [3] will be discussed. Enabled by an in-situ sputtering technique, we introduce also a revised workflow to simplify APT specimen preparation for 2D materials from a free-standing film, i.e. a macroscopic stack of nanosheets, following common specimen preparation protocols [4]. As the film cannot withstand the high electrostatic field applied during APT analysis, the specimens are coated with a thin layer of metal, thereby mechanically stabilizing the sample. This workflow significantly simplifies specimen preparation, and opens up new possibilities for further analysis of 2D materials using APT.

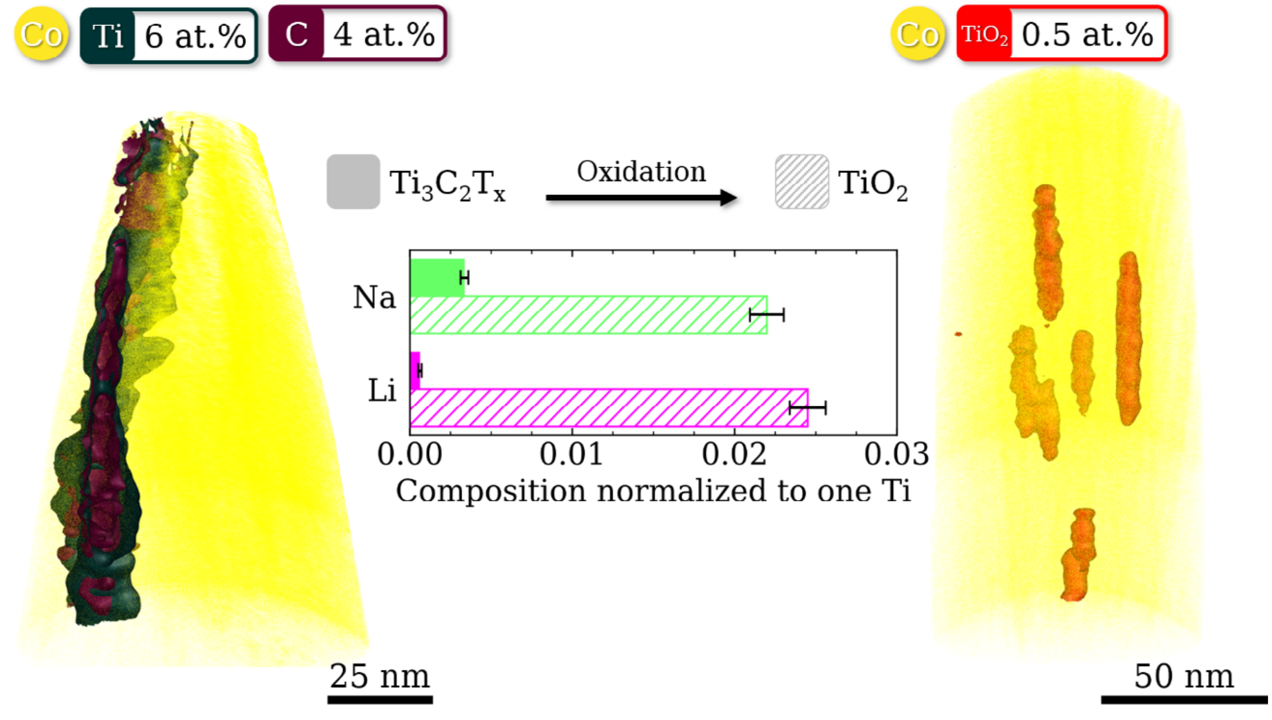

Figure 1: Oxidation experiments on $Ti_3C_2T_x$ MXenes stored in colloidal solution. APT analysis reveals concentration of alkali elements from synthesis in TiO_2 nanowires resulting from MXene oxidation. Adapted from ref. [2].

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ANTI-CORROSION STRATEGY ENABLES HIGH-STABLE MXENE POSITIVE ELECTRODES FOR ADVANCED PSEUDOCAPACITIVE ENERGY STORAGE

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2D MXenes have sparked great interest in recent years, however, their intrinsic chemical/electrochemical instability hinders their practical applications. Herein, a universal anti-corrosion strategy that suits a family of MXenes such as Nb2CTx, Ti3C2Tx, Mo2Ti2C3Tx, and Ti3CNTx is reported, which enables the stable operation of MXenes at positive (anodic) potentials and endows the MXene-based heterojunctions with remarkable capacitive performance and long-term environmental stability. The further 3D-printed asymmetric supercapacitors consisting of MXene anodes and MXene-based cathodes show wide voltage windows and deliver ultrahigh areal energy and power densities. This work paves new and exciting avenues for designing highly stable MXene-based materials for electrochemical energy storage, sensing, catalysis, and other applications.

ENHANCING MXENE STABILITIES, PROCESSIBILITY, AND STACKING ORDER VIA HIGH-PERMITTIVITY SOLVENTS

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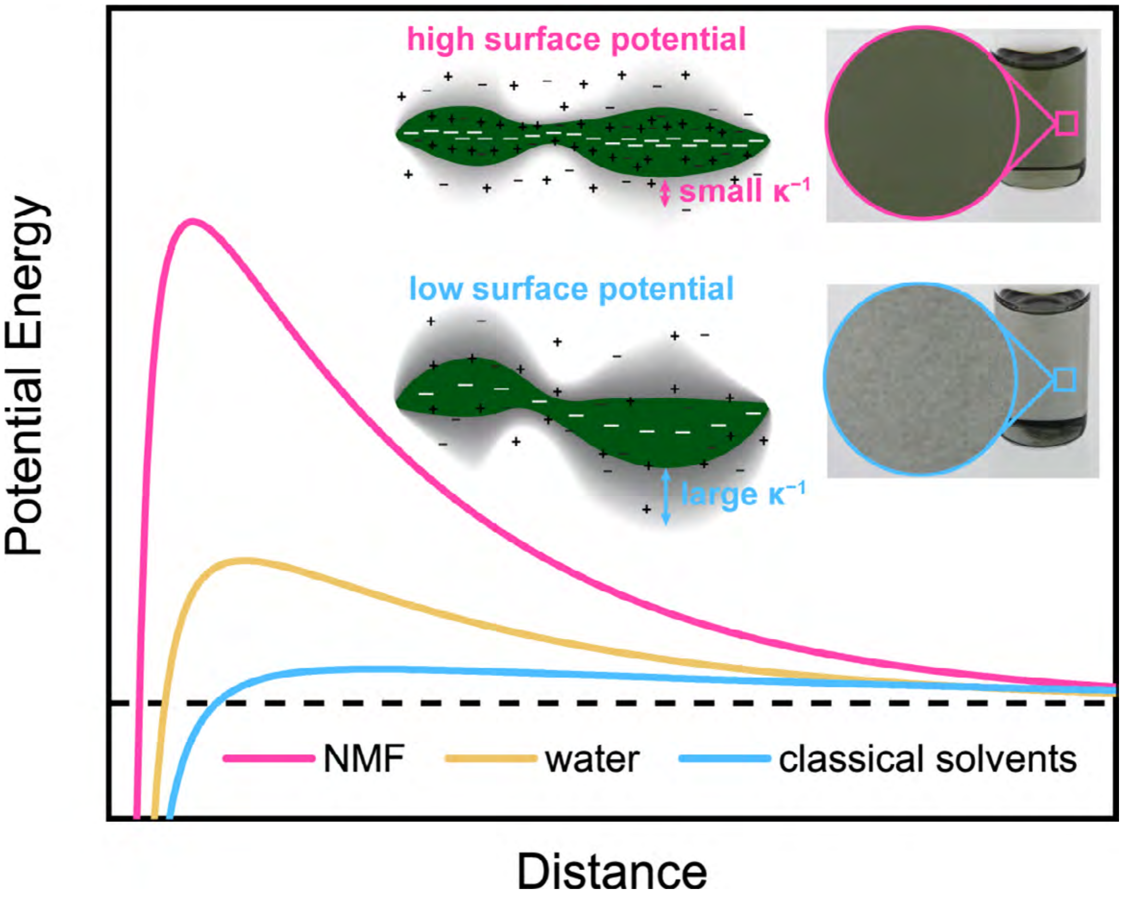
MXene has sparked remarkable attention in diverse fields and given rise to numerous pioneering applications but challenges persist in pursuing long-term stability, processibility, and highly ordered stacking structures. Various strategies were made to improve the colloidal/anti-oxidation stabilities and processing ease of MXenes, including surface coating, anti-oxidation agents, edge protecting, organic solvent exchanging, etc. Among them, the organic solvent exchanging, an additive-free strategy, can largely extend the shelf-life of MXenes without changing its chemical nature. However, compared to the most used solvent–water, common organic solvents, i.e., ethanol, DMF, DMSO, NMP, etc., could not provide sufficient colloidal stability, leading to server aggregation in the dispersion and disordered stacking in the resulting thin films. The poor dispersibility and structural disorder largely undermine MXene processibility and physical properties.

Contrary to conventional wisdom using high polarity dispersant based on high solvent polarity index and dipole moment, we find that the high permittivity of the dispersant plays a crucial role in achieving high stabilities. We show surprising colloidal and anti-oxidation stability of MXene when dispersed in high permittivity solvents, e.g., N-methylformamide and formamide (ε_r = 171 and 0109), superior to water (ε_r = 78), and commonly used polar organics, e.g., N,N´-dimethylformamide (ε_r = 37).

Selection of the high permittivity solvents also enhances the processing ease against various surfaces and reduces the stacking defects in the MXene films, leading to better physical properties. To acquire deeper scientific insights, we also employed two protocols for (semi)quantitative analysis of (1) colloidal stability using DLVO theory, and (2) mesoscopic structures using a small angle X-ray scattering model. Our characterization protocols are widely applicable for MXene research, which allows a significant advancement in understanding the MXene colloidal stability and stacking behavior. We foresee that the findings are general to address the stability and processing problems and we suggest that high permittivity solvents can be easily applied to disperse other MXenes and 2D materials, opening applications, such as energy storage devices, MXene electronics, or nanocomposites.



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DISTANCE DEPENDENCE OF MXENE-INDUCED FLUORESCENCE ENERGY TRANSFER AND APPLICATIONS IN SINGLE MOLECULE BIOSENSING

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MXenes, which were discovered in 2011, have become widely recognized as 2D materials that have potential applications in energy storage, electromagnetic shielding, and optoelectronics.[1] The energy transfer properties of these materials are still not fully understood, and this knowledge may have implications in various fields. In this study, we utilized single-molecule fluorescence (confocal) microscopy and DNA origami nanopositioners to explore the distance-dependent intensity and lifetime of an emitter[2] (ATTO 542) placed on transparent thin films made of spincoated $Ti_3C_2T_x$ MXene 2D flakes.[3] Each DNA origami structure was created to carry a single dye molecule at predetermined heights. We developed a specific immobilization chemistry for DNA origami nanostructures based on the interaction between glycine and MXene, which allowed us to control their orientation on the surface with precision. Our research showed that when the dye was positioned between 1 nm and 8 nm from the surface, the fluorescence was reduced in a distance-dependent manner of d^{-3}. These findings are consistent with the well-known Förster mechanism of near-field energy transfer with transparent conductors at the bulk level.[4] MXenes have the potential to serve as short-distance spectroscopic nanorulers for measuring biomolecular processes, providing a high level of sensitivity at a distance range that conventional energy transfer tools cannot reach.

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SURFACE TERMINATION MODULATED CATALYTIC ACTIVITY OF TI3C2 MXENE IN CARBON DIOXIDE REDUCTION AND HYDROGEN EVOLUTION REACTIONS

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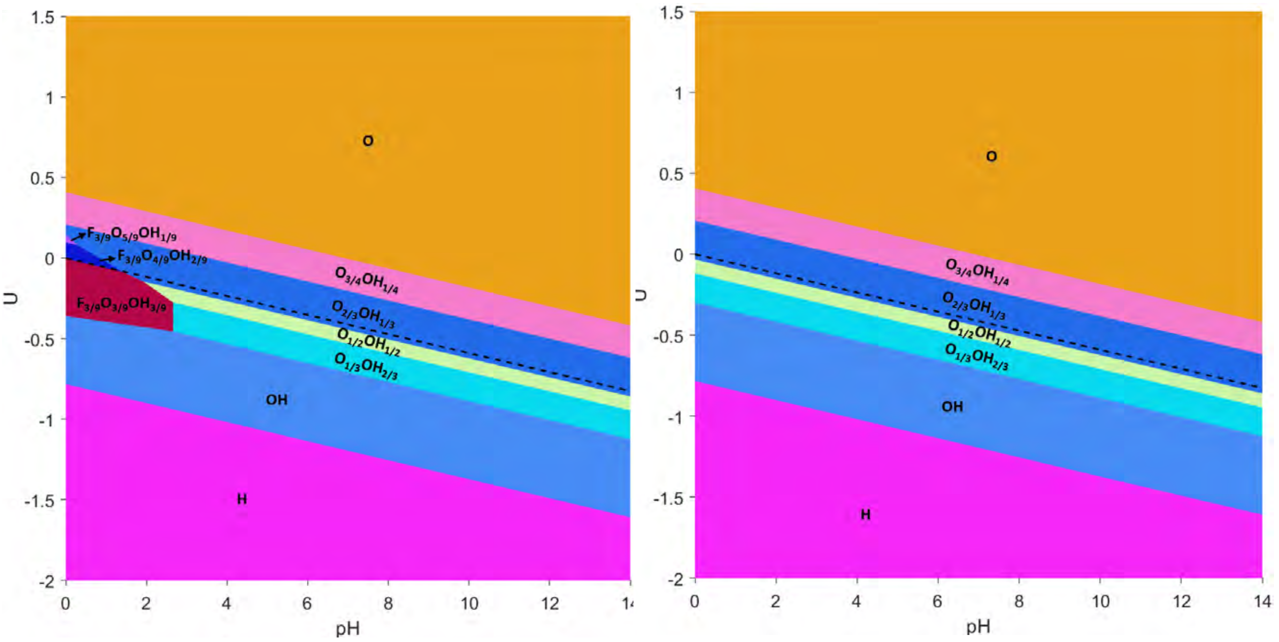
To satisfy energy needs, our society relies mostly on fossil fuels, like coal, oil, and natural gas. However, these sources contribute to climate change and resource depletion. A shift to renewable and cleaner energy is necessary. Electrocatalytic carbon dioxide reduction reaction (CO_2RR) and hydrogen evolution reaction (HER) can contribute to protect environment and sustainability by converting water into H_2 and the greenhouse gas CO_2 into commodity chemicals under mild conditions, thus closing the carbon cycle.[1]

Two-dimensional (2D) MXene materials have been identified as efficient electrocatalysts due to their high surface areas, active sites, conductivities, stability, resistance, and hydrophilicity. However, much of the focus has been on pristine MXenes, or with fully –O or –OH, neglecting the fact that synthesized MXenes often possess mixtures surface terminations. Herein, we present a comprehensive density functional theory (DFT) study taking the Ti_3C_2 MXene as a case example to explors the stability and effect of different surface terminations on HER and CO_2RR. To this end the Pourbaix diagram (see figure) of around 450 surface terminations was constructed, including pristine Ti_3C_2 and various terminations in differing ratios. Our results evidence that surface groups significantly influence catalytic performance, reducing limiting potential and cost.[2] For HER, a higher ratio of –O groups enhances catalysis by modulating hydrogen bonds.[3] For CO RR, –OH groups serve as hydrogen donors and engage in proton reduction, improving the catalytic reaction.[4] Additionally, –F groups positively affect catalysis. These findings are critical for future 2D MXene catalyst design and enhancement.



