SIGURNA I ODRŽIVA SINTEZA MXENA MEHAKOKEMIJSKOM METODOM

SAFE AND SUSTAINABLE MXENE SYNTHESIS VIA MECHANOCHEMICAL METHOD

Gabrijela Ljubek[1], Kaltrina Stajku[2], Marijana Kraljić Roković[2], Leonarda Vugrin[3], Pierluigi Bilotto[4], Markus Ostermann[5]

[1]University of Zagreb Faculty of mining, geology and petroleum engineering, Zagreb, Croatia

[2]University of Zagreb Faculty of chemical engineering and technology, Zagreb, Croatia

[3]Ruđer Bošković Institute, Zagreb, Croatia

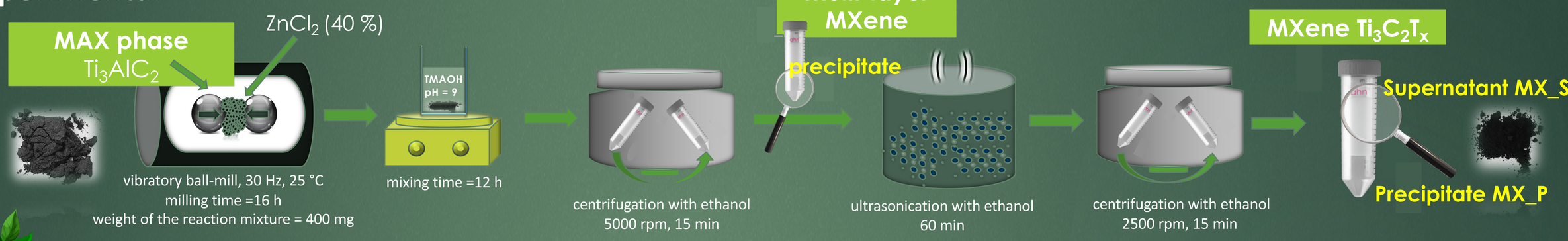
[4]Tu Wien, Group of tribology, Vienna, Austria

[5]Centre for Electrochemistryand Surface Technology, Vienna University of Technology, Vienna, Austria

Intruduction

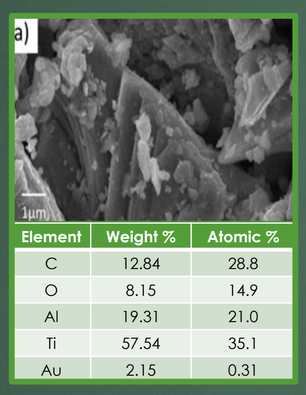
MXenes are transition metal carbides and nitrides that have emerged as one of the fastest-growing groups of 2D materials with great potential for application in supercapacitors, micro-supercapacitors, batteries, fuel and solar cells, composite materials, photocatalysis, biosensors, photodetectors, etc. To date, most MXenes have been prepared through a wet chemical etching method that involves fluoride solutions such as HF or LiF/HCl due to their high efficiency and selectivity. However, fluoride-based solutions are highly hazardous and, their use is associated with considerable safety and handling concerns that are a major barrier to scaling up MXene production. It is therefore desirable to develop simple, safe, reliable as well as sustainable synthetic routes for MXene preparation and practical application. In this work, we explore **mechanochemistry (MC)** to prepare **fluorine-free MXenes**. This is a viable approach to promote reactions of solids quickly and quantitatively that can be easily scaled-up to manufacturing levels

Experimental

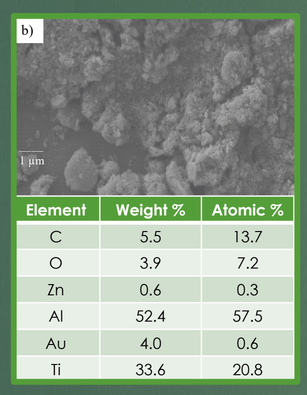


Results

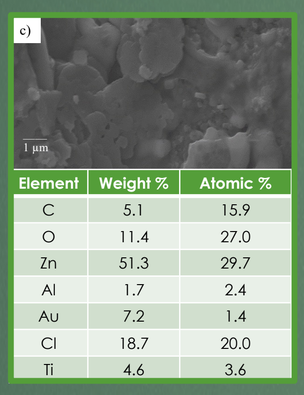
From the **experimental sheme** it is evident that there is a color change of the powdered Ti_3AlC_2 MAX phase after synthesis, from grey to black. This could be attributed to the selective etching of the aluminium. We employed $ZnCl_2$ as suitable inorganic salts for the ball-milling procedure because it provides chloride, which in combination with mechanical stress may influence Al–Ti bonds within MAX phase. Since the bond energy of Al–Cl (502 kJ mol^{-1}) is higher than that of the Al–Ti (263.4 kJ mol^{-1}), the Al can be etched by Cl− added in the form of salt. The efficiency of this process is improved by MC stress. Furthermore, Zn^{2+} and TMA^{+} can be easily intercalated between MXene layers, which contain negative surface charge, promoting the expansion and delimination od the multilayer MXene into monolayer MXene nanosheets after the ultrasonic treatment with ethanol.