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COMPUTATIONAL STUDY OF MXENES FOR WATER SPLITTING PHOTOCATALYSIS

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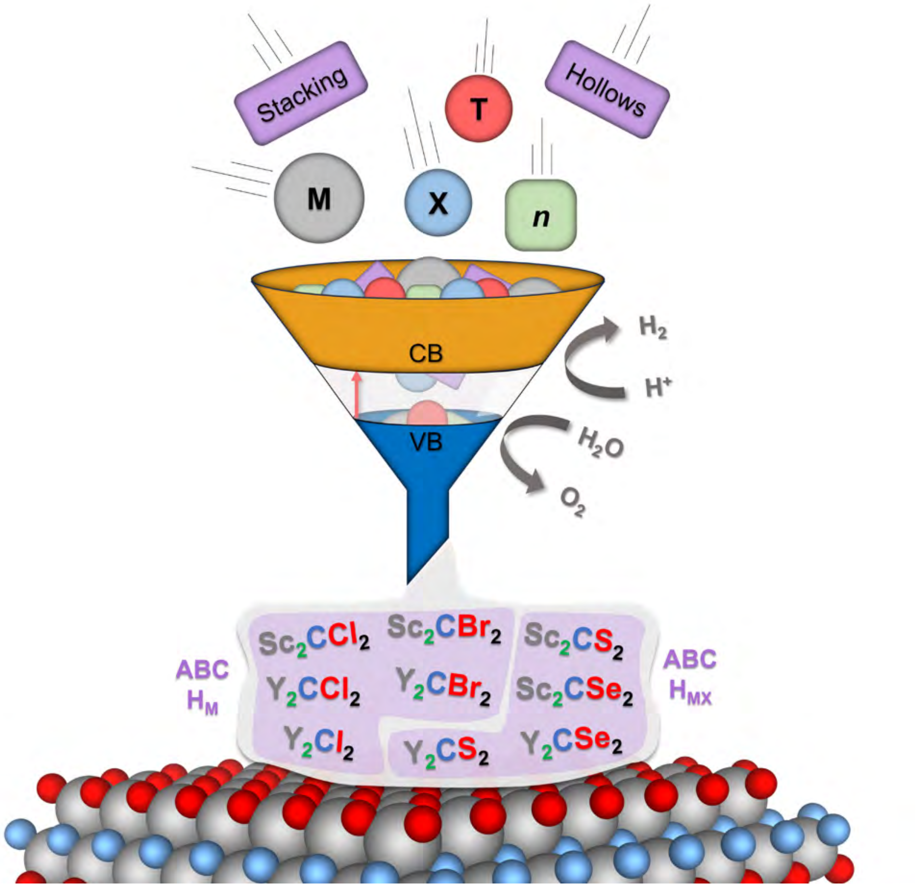
Nowadays, our energy demands still depend on traditional fossil fuels such as coal, oil, and natural gas, despite their non- renewable nature and negative impact on the environment. This reality underscores the urgent need to transition towards renewable resources to combat global warming. In this context, Hydrogen (H_2), a clean-burning fuel, emerges as a particularly promising option.

There are different methods for the H_2 production, but one of the most sustainable ones is by water splitting, where water (H_2O) is broken down into H_2 and O_2. Nevertheless, this method is very energy-demanding, and there is a crucial need to explore new materials that can catalyze this reaction. A particularly attractive solution involves using solar light as a renewable energy source for carrying out this process, and, therefore, photocatalysts have proved to be the leading option.

This is tackled here with light shed upon MXene compounds as potential photoactive materials for water splitting. MXenes are a vast family of novel two-dimensional (2D) transition metal carbide/nitride materials which have driven considerable attention in various applied fields, ranging from electrocatalysis, energy application, up to sensors. A particular field of interest is their role in photocatalysis, especially in processes such as overall water splitting.[1] When the valence and conduction band edges of MXenes are appropriately aligned with respect to the standard potentials of redox half-reactions, they can be potential candidates to generate green H_2 from abundant water using solar light as an energy vector.

Given the vastness of the MXene family, specially with new synthesis methods that have led to novel terminations,[2] the experimental assessment of MXenes for water splitting photocatalysis can be cumbersome and expensive. Therefore, a rationally driven search based on suited and accurate computational simulations can effectively seize their bandgap width and level alignment as a function of composition, layer stacking, and termination. This is done here with a comprehensive high-throughput screening of over 4,400 MXene structures, resulting in a list of suited MXenes for water splitting applications. The most promising cases are Sc_2CT_2, Y_2CT_2 (T = Cl, Br, S, and Se), Y_2Cl_2 and Zr_2CO_2, which have been further evaluated by assessing their band alignment, charge carrier mobilities, optical absorbance and charge density at the band edges.



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ROLE OF PRE-INTERCALATION ON THE ELECTROCHEMICAL PERFORMANCE OF TI3C2TX MXENE IN AQUEOUS AND ROOM TEMPERATURE IONIC LIQUID ELECTROLYTE SUPERCAPACITORS AND IN SODIUM-ION CAPACITORS

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MXenes have been investigated for energy storage applications since they were first discovered. Their layered structure, conductivity, and affinity for surface reactions makes them attractive candidates for battery electrodes as well as supercapacitor electrodes. The best performance for Ti3C2Tx MXene supercapacitors has typically been found for delaminated MXene in aqueous H2SO4 electrolyte. However, aqueous electrolytes are limited because of the narrow electrochemical stability window of water (only about 1.3 V). MXenes have been used in ionic liquid and organic electrolyte supercapacitors but the capacitance is very low. The scalability of delaminated MXene is also a challenge, as the delamination process is time consuming and relatively low yield. Further, the thickness of delaminated MXene electrodes is limited to a few microns, as the capacitance decreases significantly when thickness is increased.

One of the advantages of MXenes is their ability to host a variety of species in their interlayer spaces. The intercalation of cations is typically straightforward, since the positively charged ions are attracted to the negatively charged MXene sheet surfaces. Intercalation can even be done as part of the etching process, which streamlines synthesis.

In the first work, intercalation of metal cations (viz. K+, Na+, and Mg2+) has been used to produce multilayer Ti3C2Tx MXene electrodes for aqueous H2SO4 electrolyte supercapacitors. The pre-intercalation of these cations is done during the etching process. These electrodes demonstrated gravimetric capacitance similar to that observed in delaminated MXene electrodes, but at thicknesses of 30-100 microns, which is comparable to commercially prepared electrodes. These thicker electrodes are still free-standing and flexible, but the capacitance is only slightly affected by the increasing thickness.

Because of this, we were able to achieve up to 5.6 F/cm2 in areal capacitance while maintaining ~300 F/g gravimetric capacitance. Additionally, the manufacture of these electrodes is more similar to industrial roll-to-roll fabrication, as compared to the process used to produce delaminated MXene electrodes. Interestingly, the cations are not maintained in the interlayer spaces, but the capacitance is maintained for 10,000 electrochemical cycles, suggesting that the impact of the cations on the surface chemistry of the MXene is maintained even without the cations. These materials were investigated electrochemically, using X-ray absorption spectroscopy, and investigated with DFT and molecular dynamics to understand the results.

In the second work, alkylammonium cations with carbon chain lengths between 6 and 16 carbons were intercalated into multilayer Ti3C2Tx MXene for use as electrode materials in ionic liquid supercapacitors. Like in the previous study, the intercalation was done as part of the etching process and the MXene produced was made into flexible freestanding electrodes. These electrodes were used in supercapacitors using EMIMTFSI electrolytes. The supercapacitors using the 12 and 16 carbon chain alkylammonium cations were able to achieve very high specific capacitances of over 250 F/g. It can be shown using XRD measurements that these intercalated MXenes have a larger interlayer spacing that traditional Ti3C2Tx MXene. Ex situ XRD shows that the MXene layers are able to expand and contract to allow the electrolyte ions to move in and out of the MXene during electrochemical cycling. These materials were further investigated using neutron scattering, HRTEM, and molecular dynamics to investigate the structure and dynamics and the orientation of the large electrolyte and intercalant molecules.

Finally, a radical anion mechanism was used to intercalate elemental sodium into Ti3C2Tx MXene. High loadings of up to 2 atoms of sodium per Ti3C2Tx formula unit were achieved with this mechanism. Electrodes made from these materials were able to be used directly in sodium ion capacitors without the need to pre-charge them in a half cell and then remove them to place into the metal ion capacitor without loss of capacitance. Here, neutron total scattering with pair distribution function and density functional tight binding were used to fully resolve the structure of the intercalated materials and understand how the sodium atoms are distributed on the Ti3C2Tx MXene surfaces.

These three studies show the power of intercalation to tune MXene materials for electrochemical applications. One of the great advantages that MXene offers is in tunability, and intercalation can be a very straightforward method for tuning materials to the exact application. These methods can be used for a variety of MXenes in many applications.

DEFECT ENGINEERING OF MO2-XCTZ MXENE THROUGH PRECURSOR ALLOYING AND ITS EFFECT ON ELECTROCHEMICAL PROPERTIES

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Defect engineering of $Mo_{2-x}CT_z$ MXene through precursor alloying and its effect on electrochemical properties

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The formation of vacancies and/or pores into two-dimensional materials, like graphene and MXenes, have been shown to increase their performance for numerous sustainable applications [1,2]. Several methods have been reported to create pores in MXenes, however, a simple and affordable method with controlled and tailorable vacancy concentration and/or pores size remains challenging. Herein, we address this issue by proposing a simple and reproducible method for controlled synthesis of $Mo_{2-x}CT_z$ MXene with randomly distributed vacancies and pores.

The $Mo_{2-x}Cr_xGa_2C$ MAX phase was synthesized following a two-step procedure: (i) synthesis of a 3D $Mo_{2-x}Cr_xC$ alloy and (ii) reaction between $Mo_{2-x}Cr_xC$ and Ga. Through both experimental and theoretical analysis, Cr was shown to be homogeneously distributed on the metal site with a wide solubility range. During HF etching, both Ga and Cr atoms were removed, evident from XPS evaluation shown in Figure 1a. Moreover, the as-produced $Mo_{1.74}CT_z$ MXene exhibited defect-rich sheets with vacancies and pores in the structure (Figure 1b), originating from selective etching of Cr atoms in the 3D precursor alloy.

Notably, the incorporation of Cr in the MAX phase facilitated a shorter etching time and an improved MAX to MXene conversion yield. Furthermore, electrochemical characterizations indicated that the presence of defects results in an excellent capacitance, approximately 65% higher when compared to its stoichiometric counterpart Mo CT [3] (a comparison with different MXenes can be seen in Figure 1c).

This study shows defect engineering, schematically showed in Figure 1d, as a viable path for improving the MXene performance and further suggests its applicability for different MAX phases and/or for further optimization of MXene properties for various applications.

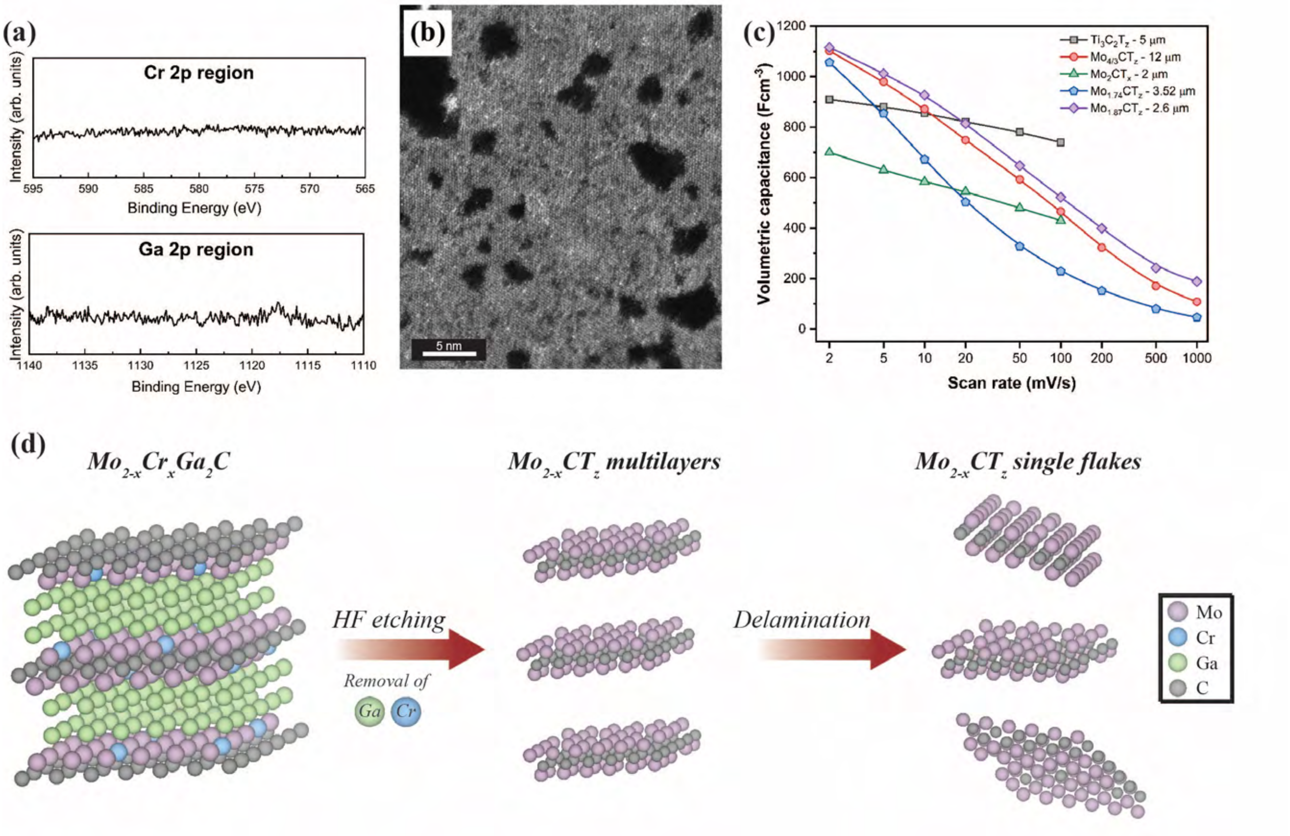

Figure 1: (a) Schematic MXene synthesis procedure, (b) XPS spectra of Cr 2p and Ga 2p regions. (c) High magnification image showing the range of pore distributions (d) Comparison of the volumetric capacitance of the present work with previously reported values.

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MXENES IN THE FRAMEWORK OF CLAYS AND RELATED 2D SOLIDS

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Practically since their discovery, various researchers have referred to MXenes as clays. In fact, many of their physicochemical characteristics are very similar, especially with regard to their 2D structural arrangement, morphological appearance, colloidal and surface properties, biocompatibility, etc., which means that both types of solids have a large number of actual or potential applications. However, some characteristics, such as their chemical composition (clay minerals: silicates; MXenes: carbides/nitrides) or their electrical behavior are totally different and, therefore, MXenes must be clearly differentiated from clays even in their nomenclature.

In any case, clays are a large family of widely studied 2D solids that represent an excellent model that may be well suited to develop new nanostructured materials derived from MXenes. For example, the broadly studied intercalation processes in clay minerals can be exploited as a useful strategy to prepare very diverse hybrid and nanocomposite materials derived from MXenes. In addition, other layered solids, such as certain transition metal oxides like vanadium pentoxide xerogel, as well as transition metal phosphates and dichalcogenides, are also 2D solids that can act similarly giving rise to corresponding derivatives endowed with desirable behavior.

In this communication, we introduce a comparative study between both types of 2D solids, clay minerals and MXenes emphasizing on the ability of smectite silicates (e.g., montmorillonite) and Ti3C2Tx carbide to produce functional derivatives via delamination (exfoliation) and intercalation processes. In this context, we present here selected examples of hybrid and nanocomposite materials derived from both clay minerals and MXenes resulting from their assembly with various guest species, from carbon and silica nanoparticles to polymers and biopolymers. We will also report on recently developed nanostructured materials derived from MXenes following processes similar to those adopted for clays that can be applied as superabsorbents, piezoelectric sensors, antimicrobial and hemostatic materials, among other potential uses.

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NI DECORATED MXENES FOR HDO OF M-CRESOL

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The Hydrodeoxygenation of lignocellulosic fast pyrolysis bio-oil is a well investigated reaction, aiming to transform the highly reactive and corrosive pyrolysis oil with oxygen containing compounds, into oxygen free aromatic compounds.

In this work, we are employing Mo-MXenes, and Ni decorated Mo-MXenes for HDO of m-cresol, an abundant species in pyrolysis oil, in a vapor-phase fixed-bed flow reactor system, operating at atmospheric pressure of H_2 and 300 °C. With their tunable surface chemistry, and versatile properties, MXenes have the potential for use as catalysts or supports for various catalytic reactions. These catalysts were extensively characterized with XRD, H_2-TPR, ICP, TGA TEM and SEM before and after reaction. Figure 1 a-c represent some SEM images of pristine Mo_2CTx, $Mo_4VC_4T_x$ and $Mo_{1.33}CTx$, showing the accordion like structure of MXene multilayers. XRD diffractograms are shown in figure 1 d for the different catalysts; the formation of the MXene is confirmed by the shift of the (002) peak to lower 2θ indicating an increase in interlayer spacing. Whereas Figure 1 d is an HAADF image of Mo_2CTx in the zone axis [0001] showing the hexagonal array of Mo atoms.

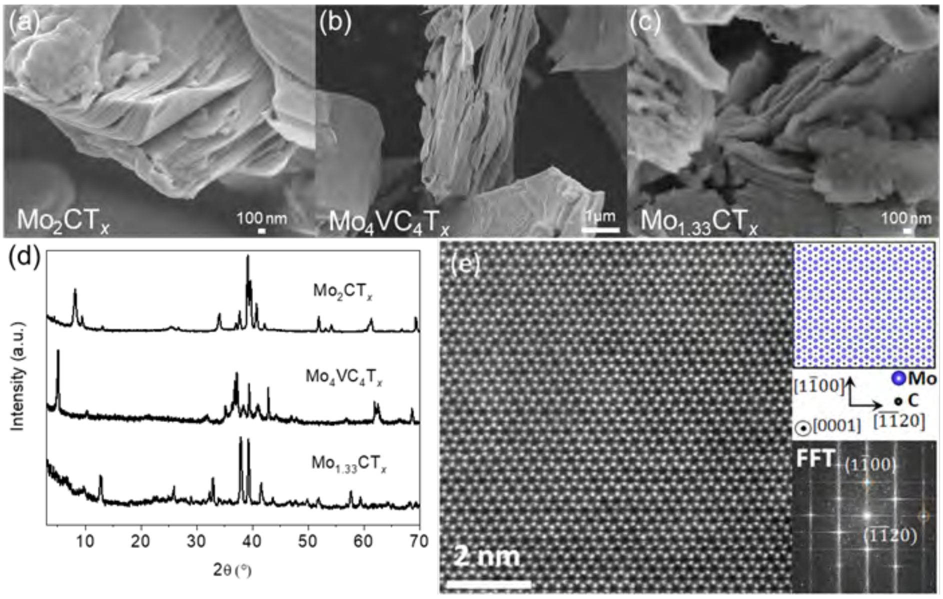
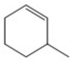
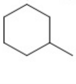
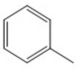
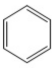
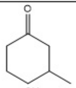
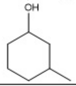


Table 1 reports the HDO reaction rate, distribution of products, and selectivity at low conversion using m-cresol as a model molecule. 5-Ni-Mo_2CTx-MI exhibited the highest deoxygenation activity, which was 16-fold higher than that for Mo_2CT_x. Concerning product distribution, $Mo_{1.33}CTx$ and $Mo_2Ti_2C_3Tx$ were quite selective, producing only toluene. . The selectivity to toluene followed the order: $Mo_{1.33}CTx$ (100) = $Mo_2Ti_2C_3Tx$ (100) > 5-Ni-Mo_2CTx-MI (95) > Mo_2CTx (90) > 5-Ni-Mo_2CT_x-WI (65). The results obtained in our work suggest that the Mo based MXenes promote direct deoxygenation to toluene, which is characteristic of oxophilic metals such as Ru. Therefore, $Mo_{1.33}CTx$ and $Mo_2Ti_2C_3Tx$, with 100% selectivity to toluene, are promising catalysts for HDO of bio-oil.

Table 1 – m-cresol conversion, HDO reaction rate, and selectivity for the HDO of *m*-cresol over 2D Mo carbides catalysts at 300 ◦C and 1 atm.

Catalyst	Conversion (%)	W/F (g.min.mmol$_{Cresol}^{-1}$)	HDO rate (mmol$_{Cresol}$.gmo^{-1})	Seletivity (%)				
				CH_4	 			 
$Mo_{1.33}CT_x$	8.52	5.54	0.0168	0	0	100	0	0
Mo_2CT_x	9.83	11.15	0.0088	7.94	0.34	89.95	1.77	0
5-Ni-Mo_2CT_x-MI	11.50	0.89	0.1442	1.41	3.55	95.03	0	0
5-Ni-Mo_2CT_x-WI	10.58	4.49	0.0255	2.65	29.52	64.56	0	3.27
$Mo_2Ti_2C_3T_x$	4.22	10.91	0.0065	0	0	100	0	0

NOVEL TECHNIQUE FOR DEVELOPING E-TEXTILES: PRINTING MXENE SUPERCAPACITORS ON FABRICS FOR WEARABLE ELECTRONICS

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The escalating demand for miniaturized, flexible wearable electronics propels the rapid growth in the field of e-textiles. As e- textiles necessitate energy storage solutions that are not only compact but also conformable, microsupercapacitors emerge as an attractive option due to their exceptional power density and prolonged operational lifespan. Leveraging the inherent properties of textiles — flexibility, breathability, and strength retention — offers a promising avenue for seamlessly integrating electronic functionalities into everyday fabrics.

This study presents a pioneering approach to fabricating e-textiles via aerosol-jet printing (AJP) utilizing additive-free aqueous $Ti_3C_2T_x$ MXene inks. AJP proves to be a superior fabrication technique, offering unparalleled resolution and cost-effectiveness for rapid prototyping. Meanwhile, $Ti_3C_2T_x$ MXenes exhibit outstanding electrical conductivity, mechanical flexibility, and facile processability in stable, viscous, aqueous, additive-free colloidal suspensions.

Through a systematic exploration encompassing cotton, polycotton, and polyester textiles, we demonstrate the feasibility of achieving flexible electrodes with remarkable areal capacitances of up to 540 mF cm^{-2} with as few as 10 layers. These electrodes exhibit exceptional high-rate performance, capacitance retention, minimal equivalent series resistance, and outstanding cycling stability. Furthermore, we optimize current collector-free symmetrical microsupercapacitors on cotton fabrics and evaluate their performance at various angles to elucidate their versatility and applicability. A prototype comprising 30 layers attains an impressive areal capacitance of up to 381 mF cm^{-2} (at 2 mV s^{-1}) when coupled with a poly(vinyl alcohol)/sulfuric acid gel electrolyte, surpassing existing printed MXene/textile-based microsupercapacitors.

This study marks a significant leap forward in integrating AJP-fabricated microsupercapacitors, thus paving the way for utilizing a broader spectrum of fabrics for diverse applications in wearable electronics, smart textiles, and beyond.

PH DEPENDENT HYDROLYSIS OF V2CTX MXENE STUDIED USING IN SITU SCANNING TRANSMISSION X-RAY MICROSCOPY

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The emerging class of two-dimensional (2D) transition metal carbides and nitrides called MXenes have attracted much attention in a varied range of applications, thanks to their layered structure, hydrophilicity, and surface terminations1. Ti3C2Tx remains the most explored member of the family, despite of more than 20 other members. V2CTx MXenes were less studied so far due to stability issues, but a new synthesis protocol has significantly improved the quality and shelf life of V2CTx 2.

This study focuses on the behavior of V2CTx MXene in aqueous solutions studied using In-situ Scanning Transmission X-Ray Microscopy3 (STXM) with dedicated electrochemical flow cell at the synchrotron BESSY II. STXM allows an element-specific characterization of the electronic structure of nanomaterials with ~50nm spatial resolution and can be applied directly in liquid.

Here, we characterize the electronic structure of pristine and aged V2CTx MXene in air, water, acidic and basic electrolytes using X-ray Absorption Spectroscopy (XAS) at V L-edge and O K edge. The stability of individual V2CTx MXene flakes is monitored through high resolution chemical imaging over several hours in aqueous electrolytes. The influence of water and pH on the chemical environment of V atoms will be discussed. In this work we stress upon on the relevance of chemical imaging allowed by STXM for insights into oxidation and hydrolysis of MXene in aqueous environment at the nanoscale.

HETEROSTRUCTURED 3D MXENE@MXENE ELECTRODES FOR ENHANCED ELECTROCHEMICAL PERFORMANCE

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Maximizing the energy and power density of supercapacitors requires high areal loading and thick electrodes. Simultaneously, a sophisticated, hierarchical pore structure for the active material is needed, granting access to electrons and ions.

Using a sacrificial ZnO template, we can create hierarchical electrodes from $Ti_3C_2T_x$ nanosheets in the form of interconnected 3D microtubes, with thin film walls up to ~220 nm thick.[1] We have demonstrated electrodes with areal loading of up to ~7.2 mg cm^{-2}, material density of ~1440 mg cm^{-3}, and electrochemical performance of 240 F g^{-1}, 140 F cm-3 and 1.4 F cm^{-2} at 200 mV s^{-1}. This makes good use of the properties of $Ti_3C_2T_x$ without compromising on areal loading or density.

Expanding on this work, treatment with nitrogen-rich species can greatly improve the intrinsic capacitance of $Ti_3C_2T_x$ [2] but comes at the expense of conductivity, which is reduced by roughly an order of magnitude. By using our template-based approach, a 3D electrode can be built in a heterogenous manner, using alternating layers of treated MXene (N-MX), and pristine MXene (MX), shown schematically in Figure 1A. This results in a porous network of microtubes (Figure 1B) where a highly conductive MX thin film is sandwiched between thin films of high capacitance N-MX. In this way, the MX thin film effectively forms a 3D current collector for the structure (N-MX@MX 3D heterostructure). This offers lower ESR (0.87 vs. 1.44 Ω) and higher capacitance (456 vs. 372 F g^{-1} at 2 mV s^{-1}) than an equivalent electrode prepared using a homogenous mixture of N-MX and MX in the same ratio (N-MX/MX 3D composite), see Figure 1C. Conventional methods for preparing porous structures such as freeze-drying [3] need to rely on a homogenous mixture of materials, as creating similar heterostructure in a controlled manner would be difficult, if not impossible.

We anticipate that this concept will pave the way for advances in electrode architecture, allowing the exceptional properties of thin films to be transferred to high areal loading electrodes, especially in cases where the active material lacks the necessary conductivity or mechanical stability to be suitable for conventional methods.

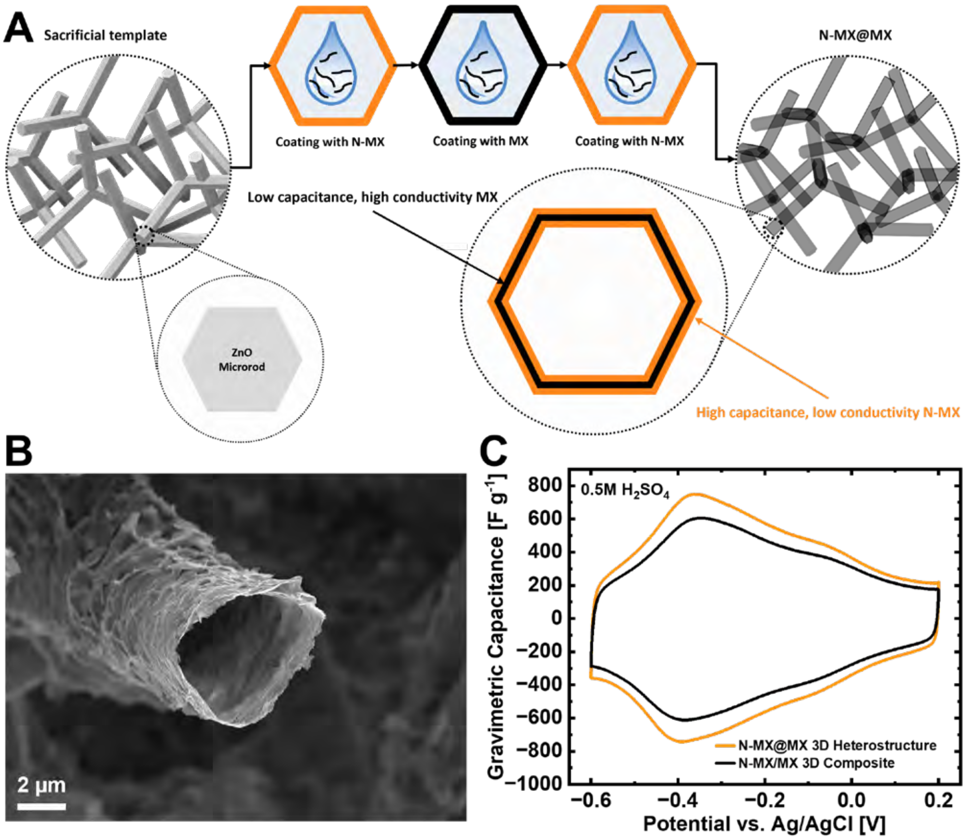

Figure 1. A: Schematic of the preparation of an N-MX@MX 3D heterostructure. B: SEM micrograph of an N-MX@MX microtube. C: Cyclic voltammogram at 2 mV s^{-1} comparing an N-MX@MX 3D heterostructure electrode to an N-MX/MX 3D composite electrode.

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BINDER FREE ENHANCEMENT OF LONG-TERM STABILITY OF 3D-MXENE THIN FILM STRUCTURES FOR SUPERCAPACITOR APPLICATIONS USING INITIATED CHEMICAL VAPOR DEPOSITION

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Binder free enhancement of long-term stability of 3D-MXene thin film structures for supercapacitor applications using initiated chemical vapor deposition

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MXenes have been found to be promising electrode materials for supercapacitor applications. They achieve high power output and fast charging/discharging by faradaic redox reactions at the surface, which has made them a focus of supercapacitor research in recent years[1.]

The titanium carbide MXene ($Ti_3C_2T_x$), has been shown to hold significant promise, as it offers great pseudocapacitive properties combined with a high electronic conductivity. Thin film electrodes made up of $Ti_3C_2T_x$ have shown exceptional capacitance of up to 450 F g^{-1} and a good rate performance even up to 100 V s^{-1} [2].

Herein we advance our previously developed method based on the fabrication of interconnected MXene ($Ti_3C_2T_x$) 2D thin films in a 3D macroscopic assembly, by an additional coating of the electrode structures with the co-polymer poly (2-hydroxyethyl methacrylate-co-ethylene glycol dimethacrylate), (p(HEMA-co-EGDMA)) using initiated chemical vapour deposition (iCVD) [3 4]. The solvent free iCVD process enables polymerization of ultrathin polymer thin films directly on the substrate surface from the gas phase. The CVD-typical growth characteristics enable conformal coating of complex 3D structures, which would be difficult by other means [5]. The applied co-polymer p(HEMA-co-EGDMA) thin film is a hydrogel with minimal swelling and great long-term stability in an aqueous environment, which turn it into a promising material for supercapacitor applications.

At a thickness of 50 µm and areal loadings of more than 5 mg cm^{-2}, the uncoated electrode networks demonstrated volumetric and specific capacitances of up 140 F cm^{-3} and 240 F g^{-1} respectively, at a scan rate of up to 200 mV s^{-1} [3]. At the same scan rate an areal capacitance of ~1.4 F cm^{-2} is recorded, outperforming that of state-of-the-art MXene based electrodes by a factor of ~2 [3]. However, during long term cycling (>10000 cycles) MXene based electrodes decrease in performance due to delamination of the individual flakes. This negatively influences the overall conductivity and capacitance of the structure. To address this problem, the additional p(HEMA-co-EGDMA) hydrogel thin film applied to the 3D MXene thin film structures, where it acts as a supportive outer layer, fixing the MXene flakes in place and inhibiting the performance loss during cycling, without the need for an insulating binder in the electrode.

With the hydrogel coatings, the cycling stability at 10 A g^{-1} of these network electrodes showed only a 10% capacitance loss across 30000 cycles, whereas the uncoated electrode lost 25% of its initial capacitance (see Figure 1a).

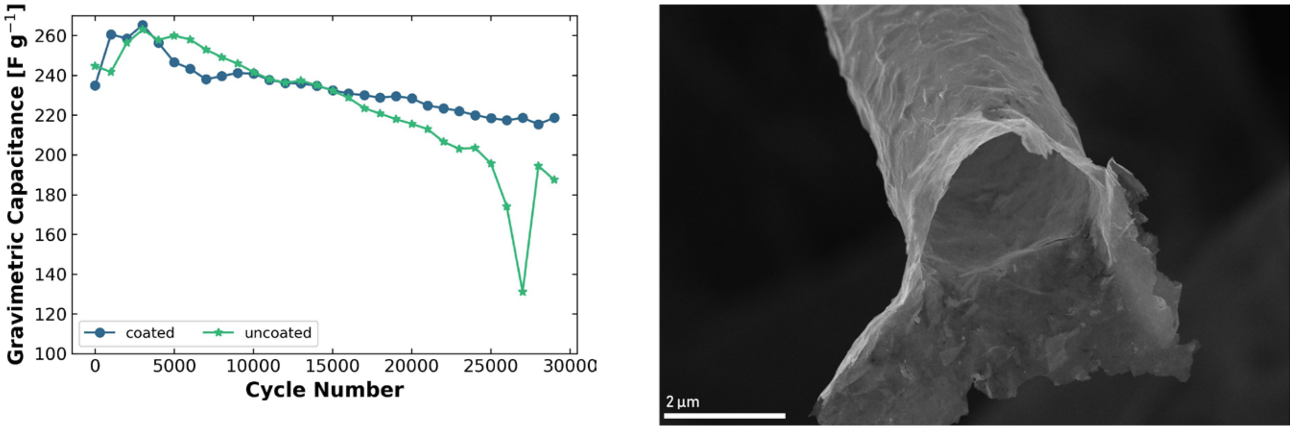

Figure 1: (left)Comparison of the long-term cycling performance of an iCVD coated sample (blue), and an uncoated sample (green) across 30000 cycles at 10 A g-1, (right)SEM image of an iCVD Coated 3D MXene thin film

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DENSITY FUNCTIONAL THEORY AND MACHINE LEARNING EXPLORATION OF NOVEL PROPERTIES IN MXENE AND RELATED MATERIALS

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This presentation will highlight recent progress by our group on the combination of density functional theory (DFT) calculations and machine learning models to predict the properties of potential novel MXene and related materials.

We use DFT with the Hubbard U correction to characterize the structure, termination, and magnetism in an out-of-plane ordered rare-earth containing MXene, Mo2NdC2T2 (T = O or OH). We investigated the effect of the U parameter on the stability and magnetism of two possible termination sites: the hollow sites aligned with the inner Nd atoms (Nd-hollow sites) and those aligned with the closest C atoms (C-hollow sites). We find that increasing UMo stabilizes the Nd hollow sites, to minimize the electrostatic repulsion between C and O atoms. Using UMo = 3.0 eV and UNd = 5.6 eV, obtained via the linear response method, we found that the energetically preferred termination site was C-hollow in Mo2NdC2O2 and Nd-hollow in Mo2NdC2(OH)2. Regardless of termination and the Hubbard U value, we found Mo2NdC2O2 and Mo2NdC2(OH)2 to be magnetic.

As a second example, we explore stacked MXenes as ultra-high temperature ceramics (UHTC). We focus on layered 2D MXenes as nanoceramic building blocks for layered 3D carbide and nitride zeta-like phases. Stacked MXenes can expand the domain of zeta-like phases due to the multiple possible interfacial combinations. We use DFT to investigate the thermodynamic stability elastic constants of stacked MXenes as UHTC precursors, with sequential quasi-random structures to study non-stoichiometric nanolamellar carbides. We identify both stoichiometric and non-stoichiometric nanolamellar carbides below the established convex hull. Furthermore, we use machine learning models with DFT inputs to predict the melting temperature of these materials. Our findings show that stacked MXenes could result in ceramics with properties beyond those of vacancy-ordered zeta phases and traditional UHTC transition metals via a lower-temperature synthesis pathway.

2D/2D HETEROJUNCTION BASED PORPHYRIN MOF@TI3C2 MXENE PHOTOCATALYST FOR OVERALL WATER SPLITTING

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Photocatalytic overall water splitting using natural sunlight can became available technology for renewable hydrogen production to be used as energy vector. Photocatalytic hydrogen generation from water could have the advantage respect to water electrolysis of a less costly infrastructure and a best suited technology for local decentralize solar energy conversion in geographical areas not connected to the high-power electrical grate.

A general strategy to further increase charge separation in semiconducting photocatalyst is the formation of heterojunction between two or more components. Heterojunction typically required a large interfacial contact between the components to facilitate charge carrier migration amount there. Heterojunction is there for not very efficient when large 3D microcrystals, such a as typical 2D MOFs, is one of the components since the mean path of the charge carriers from the interior to the outer surfaces of the crystal is very large, recombination being favour as the distance to be travel increases. Therefore, 2DMOFS a far most suited formed heterojunction, particularly with other 2D materials.

Herein, we reported the photocatalytic performance of a 2D MOFs/MXene pain attention to the efficient charge migration between the two components and the stability of the heterojunction. In particular, the heterojunction we have described compressed Cu2[CuTCPP] 2DMOF and Ti3C2 MXene that enjoy as a good photocatalytic activity for visible light overall water splitting. In a precedent we had already reported the photocatalytic activity Cu2[CuTCPP] 2DMOF for hydrogen and oxygen evolution as well as overall water splitting. Now as well as the photocatalytic activity further increases in the heterojunction although the stability of the heterojunction is still low.

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TI3C2TX MXENE FLAKES SIZE EFFECT ON ZINC CRYSTAL GROWTH IN ANODE- FREE ZN BATTERIES

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A demand for safe and environmentally friendly and sustainable energy storage systems is progressively increasing as a decrease of use of traditional energies, as coal and oil is becoming of paramount urgence due to environmental deterioration. However, the intermittency and instability of clean and renewable energies, such as wind, solar or tidal energies, represents a strong limitation, thus energy storage devices become essential to reliably transform and store energy in case of necessity [1]. Zinc-based batteries have attracted great interest. However, zinc-ion batteries suffer from critical issues as dendritic growth, which results in battery failure. This phenomenon is associated to an uneven distribution and nucleation of Zn on the anodic surface. This effect, however, can be smoothened and regulated by treating the surface to improve a “zincophilic” character to the surface [2]. In this context, MXenes have attracted great interest. In particular, MXenes are obtained by selective etching of a precursor layered material, known as MAX phase, and characterized by the general formula Mn+1XnTx, where M is a transition metal with n =1-4, X represents carbon and/or nitrogen atoms and Tx represents surface terminations of different nature (-O, -OH, -F and -Cl). Specifically, Ti3C2Tx has attracted great interest because of its high electrical conductivity and its HCP crystal structure which has been proven to favor a homogenous growth of Zn [3]. Given our previous work [4], we identified a possible effect of the Ti3C2Tx flakes dimension on how the Zn crystals grow on the MXene-based substrate. In this context, Ti3C2Tx MXene are synthetized and characterized through multiple approaches (SEM, XRD and UV-vis). Then, multiple flake sizes are considered, and a MXene-based coating is produced obtained accordingly to obtain an electrode. The electrodes then are electrochemically tested through EIS and cyclic voltammetry. Zn deposition will be also conducted through a Hull cell and the deposits will be analyzed through XRD and SEM to understand whether the preferential (002) orientation of Zn was favored or not according to a specific flake dimension of the MXene substrate.

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ISOTOPIC ANALYSIS OF INTERCALATED PROTONS IN TI3C2TX MXENE FOR ELECTROCHEMICAL ENERGY STORAGE USING OPERANDO FTIR SPECTROSCOPY

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MXenes, a family of 2-dimensional transition metal carbides, are a promising candidate for use in energy storage applications due to their high capacitance. Here, we monitor the confined water and protons in $Ti_3C_2T_x$ MXene electrodes during cyclic voltammetry using operando FTIR spectroscopy. Isotopic exchange with deuterium oxide is used to allow a better understanding of the proton dynamics inside the MXene interlayers.

Operando FTIR measurements are being performed with a dedicated electrochemical cell able to measure the different vibrational modes of the confined species. The measurements are conducted in attenuated total reflectance mode (ATR) employing structured Si substrates as the reflective barrier between the optical chamber and the electrochemical reactor. A three-electrode setup is used, where the $Ti_3C_2T_x$ MXene acts as the working electrode as demonstrated in our previous work[1]. The IR spectra are taken during electrochemical cycling. This method has been demonstrated to be very well suited to analyzing confined electrolytes in the interlayer spacing of two dimensional MXenes, as the probing depth is generally shorter than the thickness of the MXene films.

The focus of this presentation will be on analyzing the change of the vibrational modes of water and deuterium during electrochemical cycling versus the applied potential to the working electrode. This behaviour will be discussed regarding the intercalation of protons and the reordering of the intercalated water or deuterium. The results will be placed in the context of MXene in the role of an electrode for pseudocapacitor applications.

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ROBUST 2D TI_3C_2-MXENE/AUNPS COMPOSITE FOR SENSING E-COLI IN DRINKING WATER

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Robust 2D Ti_3C_2-MXene/AuNPs composite for sensing E-Coli in drinking water

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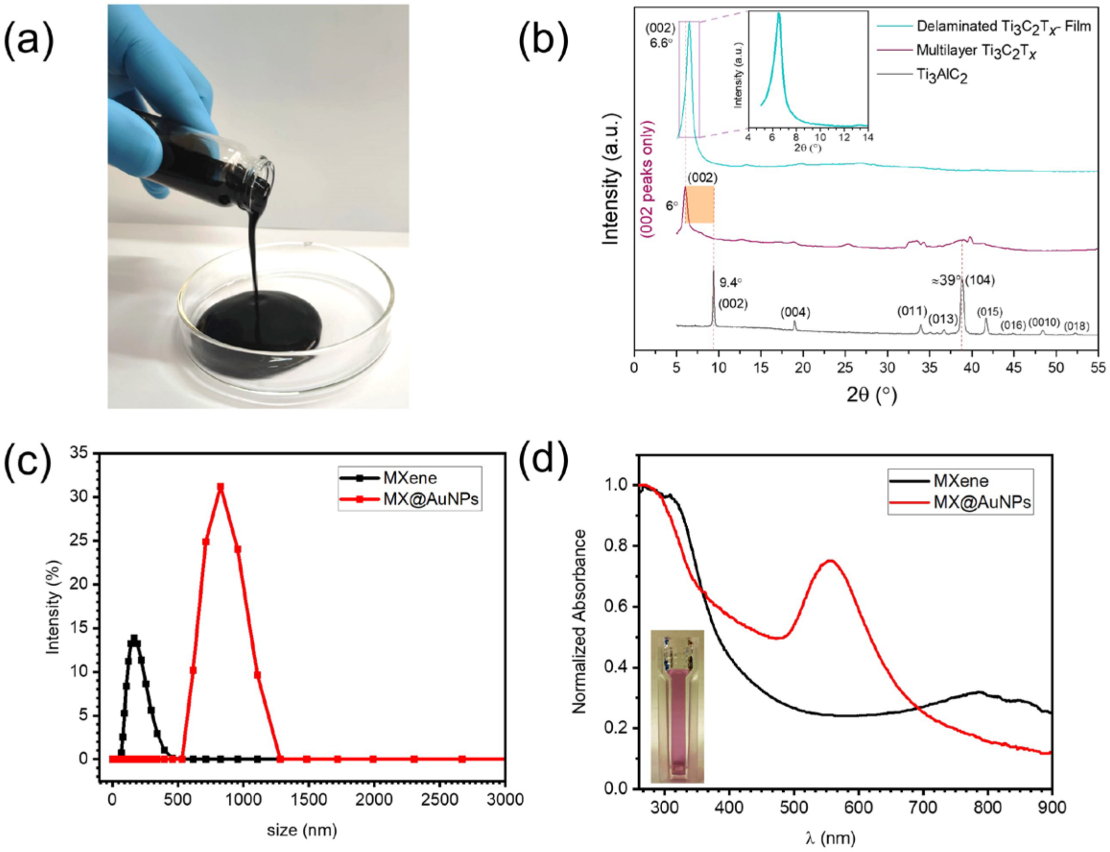
Abstract

Biosensors offer a rapid, efficient, affordable, and real-time monitoring solution for detecting Escherichia coli in drinking water, a pathogen responsible for many infectious diseases. Here, we introduce a cost-effective immunosensor based on screen-printed electrodes, employing 2D-Ti_3C_2 MXene and gold nanoparticle composites (MX@AuNPs). The MAX phase was etched via an HF + HCl etching approach and delaminated using lithium chloride (LiCl) to obtain a stable colloidal suspension containing single/few-layer MXene flakes (Figure-a). The MX@AuNPs were prepared by in-situ self-reduction method, followed by an innovative photochemical immobilization technique (PIT) to covalently immobilize antibodies over MX@AuNPs. The etching and subsequent delamination processes were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDXS). In XRD, the disappearance of the peak at $2\theta \approx 39°$ indicates the removal of interleaved aluminum (Figure-b). Additionally, the broadening and downshifting of the (002) peak to a lower angle ($2\theta \approx 6°$) correspond to a larger c-spacing, indicating successful exfoliation and subsequent delamination. Confirmation of successful MX@AuNPs synthesis was achieved through dynamic light scattering (DLS), ultra- violet-visible (UV-vis) spectroscopy and scanning electron microscopy (SEM). DLS analysis reveals an increase in the hydrodynamic radius of the flakes after decorating MXenes with AuNPs, confirming composite formation (Figure-c). UV-vis spectra exhibit a prominent peak of AuNP alongside the typical MXene peak, further indicating MX@AuNPs formation (Figure- d). The fabricated biosensor demonstrates the combined synergistic properties of both MXene and AuNPs, capable of reaching a low detection limit and rapid response time. Our groundbreaking approach, which streamlines water quality monitoring by utilizing commercial screen-printed electrodes, holds promise for detecting various other pathogens and environmental pollutants.

Figure. Production and characterization of MXene and MX@AuNPs. (a) Single to few layer MXene Ink. (b) XRD patterns of Ti_3AlC_2 MAX, Ti $_3C_2$ multilayers powder, and delaminated MXene film shows successful etching and delamination. (b) UV-vis spectra of colloidal solution of MX@ AuNPs. (c) DLS analysis of MXene, and MX@AuNPs. (d) The extinction spectra of MXene and MX@AuNPs.



FEMTOSECOND TRANSIENT ABSORPTION SPECTROSCOPY INVESTIGATION IN S-SCHEME PHOTOCATALYSTS

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The biggest challenge in the photocatalytic filed is the low photocatalytic efficiency, essentially due to the rapid recombination of photogenerated electrons and holes. In single-component photocatalyst, most photogenerated carriers are recombined inside photocatalyst (in picoseconds to nanoseconds) before migrating to the photocatalyst surface (in picoseconds) and participating in the redox reaction (in nanoseconds to microseconds). To address this issue, constructing S- scheme heterojunction photocatalysts is an effective method. S-scheme heterojunction typically consists of an oxidation semiconductor (OS) and a reduction semiconductor (RS). Under photoexcitation, the photogenerated electrons in OS conduction band will transfer to RS valence band driven by built-in electric field. Consequently, photogenerated carriers with strong redox ability are spatially separated and retained in S-scheme photocatalysts. To seek the evidence of S-scheme heterojunctions, femtosecond transient absorption spectroscopy (fs-TAS) is a powerful technique that can directly monitor the ultrafast electron transfer process (in picoseconds) at RS/OS interface. Based on the fs-TAS results, the entire electron quenching dynamics of RS and OS were extracted and the lifetimes and rates of electron transfer at the RS/OS interface were obtained. In situ fs-TAS measurements with different atmospheres and solvents were also performed to simulate the actual photocatalytic process. In summary, fs-TAS can confirm the S-scheme heterojunctions from the perspective of electron transfer dynamics.

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POSTER PRESENTATIONS

LITHIUM ION-SELECTIVE SEPARATION USING MXENE-BASED NANOCOMPOSITE ADSORBENT

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With the increasing demand for lithium in industries such as electric vehicles and renewable energy, concerns have arisen regarding the depletion of global lithium reserves and the environmental impact of mining. This research focuses on the recovery of lithium from diverse water resources, including brine water, wastewater, and seawater to address the need for sustainable lithium production. Our goal is to fabricate a high-performance adsorbate and incorporate it into effective lithium recovery technologies, thereby paving the way for a circular economy in the lithium-ion battery domain. One promising approach to be explored is the utilization of 2D material-based nanocomposite, which demonstrates remarkable potential in effectively adsorbing and separating lithium from brine water sources. The lithium ion-selective adsorbent has been constructed with rationally-designed nanocomposite consisting of 2D sulfonated graphene oxide/MXene-based hydrogel.

These materials have demonstrated the ability to remove over 98% of lithium ions from brine, exhibiting remarkable selectivity amidst various co-existing ions. The successful application of sulfonated graphene oxide/MXene-based nanomaterials underscores their potential as efficient solutions for lithium-ion recovery from brine water, offering a pathway to lessen the environmental footprint of lithium extraction and enhance the cost-effectiveness of lithium recovery processes. Such advancements are critical for ensuring the long-term sustainability of the lithium-ion battery industry.

SYNTHESIS AND PHOTOCATALYTIC ACTIVITY STUDY OF LAYERED TINα NANOSHEETS AS EMERGING MATERIALS TOWARDS GREENER N2 FIXATION TO AMMONIA

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MXenes are a novel family of two-dimensional (2D) transition metal carbides, carbonitrides and nitrides, directly prepared from selective etching of the A-site element in MAX phase precursors. Their general chemical formula $M_{n+1}X_nT_x$ describes comprising n+1 layers (n=1–4) of early transition metals ('M'), interleaved by n layers of carbon and/or nitrogen atoms ('X'), with T_x representing surface terminations bonded to the outer M layers (i.e. –F, –O, –OH). Thus, their unique morphology and functionalities, together with a fascinating integration of mechanical, electronic, chemical, and optical properties makes them promising materials for advanced applications [1]. Owing to their consolidated role in the field of photocatalysis [2] and along with the increasing demand for high-performance renewable energy sources for chemicals production.

In this presentation, we will focus on the application of titanium nitride-derived Mxenes in the nitrogen fixation reaction to ammonia. It will be firstly discussed whether photothermal or thermal mechanism of catalysis is followed, then delving into their main methodology of synthesis and different strategies of purification.

Mxenes were obtained from two different MAX phases (Ti_3AlN and Ti_2AlN) and the required the etching of Al layers was carried out through Lewis acid molten salt method, under Argon atmosphere and high excess of $CuCl_2$ [3]. As a fundamental synthetic parameter, the increasing etching temperature (from 600°C to 950°C) effect has been evaluated first. Subsequently, a purification step was needed to remove deposited metallic copper over the raw Mxene: parameters such as purification temperature, persulfate oxidating agent-nature (i.e. ammonium, potassium and sodium persulphate) and its concentration (i.e. 0,1-0,4 M) led to several multi-layered Ti_3N_2 and Ti_2N nanosheets. All these variables are proved to directly affect the formation of equilibrium phases as well as their final morpho-structural properties.

Extensive physico-chemical characterization of the material were performed to get a comprehensive structural and electronic properties of each Mxene.

Moreover, each as-synthetized MXene has been tested in batch reaction under irradiation or dark, whereas the confirmation of nitrogen source of the produced NH_3 was occurred though $^{15}N_2$ isotope labelling experiment. Additionally, optimization of reaction conditions was carried out considering different external conditions of light intensity, pressure and temperature too.

Finally, in this work we discuss the ammonia quantification by means of both indophenol blue method and ^1H NMR.

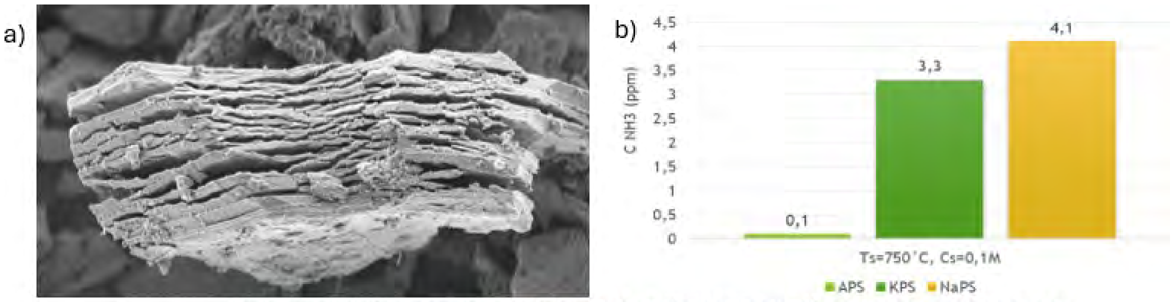

Figure 1: a) SEM image of Ti_3N_2 MXene; b) oxidating agent effect over the photocatalytic activity of 750°C-synthetized Ti_3N_2 MXene

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HYPERSPECTRAL BULK- AND SURFACE-SENSITIVE IMAGING OF TITANIUM CARBIDE MXENES

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Two-dimensional layered materials, such as transition metal carbides or nitrides, known as MXenes, offer an ideal platform to investigate charge transfer processes in confined environments, relevant for energy conversion and storage applications, such as supercapacitors and Li-ion batteries[1]. Their rich and tunable surface chemistry plays an essential role in the pseudocapacitive behavior of $Ti_3C_2T_x$MXenes[2], where T_x=O, OH, F, Cl etc. However, the local distribution of surface functional groups over single flakes and within few- or multilayered flakes remains unclear.

In this presentation, we introduce synchrotron-based scanning X-ray microscopy (SXM) with simultaneous transmission and electron yield detection (EY), enabling multimodal nanoscale chemical imaging with bulk and surface sensitivity, respectively, of individual MXene flakes[3]. Soft X-rays absorption spectroscopy (XAS) allows the probing of fine electronic structure of the metal valence electrons and light elements present in the layered transition metal compounds and electrolytes[4]. Specifically, for transition metal structures with termination groups found in MXenes, the crystal field interaction determines the shape, strength, and occupancy of electronic orbitals. Transmission imaging techniques with soft X-rays are ideal for monitoring changes in the local chemistry of few-layered materials, with guest-species between the interlayers or exposed to different environments. Microscopy techniques, other than SXM, offer limited spatial resolution (optical microscopy), only surface sensitivity (Scanning probe microscopy, XPEEM), only bulk sensitivity (TEM, TXM) or lower energy resolution (EELS).

Single and few-layered $Ti_3C_2T_x$ MXenes, synthesized with hydrofluoric acid (HF-etched), and multilayered $Ti_3C_2T_x$ MXenes, synthesized via the molten salt route (MS-etched)[5], are imaged by multimodal SXM at the Ti L- and O K-edge. Transmission detection mode is used for bulk sensitivity, required to probe the surface chemistry in the MXene interlayer, while EY mode allows high surface sensitivity for probing the top MXene layer. SXM allows the monitoring of MXene flake thickness and electron emission properties at the sub-flake level. Local XAS measurements have a high chemical sensitivity to the Ti and O bonding configurations, hence to the surface chemistry of MXene. The Ti chemical bonding differs dramatically between HF- etched and MS-etched $Ti_3C_2T_x$ MXenes explained by the larger content of O-termination in MS-$Ti_3C_2T_x$. Thus, different surface chemistry and electronic properties are identified for MXenes, synthesized via different routes.

SXM also enables the chemical identification of the different components found in post-mortem analysis of battery components cycled in a Li-ion battery with $Ti_3C_2T_x$ MXene, as working electrode. Adsorbed electrolyte (surface) and electrolyte-electrode interaction (bulk) can be probed with high chemical sensitivity. Changes in the chemical bonding configuration of electrochemically cycled MXene electrode are recorded in the bulk of MXene, related to interaction of MXene with intercalated lithium cations, and its top layer, due to interaction with the electrolyte. Specifically, upon comparison of XA spectra at Ti L- and O K-edge between cycled and pristine MXene in bulk, we identify increased Ti oxidation state in cycled MXene, related to the bonding of lithium cations with oxygen surface termination groups. Furthermore, surface-sensitive TEY measurements hint at surface reactions between the MXene and the electrolyte during the electrochemical cycling process. This distinction underscores the complex interplay of bulk intercalation and surface phenomena in these materials.

Multimodal SXM can be applied to other laminated materials, such as graphene, layered transition metal dichalcogenides, thin film solar cells and multilayered polymer films, thereby opening new insights into intercalation and surface redox processes.

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EXPLORING THE IMPACT OF ENVIRONMENTAL FACTORS ON LONG-TERM TI3C2TX ELECTROMAGNETIC SHIELDING PERFORMANCE

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Exploring the Impact of Environmental Factors on Long-Term Ti3C2Tx Electromagnetic Shielding Performance

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Keywords: MXene, Electromagnetic interference EMI, Shielding effectiveness SE, Chemical stability.

MXenes, a promising class of 2D transition metal carbides/nitrides, are renowned for their exceptional electronic conductivity and robust mechanical properties, rendering them highly attractive for advanced electromagnetic interference (EMI) shielding applications. However, despite these inherent advantages, challenges persist in refining MXene synthesis techniques and enhancing their resistance to oxidation[1]. Various factors related to the synthesis methods employed to produce MXene materials, such as the presence of intercalants between the flakes or surface defects, significantly affect their electronic properties, impeding charge transport and accelerating the oxidation process[2].

To address these challenges, we propose a novel synthesis approach derived from the conventional minimally invasive layer delamination (MILD) method[3]. Our method incorporates two additional steps aimed at improving process yield, a key challenge faced by conventional methods that often yield high-quality individual MXene flakes but struggle to produce sufficient quantities for bulk material fabrication. Through our approach, we successfully fabricated Ti3C2Tx films (~4 µm thickness) exhibiting excellent conductivity (3973.72 ± 121.31 Scm-1) and an average electromagnetic interference (EMI) shielding effectiveness of 56.09 ± 1.60 dB within the 1.5 to 10 GHz frequency range at 35% relative humidity (RH).

Furthermore, our study investigated the long-term oxidation stability of these films under varying RH conditions. Our results highlight the efficacy of this innovative synthesis approach in enhancing process yield and delivering exceptional values for both conductivity and EMI shielding capabilities of MXene materials. This advancement represents a significant step toward harnessing MXenes for practical applications requiring robust EMI shielding solutions. Additionally, insights into long-term stability provide crucial considerations for the implementation of MXenes in real-world environments.

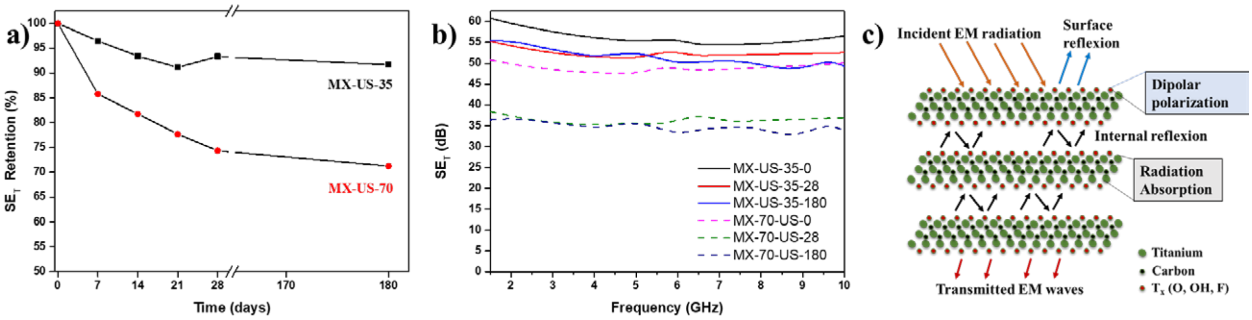

Figure 1. a) depict the retention capacity of EMI shielding effectiveness at 35 and 70% of relative humidity. b) illustrates the EMI shielding effectiveness performance from 1.5 GHz to 10 GHz for MX-US-35 and MX-US-70 results after keeping the samples for 0, 28 and 180 days in controlled humidity test conditions. c) represents the EMI shielding mechanism suggested for Ti3C2Tx material.

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HIGH PERFORMANCE ELECTRODE MATERIALS FOR HYBRID AQUEOUS SUPERCAPACITORS BASED ON MXENES

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A class of two-dimensional (2D) transition metal carbides, carbonitrides and nitrides with excellent physicochemical properties, called MXenes, is quickly emerging as a promising method of obtaining electrodes for aqueous supercapacitors. Because of their two-dimensional structure, the MXene nanosheets are not only able to be assembled into simple films through vacuum filtration, but they can also be loaded on flexible substrates and is even possible to print them on paper as micro capacitors because of their two-dimensional structure. It should be noted that such materials are commonly found at low operating voltages, but also at high capacity values under high-rate charge-discharge processes, which are mainly caused by the surface sorption of working ions and the formation of a layer on the surface. As a result of such properties, they are considered to be promising candidates for use in environmentally friendly and economical water supercapacitors. We present here the results of electrochemical tests performed on M_3X_2 MXenes in aqueous supercapacitors with activated carbon as anode to see how they respond to the electrochemical environment.

For MXenes M_3X_2 preparation, we used classical high temperature synthesis process with calcination in argon atmosphere. Filmsnanosheet suspensions were prepared by etching the Al layers from precursors using LiF and HCl mixtures. As anode materials we used activated with KOH carbon with high porosity and optimal micro- and mesopores distribution. The cyclic voltammetry (CV) tests and charge-discharge measurements were performed using Gamry 5000P equipment. Our electrochemical measurements have shown that this combination of electrode materials is able to provide high specific power and capacity as a result of its electrochemical properties. As a result of the high operational stability at long time cycling, it indicates the possibility of cycling over thousand of cycles without losing the Coulombic efficiency and capacity.

COMPUTATIONAL INSIGHT INTO THE GUANYLATION OF CARBODIIMIDES BY MEANS OF TI3C2TX MXENE AS A HETEROGENEOUS CATALYST

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Guanidines are a class of compounds with widespread use in thanks to its presence in aminoacids and nucleobases. This moiety serves a crucial role in a wide array of medicinal products, either as a standalone aromatic guanidines or as guanidine moieties in other pharmaceuticals such as antimicrobial drugs, among other uses.

We report that Ti3C2Tx Mxenes, synthesized by exfoliation of Ti3AlC2 with a NH4F/HCl mixture, exhibit catalytic activity as heterogeneous catalyst for guanylation of aromatic amines with carbodiimides, exhibiting among the highest turn over frequencies (TOFs) ever reported. According to XPS analysis, the Ti3C2 surface is functionalized by oxygen and fluorine groups, accompanied by both vacancies and defects that confer this material unique Lewis-acid catalytic properties for this reaction.

These unique structural properties have been modelled computationally, by means of quantum chemical DFT calculations at the m06/Def2SVPD level of theory. After modelling a 35-atom cluster of the described Mxene, a full reaction coordinate analysis has been carried out in order to determine the underlying reaction mechanism.

Three transition states have been characterized for this mechanism, with different reaction routes, and their relative energies have been compared. The transition states include:

a) Cycloaddition of the carbodiimide on the catalyst.
b) 1st proton transfer on the product, either to amine or carbodiimide nitrogen.
c) 2nd proton transfer on the product, to carbodiimide if the first was on amine, or either amine or the other carbodiimide nitrogen.

HIGH-PERMITTIVITY SOLVENTS INCREASE MXENE STABILITY AND STACKING ORDER ENABLING ULTRAEFFICIENT TERAHERTZ SHIELDING

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2D transition metal carbides and nitrides (MXenes) suggest an uncommonly broad combination of important functionalities amongst 2D materials. Nevertheless, MXene suffers from facile oxidation and colloidal instability upon conventional water-based processing, thus limiting applicability. By experiments and theory, It is suggested that for stability and dispersibility, it is critical to select uncommonly high permittivity solvents such as N-methylformamide (NMF) and formamide (FA) (ε_r = 171, 109), unlike the classical solvents characterized by high dipole moment and polarity index. They also allow high MXene stacking order within thin films on carbon nanotube (CNT) substrates, showing very high Terahertz (THz) shielding effectiveness (SE) of 40–60 dB at 0.3–1.6 THz in spite of the film thinness < 2 μm. The stacking order and mesoscopic porosity turn relevant for THz-shielding as characterized by small-angle X-ray scattering (SAXS). The mechanistic understanding of stability and structural order allows guidance for generic MXene applications, in particular in telecommunication, and more generally processing of 2D materials.

HYBRIDS BASED ON MXNES AND LAYERED HYDROXIDES, AS A NEW ALTERNATIVE FOR ELECTROCHEMICAL ENERGY SYSTEMS

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The growing energy demand and the necessity to transition from fossil fuels pose a significant challenge for the scientific community. While approaches utilizing renewable energies have partially met this demand, intermittency plays a significant role in the drawbacks of these technologies. Consequently, efforts have been directed towards the development of highly efficient energy storage and conversion systems.

In recent years, 2D materials have emerged as a promising alternative due to their electrical, electrochemical, mechanical, and optoelectronic properties. Among these materials, a particular type known as 2D transition metal carbides and nitrides, or MXenes, have garnered significant attention for their potential use in energy applications. MXenes offer high energy density attributed to their shorter ion diffusion pathways, large surface area, and high conductivity.1,2 However, their industrial applications are restricted by their specific elemental composition and synthetic procedure. Conversely, layered hydroxides constitute a family of materials that have proven intriguing for electrochemical applications, exhibiting considerable chemical versatility.3–5 Some variables such as composition, cations, crystalline structure, morphology, and interlayer anions can be modulated, providing a wide array of materials for exploration, that can be produced on a large- scale, making them relevant for industrial applications.

In this context, here in this work, we aim to explore and study the hybridization of Ti-based MXenes, which are obtainable at large-scale production, with Co & Ni-based layered hydroxides. This process allows obtaining materials with compositions with an interest in energy storage (supercapacitors) and conversion applications (OER catalysts) leveraging the advantages offered by both materials. As well, the hybridization process could be scalable, making it ideal for industrial applications.

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INFLUENCE OF ANNEALING TEMPERATURE ON THE MECHANICAL PROPERTIES OF TI3C2TX MXENE FILMS

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Two-Dimensional (2D) materials are materials that are one or a few atoms thick. These prominent materials have unique electrical, chemical, and mechanical properties. On this basis, they are deemed to be typical candidates for ubiquitous engineering applications. Transition metal carbides and nitrides (MXenes) are an emerging family of 2D materials that exhibit extraordinary properties. Freestanding MXene films have highly compacted structure of hierarchically assembled pristine nanoflakes. Films and three-dimensional (3D) structures made from 2D materials introduce a distinct assembly structure that imparts the inherent properties of pristine 2D materials into a macroscopic scale. Acquiring adequate strength and toughness of 2D materials' structures is of interest due to the intense demand in numerous industrial applications.

This work aims to investigate the mechanical properties of robust films composed of $Ti_3C_2T_x$ MXene, and for them to attain other extraordinary properties such as flexibility, electrical conductivity, and electromagnetic interference shielding. The various parameters, such as the fabrication technique of the films, films' thickness, thermal annealing treatment, and strain rate that affect the mechanical behavior of $Ti_3C_2T_x$ MXene film were studied. To emphasis the effect of the fabrication technique of the MXene films, vacuum assisted filtration (VAF) and casting processes were utilized to fabricate $Ti_3C_2T_x$ MXene films with various thicknesses. Additionally, the influence of annealing temperature on the acquired mechanical properties of $Ti_3C_2T_x$ MXene films, under various strain rates, was elucidated. X- ray diffraction (XRD) was used to confirm the successful synthesis of $Ti_3C_2T_x$ MXene and monitor c-lattice parameters at different annealing temperatures. Additionally, X-ray photoelectron spectroscopy (XPS) was utilized to track the changes of surface chemistry due to thermal annealing. The deformation of individual MXene flakes within the $Ti_3C_2T_x$ MXene film was detected via Raman spectroscopy to show the changes of vibrational modes of $Ti_3C_2T_x$ MXene atoms. The fracture surface and the alignment of nanoflakes were observed via scanning electron microscope (SEM).

The annealing temperature, ranging between room temperature (RT) and 300ºC, has a significant impact on the obtained mechanical properties of $Ti_3C_2T_x$ MXene films. For all strain rates, ranging between 0.1 min-1 and 10-5 min-1, the tensile strength increases with high temperatures, peaking at 200ºC. In contrast, there is a decline of the failure strain as the annealing temperature increases. This behavior was independent of the fabrication technique and the thickness of $Ti_3C_2T_x$ MXene film. However, thin $Ti_3C_2T_x$ MXene films showed slightly higher mechanical properties compared to thick films. Additionally, casted films exhibited lower mechanical properties compared to those fabricated via vacuum assisted filtration (VAF) process. The annealing treatment not only enhances the tensile strength of the MXene films, but also improves the electrical conductivity and electromagnetic interference shielding performance. The obtained deformation mechanism seemed to be highly dependent on the alignment of individual $Ti_3C_2T_x$ MXene nanoflakes within the film and the characteristics of interlayer between adjacent nanoflakes.

HIGHLY CONDUCTIVE MXENE INK: VERSATILE COATINGS FOR ENGINEERED METAL POWDERS IN 3D PRINTING APPLICATIONS

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The development of nanotechnology combined with additive manufacturing has led to the rapid transformation of the electronics industry. The conversion of technology from analog to digital through microchips (computers, automotive/aerospace, electronics), is undeniable, with a new problem arising this time: heat anticipation due to electronics' operation. It is estimated that the electric centers use 40% of their total energy to solve to this problem. For this reason, there is an emergent need for new materials with high thermal conductivity to prepare heat dissipation devices.

Traditionally, synthetic diamond and metal powders (such as copper) are characterized by high thermal conductivity, however the high cost discourages their use in mass produced applications. The upcoming development of 2D materials has reshaped in this field to this direction, with the most promising of it being MXenes due to their processability and excellent properties. We present a highly viscous MXene based ink, suitable to cover a wide variety of different metal powders with thermal properties and 3D printables, along with their characterization via UV-Vis, TEM, XRD, and XPS.

TI3C2 MXENE CATALYSTS FOR STYRENE OXIDATION TO BENZALDEHYDE: INFLUENCE OF THE ETCHING CONDITIONS

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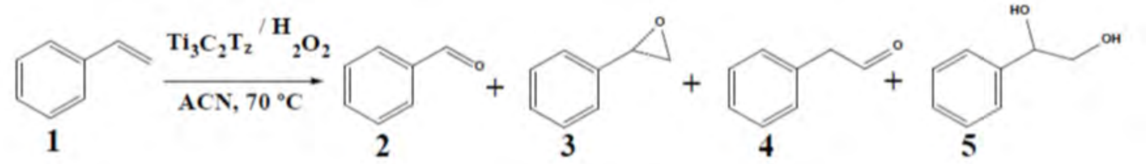
$Ti_3C_2T_z$ MXenes have been prepared under different etching conditions and the resulting materials have been tested as heterogeneous catalysts for the selective oxidation of styrene to benzaldehyde[1]. A clear dependence is observed between the etching conditions (hydrofluoric acid concentration and etching time) and the morphology and surface chemistry (viz., T_z terminations and impurities) of the MXene, which have a direct impact on the catalytic performance of the resulting material, as summarized in Table 1. Under appropriate conditions, etching of the Ti_3AlC_2 MAX phase precursor with concentrated HF produces $Ti_3C_2T_z$ MXenes with highly accessible accordion-like structures and accessible Ti–O surface terminations that can act as active species for the catalytic process, keeping up with the best catalysts reported so far for this reaction.

The present study represents one of the few existing reports on catalytic properties of MXenes under mild liquid-phase conditions, paving the way for future developments of this new family of 2D materials for fine chemical applications.

Table 1. Summary of the catalytic results obtained for styrene oxidation over synthetized MXenes, MAX phase, TiO2.



				Selectivity (%)		
Entry	**Catalyst**	**Time (h)**	**Conv. (%)[b]**	**2**	**3**	**4+5**
1	Blank	6	0	0	0	0
2	Ti_3AlC_2 (MAX)	6	1.6	86.7	13.3	0
3	$Ti_3C_2T_z$-10HF-24	2	2.4	85.5	14.5	0
		6	11.7	83.4	16.6	0
4	$Ti_3C_2T_z$-40HF-6	2	36.8	95.4	2.8	1.8
		6	71.7	76.1	3.9	20
5	$Ti_3C_2T_z$-40HF-24	2	64.6	80.8	6.8	12.4
		6	79.3	73.8	4.7	21.5
6	$Ti_3C_2T_z$-40HF-24 [a]	2	85.3	67.8	1.3	30.9
		6	98.3	69.9	2.5	27.5
7	$Ti_3C_2T_z$-40HF-24-DMSO	2	47.1	73.3	5.1	21.6
		6	69.5	60.6	5.7	33.8
8	TiO_2	2	18.1	82.5	17.5	-
		6	**34.8**	**87.9**	**9.4**	**2.7**

Reaction conditions: Styrene (0.5 mmol), acetonitrile (2 mL), catalyst (10 mg), 70 °C, aqueous 50 % H_2O_2 (1 mmol), under a N_2 atmosphere. [a] 2 mmol of aqueous 50 % H_2O_2 is used; [b] Conversion (mol %), determined by GC.

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3D PRINTED SILICON/MXENE ELECTRODE FOR ENHANCED SODIUM-ION BATTERIES

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Silicon stands out as a promising material for negative electrodes in sodium-ion batteries due to its high theoretical capacity, low working potential, and abundance. However, challenges such as volume expansion, unstable solid electrolyte interphase, low conductivity, and capacity retention hinder its performance. Attempts to mitigate these issues include strategies such as particle size reduction, creating porous structures, and incorporating conductive materials.

MXene, a class of 2D transition-metal carbide and nitride, in particular, Ti3C2Tx, shows promise in enhancing the electrical conductivity and mechanical properties of silicon particles. Previous studies have demonstrated MXene's effectiveness as a conductive additive for metal-ion battery electrodes, improving structural stability and enabling the fabrication of thick electrodes for high-energy applications[1].

We explored the synergy between MXenes and 3D printing technologies to further enhance the mechanical properties and ion diffusion pathways within the electrode structure. 3D printing has emerged as an alternative to conventional electrode fabrication techniques due to its versatility in designing electrodes at a macroscopic level. Through this approach, we aim to enhance the porosity and conductivity of electrodes, facilitating increased exposure of active materials for ion intercalation. Electrochemical and physical characterization techniques such as SEM, AFM, and XRD were employed to evaluate the performance of the resulting electrodes.

This research presents a novel approach to optimizing sodium-ion battery electrodes, leveraging the high capacity of silicon with the unique properties of MXene and the versatility of 3D printing technology.

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MXENE-BASED MATERIALS FOR CATALYTIC APPLICATIONS

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MXenes, a novel class of two-dimensional (2D) transition metal carbides, nitrides, and carbonitrides, have gained significant attention in recent years due to their physicochemical and surface properties for heterogenous catalysis. These novel materials are produced by selectively etching layers of sp elements from their corresponding three-dimensional (3D) MAX phases, this procedure leads to the MXene surface terminations groups (–OH, –O and/or –F groups), providing a strong interfacial coupling with metal ions and nanoparticles. [1-2]

In addition, first-row metals can be used to design inexpensive earth-abundant materials. Specifically, nickel have been extensively explored for hydrogen transfer reactions due to their high activity. Some of the main difficulties with Ni-based catalysts are the low yields and selectivity that have been reported for catalytic applications. However, combining Ni nanoparticles with 2D materials like MXenes, can improve their stability and increase their activity in organic transformations, minimizing the formation of unwanted byproducts. [3-4]

In this work, we propose the synthesis of a new MXene-based materials as support for nickel nanoparticles and its potential application for organic transformations.

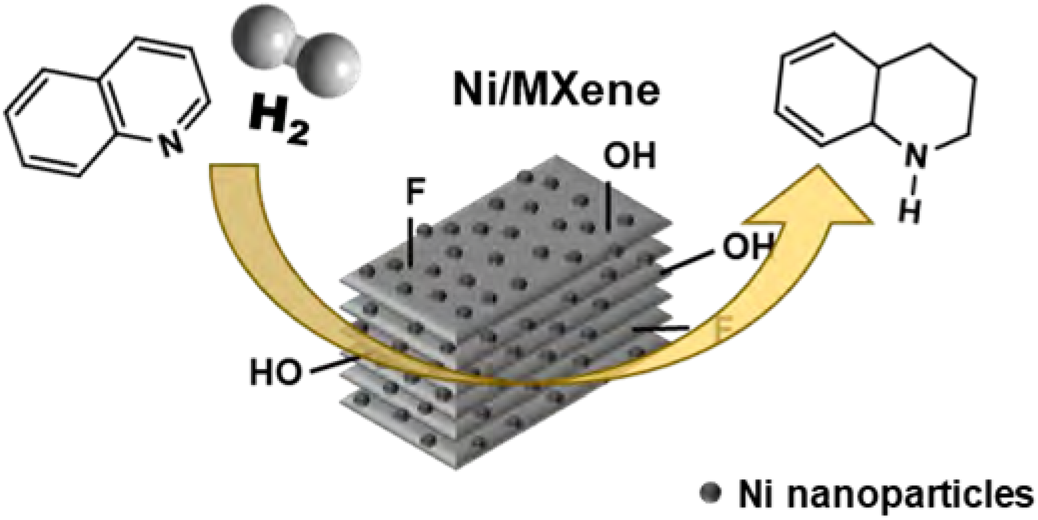

Figure 1. Reaction scheme in catalytic hydrogenation of quinoline using Ni/MXene-based materials

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PEROVSKITES NANOCRYSTALS SUPPORTED ON MXENE (TI2N) FOR PHOTOCATALYTIC CO2 REDUCTION

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Nanocrystals (NCs) composed of entirely inorganic cesium lead bromide ($CsPbBr_3$) stand out as significant entities within the family of metal halide perovskite semiconductor materials with photoluminescence quantum yield (PLQY) near 100% and easy manufacture procedures.[1] They exhibit remarkable stability and exceptional optoelectronic characteristics, paving the way for a multitude of potential applications, including CO_2 photoreduction.[2] On the other hand, recent advances have shown that MXenes supported semiconductors based photocatalysts can be expected to emerge as the most advantaged and encouraged novel photocatalysts in the photocatalytic and photoelectrochemical applications.[3]

In this study, we propose the use of NCs of $CsPbBr_3$ as a co-catalyst, prepared by hot-injection method. The influence of the capping ligand is studied, as it can determine the morphological and optical properties of the perovskite NCs and consequently, their catalytic activity. These NCs are supported on a matrix of Mxene (Ti_2N) and graphene[4] to achieve methane through photocatalytic CO_2 reduction. Moreover, the self-supported $CsPbBr_3/Ti_2N$ Mxene catalyst enables lower reaction temperatures compared to those reported with other catalysts in the literature.

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CO ADSORPTION IN MXENES TIXCX-1 (X=2,3) AND ITS MAX SLABS

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This work is focused on the carbon monoxide molecule (CO) adsorption study on the MXenes Ti2C, Ti3C2 in its MAX slabs phases Ti2AlC, Ti3AlC2. The adsorption of the CO was performed using the density functional theory (DFT) as is implemented in the Vienna Ab initio Simulation Package (VASP)[1]. Since the structures are arranged in layers, Van der Waals dispersive force interactions were considered. A 3 x 3 x1 supercell was used to study the different structures. The consecutive slabs were separated by a vacuum of ~15 Å to reduce self-interactions due to periodic conditions.

The structure of the MXenes were built from the corresponding MAX phase, by removing the Aluminium. The slabs were obtained by cuts of the MAX phase with different surface terminations like Titanium, Aluminium or Carbon. The stable one was finished in titanium, and we used it to construct slabs with stoichiometries: Ti2AlC, Ti2Al0.5C, Ti6Al2C3, Ti3AlC2, Ti3Al0.5C2 Ti9Al2C6, were we adsorbed CO.

There are four sites of high symmetry: “Top”, over a Ti atom of the outmost first layer; “Hollow-M (HM)”, over a metal atom (Ti) of the second layer; “Hollow-C (HC)”, over a carbon atom and “Bridge”, between two adjacent Titanium atoms from surface. Furthermore, the CO was placed in 3 different positions with respect to the surface: horizontal, vertical with the C pointing at the surface and vertical with the O pointing at the surface. Vibrational frequencies for adsorbed CO were determined by freezing all MAX and Mxenes atoms from the support, this is, the normal vibrational modes of the CO have been uncoupled from the surface phonons and every atom displaced independently of its equilibrium position. The CO- surface interaction was neglected and only the adsorbate was calculated.

We optimized the MAXs phases, their corresponding MXenes and different configurations for the MAXs phases, where we varied the proportion of Al:Ti:C. We organized them into 2 groups named: I (MAX Ti2AlC and its derivatives) and II, MAX Ti3AlC2 and its derivatives. All optimizations were carried out under the same calculation conditions. CO adsorbed perpendicular to the titanium surface is placed on both the C and O atom sides. The adsorption energy:

$$E_{ads} = E_{AS}-(E_A-E_S)$$

Where is the system energy with the adsorbate, adsorbate energy (CO) in vacuum, clean surface energy. The configurations with lower adsorption energy were selected to calculate the vibrational frequencies, where only the CO displacements perpendicular to the surface were considered to be active.

In group I the value of the calculated frequency is slightly increased as the proportion of aluminum increases, the variation in intensity is negligible. The frequency and intensity values are very similar for group II, with the exception of MXene which has a lower value, indicating that Aluminum is not present inside the cell. Because the differences in adsorption energy, as well as in frequencies and intensities, between these MXenes and Slabs of their MAX phases are very close to each other so we considered that any of these stoichiometries can be used for the CO adsorption.

Acknowledgments

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PHASE-ENGINEERED DICHALCOGENIDES/FLUORINE-FREE MXENE (T=OH, O) HETEROSTRUCTURES FOR PH-UNIVERSAL HYDROGEN EVOLUTION REACTION

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The study addresses the pH-dependent limitations in electrocatalytic hydrogen evolution reactions (HER) by developing heterostructures via chemical bonding between 2D-dichalcogenides and MXene planes. The MXene was prepared in an alkaline environment to eliminate fluorine. Employing a one-step solvothermal synthesis method, the study creates synergistically interacting 1T phases of materials like MoS2 and MXene. These heterostructures demonstrate improvements in catalytic stability, active site exposure, surface area enlargement, electrical conductivity, and thereby enhance water dissociation activities in all directions. Additionally, the 1T dichalcogenide-MXene catalyst exhibits pH-universal catalytic properties, surpassing platinum in HER performance across various environments.

Despite significant progress in developing hydrogen production catalysts with outstanding performances, a notable gap persists in the availability of durable catalysts capable of operating effectively under high current densities (>500 mA cm-2). The synthesized crystals show remarkable activities under current densities of 1000 mA cm−2, requiring low overpotentials in 0.5 M H2SO4, 1 M KOH, and 0.1 M phosphate buffer (PBS) electrolytes. Moreover, they demonstrate excellent HER performance with minimal overpotentials to achieve current densities of 10, 500, and 1000 mA cm−2, respectively, with outstanding stability observed over 1000 CV cycle HER tests without degradation in acidic media. Enhanced HER performance is also observed in other 2D-dichalcogenides/heterostructures, suggesting promising prospects for phase- engineered dichalcogenides/ fluorine-free composites for pH-universal HER.

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MXENE SYNTHESIS UNDER DIFFERENT BASE CONDITIONS

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The great strides in MXene synthesis have been made under acidic condition in presence of fluorine. Until now, MXene fabrication has lacked data to analyze the contribution of base synthesis. Notably, fluorine decreases conductivity, while hydroxide groups enhance it. Base synthesis methods offer a promising approach to introduce hydroxide groups onto MXene, boosting its suitability for energy storage devices. Following the Bayer's process for MXene synthesis [1], using sodium hydroxide for etching and exfoliation the paper highlights the potential risk posed by alkaline compounds (Na/K-Ti-O compounds) that may impede the aluminum etching process. To overcome this challenge, we have redirected our efforts towards employing organic bases for MXene synthesis. Following the success of MXene fabrication from tetramethylammonium hydroxide (TMAOH) [2], we have been investigating different milder synthesis conditions using TMAOH and obtained MXene structures. In the initial phase of this research, XRF analysis confirmed a reduction in aluminum content in the product, indicating a promising approach for etching aluminum from the MAX phase. Despite the relatively low yield of MXene achieved under these conditions, the potential of synthesizing MXene using basic condition is highly promising. Our ongoing experiments with tetraethylammonium hydroxide (TEAOH) also show the positive results of MXene formation under the same mild conditions. The work will further explore the potential of organic base and discuss on limitation and improvement.

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MXENE FOR GREEN SYNTHESIS OF AMMONIA

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MXenes, a class of two-dimensional (2D) materials composed of transition metal carbides, nitrides, or carbonitrides, have garnered attention for their diverse range of applications due to their unique properties, such as high electrical conductivity, mechanical strength, and tunable surface chemistry. While MXenes have primarily been explored for applications in energy storage, sensing, and catalysis, their potential for catalyzing ammonia synthesis is an intriguing area of research.

Ammonia synthesis is a crucial industrial process to produce fertilizers, chemicals, and various materials. Traditionally, this process relies on the Haber-Bosch process, which operates under high temperature and pressure conditions using iron-based catalysts. However, this process is energy-intensive and produces a significant amount of greenhouse gases. Exploring alternative catalysts, such as MXenes, for ammonia synthesis offers the potential for more efficient and environmentally friendly processes. MXenes exhibit several properties that make them attractive candidates for catalysis, including their high surface area, ability to accommodate various functional groups, and electronic conductivity.

In this study, we experimentally compared, different MXene throughout the periodic table for electrochemical nitrate reduction properties for the first time. The Faradic Efficiency, Yield rate, and stability of every MXene were explored. This study will pave a path for further deep exploration and utilization of MXene and MXene-derived electrocatalysts for ammonia synthesis.

MXENES-SILICA POROUS NANOSTRUCTURED MATERIALS WITH PHOTOTHERMAL PROPERTIES

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In the present communication we introduce new experimental approach for the preparation of functional porous nanoarchitectures from exfoliated Ti3C2Tx MXene. The procedure involves the previous intercalation of a cationic surfactant (CTAB) followed by nanoparticles formation after hydrolysis of an alkoxysilane such as tetramethylorthosilicate (TMOS) leading to delaminated MXene assembled to SiO2 network (Fig.1).

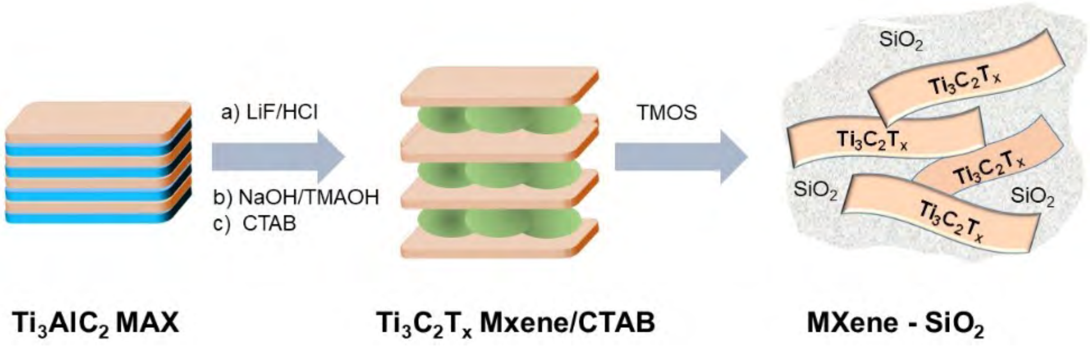

FIG. 1 Scheme showing the strategy followed to synthetize MXenes-silica porous nanostructured materials

The formation of the Ti3C2Tx MXene from the MAX phase by reaction with LiF/HCl solution as well as the intercalation of the MXene and further delamination by the silica generation are confirmed by X-Ray diffraction (XRD), the solids being characterized by FTIR, FE-SEM and TEM-EDX techniques. The resulting nanoarchitectures show enhanced adsorption properties conferred by the generated silica together photothermal response, which is attributed to the presence of the MXene. In fact, the specific surface area of the starting MXene (ca. 60 m2 g-1) increases to values greater than 200 m2 g-1, which make these materials as very attractive adsorbents. The photothermal response of these porous nanoarchitectures is evidenced by the significant increase of temperature produced under laser NIR irradiation (808 nm). This characteristic is a rare feature in materials science and therefore gives us the opportunity to thermally activate organic reactions by laser irradiation with the possibility to act at a distance from the reactor device opening the way to diverse applications including heterogeneous catalysis field.

In this preliminary study, as a proof of concept, we have tested the transformation of pinacol in pinacolone after adsorption on these MXene-silica solids doped with sulfuric acid and thermal activation using a NIR laser device. In addition, the interest of these materials is based on the presence of porous silica offering the possibility of further functionalization, for instance by anchoring functional groups via silanization openning up much broader future perspectives for the design and preparation of new multifunctional materials derived from MXenes

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VACANCY ORDERED DOUBLE HALIDE PEROVSKITE COMPOSITE WITH MXENE FOR HER APPLICATIONS

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In the realm of catalysis, lead halide perovskites have demonstrated considerable potential. Nonetheless, the presence of lead poses significant toxicity concerns, hindering their practical utility. Addressing this issue, this study introduces a pioneering approach to synthesize an environmentally friendly, lead-free double perovskite composite via an interfacial trapping system. Integrating this composite into MXene material, the resulting catalyst was evaluated for its electrocatalytic activity in the Hydrogen Evolution Reaction (HER) for the first time. The collaborative interplay between MXene and halide perovskites yields notable enhancements in catalytic stability, active site accessibility, surface area expansion, and electrical conductivity, thereby amplifying electrocatalytic activities. Investigations into the electrical conductivity of various MXene-halide perovskite combinations were conducted to further elucidate these synergistic effects.

Remarkably, the catalyst exhibited outstanding performance, characterized by low overpotential and Tafel slope, surpassing both pristine MXene and halide perovskite counterparts. Furthermore, the composite displayed exceptional cyclic stability over 1000 CV cycles. Notably, it demonstrated superior activity across both acidic and basic conditions, shedding light on its potential for broad pH electrocatalytic applications.

Furthermore, the impact of halide perovskite size variation on electrocatalytic activity was explored by altering the synthesis technique to hydrothermal. Interestingly, this alternative approach yielded less electrocatalytic activity compared to the former method.

This research underscores a viable strategy with promising implications for the development of lead-free perovskite composite catalysts, offering insights into enhancing catalytic performance while mitigating environmental concerns.

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ENHANCED ELECTROCHEMICAL SENSING PLATFORMS BASED ON “FLUORIDE” AND “FLUORIDE-FREE” SYNTETHIZED MXENES FOR CLINICAL AND ENVIRONMENTAL APPLICATIONS

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The use of low-dimensional materials for the development of nanostructured electrochemical sensors has proven to be an excellent strategy for enhancing, in terms of electrocatalytic activity, sensitivity, and selectivity, the response of these devices towards compounds of interest in various application fields. Since the isolation of graphene in 2014 by Geim and Novoselov, and due to their unprecedent properties, a search for other 2D nanomaterials has attracted a great attention taking a leading role in numerous research areas. These known 2D nanomaterials mainly include Transition Metal Dichalcogenides (TMDs), 2D carbides, Transition Metal Oxides (TMOs), graphitic carbon nitride (g-C3N4), or nitrides and carbonitrides of transition metal (MXenes), among others.

All 2D nanomaterials exhibit several common properties derived from their “surface character”, such as a large specific surface area and, therefore, a high surface area-to-volume ratio. Among these bi-dimensional materials, MXenes (with a general formula of Mn+1XnTx, where M is an early transition metal, X can be C and/or N, and T represents surface terminations such as OH, O or F), combine the metallic conductivity of M with the hydrophilic nature of the functionalized surface, which makes them excellent 2D nanomaterials for electrochemical sensors applications. Furthermore, in the case of biosensing devices, these surface groups facilitate the binding of the recognition element, while their high specific surface area allows for the immobilization of a high density of (bio)receptors, thereby enhancing device sensitivity. Additionally, MXenes offer additional advantages such as good biocompatibility, which creates a favourable environment for preserving enzymatic activity, and resistance to passivation and fouling, leading to increased device stability. These characteristics make them an excellent choice for designing and developing electrochemical (bio)sensors with improved properties applicable to both batch and flow methods.

In this work, we present different electrochemical sensors based on 2D MXenes synthetized either by: i) fluoride etching procedure1,2, ii) “in-situ” generated fluoride etching procedure3 and, iii) electrochemically fluoride-free procedure4. After the electrochemical and morphological characterization by AFM, we show the enhanced electrochemical response of the sensing platforms towards different analytes of relevance in the clinical or environmental fields. Moreover, we present the synergistic effect observed when MXenes are combined with other low dimensional materials as diamond nanoparticles, demonstrating how the intrinsic conductivity of MXenes proves promising, opening an exciting field of work and expanding the potential of 2D materials in applications related to the development of electrochemical sensors.

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THE INFLUENCE OF INTERCALATING AGENTS ON THE FORMATION AND THE EFFICIENCY OF MXENE-BASED PHOTOCATALYTIC HYBRIDS FOR LIGHT-DRIVEN HYDROGEN GENERATION

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Since the family of MXene materials was discovered in 2011, its diversity expanded rapidly. Also, the ways of MXenes application are continuously growing due to their outstanding properties, like the combination of electronic conductivity and hydrophilic surface. The model $Ti_3C_2T_x$ MXene is a promising material to be applied as photocatalytic substrate in hydrogen production via photoinduced water-splitting process. MXene-based catalysts are expected to replace platinum in photocatalysis. Nevertheless, the factors that can affect the photocatalytic activity of MXenes are numerous. Firstly, the method applied for their formation and corresponding purification processes have predominant importance. Secondly, the exact protocol of photocatalytic system preparation prior to photocatalytic test has an equally significant role. From the state-of-the-art it is known, that the intercalation agents applied during MXene formation influence the distance between MXene monolayers and stability of their colloidal solution. Hence, they also affect the available MXenes surface area and their overall photocatalytic activity.

In this work, we investigated the influence of chosen intercalating molecules onto photocatalytic activity of MXene-based photocatalytic system. Thus, $Ti_3C_2T_x$ monolayers were formed by etching of Ti_3AlC_2 MAX phases using mild LiF-HCl procedure, followed by initial purification and delamination processes. Next, MXenes were divided into three batches, namely: i) reference, ii) tetrabutylammonium hydroxide- (TBAOH), and iii) LiCl-intercalated samples. The prepared samples were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Raman spectroscopy.

As expected, all three batches of MXenes differed in terms of number and type of the intercalant layers, as well as amount and kind of the impurities. All of the above-mentioned factors can strongly influence the photocatalytic activity of MXene fractions for hydrogen generation. The photocatalytic activity of obtained MXene fractions was analyzed in photocatalytic system containing Eosin Y as a photosensitizer, triethanolamine as a sacrificial electron donor, $CoSO_4$ as a catalyst and $Ti_3C_2T_x$ flakes as a conductive support. According to achieved results, it was found that counterintuitively, the photocatalytic activity of MXenes decreased after intercalation with TBAOH, despite the increase of the distance between individual flakes (as confirmed by XRD results). This reduction in activity is thought to happen due to the diminished ability of MXenes to form co-catalytic nanohybrids, as a consequence of the MXene surfaces being fully occupied by TBAOH ions. Nevertheless, our work definitely highlights huge potential of 2D MXenes in dye-sensitized photocatalysis for hydrogen evolution.
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COMPUTATIONAL INSIGHTS INTO TAILORING OF SURFACE TERMINATION ON MXENES FOR PHOTO-THERMOCHEMICAL CYCLES OF CO2 AND H2O DISSOCIATION

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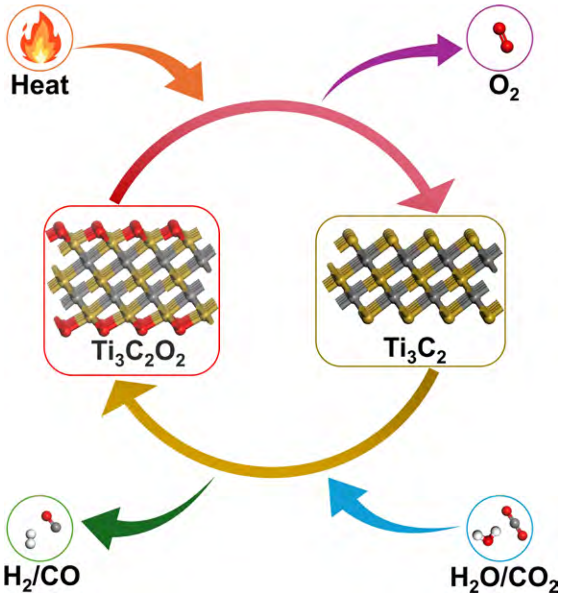
Solar-driven thermochemical approaches to CO_2 and H_2O dissociation inherently operate at high temperatures, offering an appealing route to high-efficiency solar fuel production without the need for precious metal catalysts. Two-step thermochemical cycles utilizing metal oxide redox reactions provide a solution to the CO-O_2 or H_2-O_2 separation challenge, in contrast to the direct thermolysis of CO_2 and H_2O. Cerium oxide has become a highly appealing choice of redox active material for two-step thermochemical cycling due to its rapid fuel production kinetics and exceptional selectivity.[1]

In comparison to cerium oxide, MXenes materials offer rich and adjustable oxygen-containing termination groups, as well as a lower operating temperature for tailoring surface terminations, [2,3] making them promising for two-step thermochemical cycling of CO_2 and H_2O dissociation. In this study, we employed density functional theory calculations to investigate the reduction of $Ti_3C_2O_2$ to bare Ti_3C_2, followed by re-covering bare Ti_3C_2 through dissociating CO_2 and H_2O, releasing CO and H_2 simultaneously. Our calculations suggest that the bare metallic MXene exhibits high activity, with low energy barriers for H_2O splitting (~0.45 eV) and H spillover (~0.39 eV) and no energy barrier for CO_2 dissociation under specific adsorption configurations. The rate-determining steps for H_2O and CO_2 dissociation involve the formation and desorption of H_2 and CO. The reduction step of $Ti_3C_2O_2$ requires relatively high energy (about 10 eV), which can be decreased by replacing O with OH/Cl/Br termination groups.

In summary, our results demonstrated that $Ti_3C_2O_2$ is a promising material for combining the oxygen uptake and release capacity for facile thermochemical CO_2 and H_2O dissociation, resulting in the production of CO and H_2, respectively.



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SPRAY-COATED TI3C2TX MXENE THIN FILM FOR FLEXIBLE ENERGY STORAGE DEVICES

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Thin films that display high adhesion and high conductivity are essential for flexible electronics. Two-dimensional transition metal carbides and nitrides (MXenes) have accumulated tremendous interest recently due to their high conductivity and excellent figure of merit. In this work, we demonstrate the fabrication of highly adhesive $Ti_3C_2T_x$ MXene films on a flexible substrate using the spray coating technique by varying the spray time, substrate temperature, and concentration of MXene solution. Homogenous films having thicknesses of 150 μm–100 μm with sheet resistances (R_s) ranging from 0.06 to 1 kΩ sq^{-1} are produced at ambient conditions with the figure of merit (the ratio of electronic to optical conductivities, σ_{DC}/σ_{opt}) ranging from 0.5 – 1.[1] The thin films had a layered morphology and good conductivity making them suitable for supercapacitor application. The work presents a scalable path toward creating MXene thin films for device application and hence opens up a path towards easy commercialization.[2]

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INVESTIGATION OF HIGHLY CONDUCTIVE AND HUMIDITY-TOLERANT MXENE PREPARED USING PHOSPHORIC ACID

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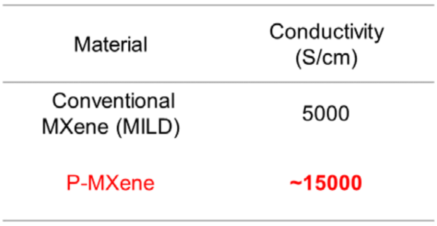
MXene, a novel two-dimensional material discovered by Naguib *et al*. at Drexel University in 2011, has attracted great interest among researchers because of its unique fundamental and application properties. These properties make MXene a promising candidate for electromagnetic shielding devices, supercapacitors and lithium-ion batteries, etc. Furthermore, the wet process capability of MXene, owing to its hydrophilic surface terminations, enables the use of environmentally friendly and abundant water as a synthesis solvent. The ease of processing suggests its suitability for mass production rather than other conventional two-dimensional materials.

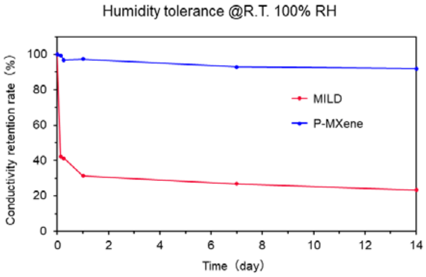
Delamination of MXene from multilayer to single layer is important for bringing out its physical properties originating from its two-dimensional structure. Conventionally, hydrochloric acid is used as a supplemental acid in an etching process to adsorb chlorine termination on its surface to improve the delamination capability of MXene. Chlorine termination enlarges the interlayer distance and facilitates the delamination of MXene easier. However, several restrictions, such as the RoHS directive, limit the total amount of chlorine in the devices to protect the environment and realize a sustainable society.

Therefore, the global trend of decreasing and eliminating chlorine will continue in the future. Delamination of MXene using tetramethyl ammonium hydroxide (TMAH) under chlorine-free conditions has been previously reported. However, TMAH is a poisonous substance; therefore, its use is not preferable. The use of TMAH lowers the properties of MXene, such as conductivity and humidity tolerance, because of its bulky structure. Electronic devices for consumer use are sometimes operated in very harsh conditions such as high temperatures and high humidity. Therefore, electronic devices that can maintain their performance in harsh conditions for a long time are required.

In this presentation, a novel method for chlorine-free delamination and the performance of chlorine-free MXene prepared using this method will be discussed. Phosphoric acid was used as a supplement for the etching process, and lithium phosphate was used as an intercalator in the intercalation process. The change in these two processes enabled chlorine-free delamination. Briefly, Ti_3AlC_2 was synthesized by the calcination of a mixture of titanium, titanium carbide, and aluminum powder. Next, the obtained Ti_3AlC_2 block was ground and passed through to obtain a uniform particle size powder. The Ti_3AlC_2 powder was etched in a mixture of hydrofluoric acid and phosphoric acid at 35 degC for 24 h. Then, Ti_3C_2 was obtained. The obtained Ti_3C_2 was washed with de-ionized (DI) water 10 times. Subsequently, a mixture of lithium phosphate, phosphoric acid and DI water was added to promote the intercalation of the lithium cation. Finally, the mixture was shaken with a conventional shaker to induce delamination and collected by centrifugation. The supernatant from the centrifugation was used for further evaluation. We refer to the product as P-MXene in the following. The free-standing film of P-MXene shows an electronic conductivity of over 14,000 S/cm and humidity tolerance of more than 90 % at R. T. 100% RH 2 weeks on the maximum. This result indicates that P-MXene has superior properties suitable for consumer electronic devices compared with conventional MXenes.



Material	Conductivity (S/cm)
Conventional MXene (MILD)	5000
P-MXene	**~15000**



The reason why P-MXene exhibits good electronic properties was also investigated. Density analysis of the free-standing film shows that MXene with high conductivity possesses a high density, typically more than 3 g/cm^3. Cross-sectional scanning electron microscopy suggests that the macropores of the free-standing film decrease the electronic conductivity by obstructing the propagation of electrons. This result is consistent with the simulation using the finite element method. The simulation suggests that the phenomenon that macropores decrease the electronic conductivity of the film is unique for two- dimensional materials. X-ray diffraction analysis revealed that MXene with high humidity tolerance possesses a short interlayer distance compared with conventional chlorine containing MXene. Time-of-flight secondary ion mass spectrometry suggests that the surroundings of lithium contained in MXene are different from those of high- and low-humidity-tolerant MXenes. These results suggest that water and lithium in the interlayer spacing draw additional water and lower humidity tolerance.

CHARGE STORAGE MECHANISM IN V2CTX MXENE FOR AQUEOUS ZINC-ION BATTERY STUDIED BY IN SITU X-RAY ABSORPTION SPECTROSCOPY

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MXenes, a family of 2-dimensional transition metal carbides, are a promising candidate for use in energy storage applications due to their 2D morphology and hydrophilic surface, offering high charge storage in aqueous electrolytes. Especially V_2CTX MXene has recently shown exciting performance in aqueous zinc ion batteries (AZIBs).

In situ/operando x-ray absorption spectroscopy (XAS) measurements have been performed in the OÆSE endstation at the storage ring BESSY II with a dedicated electrochemical flow cell capable of measuring XAS in the photon-in/photon-out regime.

In this poster, we monitor the chemical bonding of V_2CTX MXene electrodes during cyclic voltammetry using operando XAS. XAS measurements at the V K-edge reveal changes in MXene surface chemistry during electrochemical cycling in 3M $ZnSO_4$ aqueous solution. The behavior will be discussed with regard to intercalation of Zn ions versus redox reactions at the interfaces of MXene and electrolyte. After each cycle, the potential was held constant at the largest oxidative and reductive potentials and XAS measurements were conducted to understand charging dynamics and identify the storage mechanism.

Time- and potential-dependent changes in the oxidation state from V^{3+} to V^{4+} and V^{5+} were also tracked in situ and will be discussed.

This work demonstrates the relevance of operando XAS for unraveling charging processes in MXene-based AZIBs.

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