Element	Weight %	Atomic %
C	12.84	28.8
O	8.15	14.9
Al	19.31	21.0
Ti	57.54	35.1
Au	2.15	0.31



Element	Weight %	Atomic %
C	5.5	13.7
O	3.9	7.2
Zn	0.6	0.3
Al	52.4	57.5
Au	4.0	0.6
Ti	33.6	20.8



Element	Weight %	Atomic %
C	5.1	15.9
O	11.4	27.0
Zn	51.3	29.7
Al	1.7	2.4
Au	7.2	1.4
Cl	18.7	20.0
Ti	4.6	3.6

Figure 1. SEM images of the a) MAX powder, b) MX_P and c) MX_S. *Insert shows EDX analysis.*

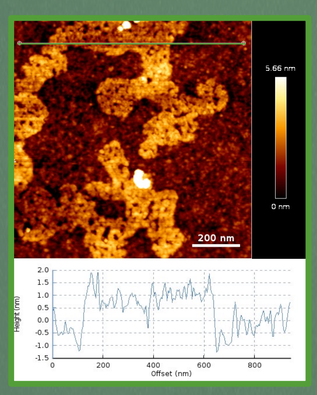


Figure 2. AFM topography image of Mxene (MX_S).

Fig. 1a illustrates the typical compact layered structure of the MAX phase Ti_3AlC_2, while the morphology of the materials obtained after MC treatment (**Fig 1b,c**) shows a smaller particle size with vaguely defined edges. From the EDX analysis it is clear that 91.2 wt % Al was removed in supernatant MX_S, while in MX_P there was no removal of Al. The precipitate (MX_P) is believed to be the MAX phase from which the MXene (MX_S) has been removed.

The topographic height profile (**Fig. 2**) obtained via AFM mapping revealed that the MXene sheets had a height of 1 – 2 nm, which corresponded to a single layer of MXene, implying the successful exfoliation of the sheets.

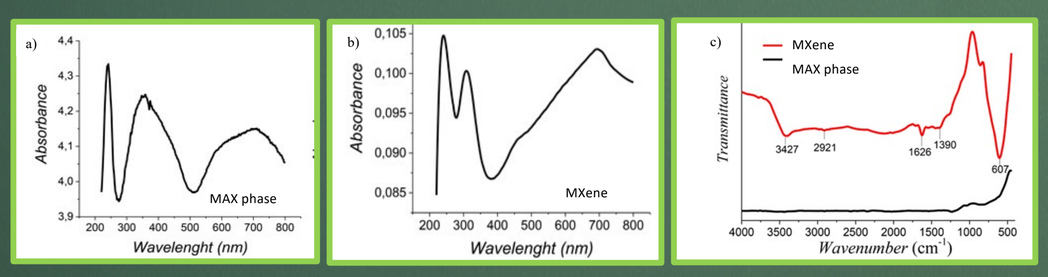


Figure 3. UV/Vis (a, b) and FTIR (c) spectra of the MAX phase and MXene (MX_S).

The UV/Vis and FTIR spectra (**Fig. 3**) of the MAX phase and MXene indicate the presence of oxygen functional groups on the MXene surface, as well as Ti oxidation and formation of TiO_2. On **Fig. 3b** it was shown that beside two $Ti_3C_2T_x$ absorbance peaks, at approximately 320 nm and 700 nm, there is one additional absorbance peak at 250 nm related to TiO_2.

Fig. 3c shows the FTIR spectrum of MAX phase and MXene, respectively. No particular peak can be visualized on the FTIR spectrum of the MAX phase, which is different from MXene (MX_S). Peaks appeared in the FTIR spectrum of the MXene can be attributed to the stretching vibrations of -OH, C-H, C=O, O-H and Ti-O bonds.

Raman spectrum of MX_S MXene (**Fig. 4**) show the characteristic resonance peak of $Ti_3C_2T_x$ at 120 cm^{-1} that emerges when the laser wavelength is coupled with the plasmonic resonance.

Next is the flake region consisting of E_g (Ti, C, O) and A_{1g} (Ti, C, O) vibrational modes, which are in-plane and out-of-plane vibrations of Ti atoms in the outer layer as well as carbon and surface groups, respectively.

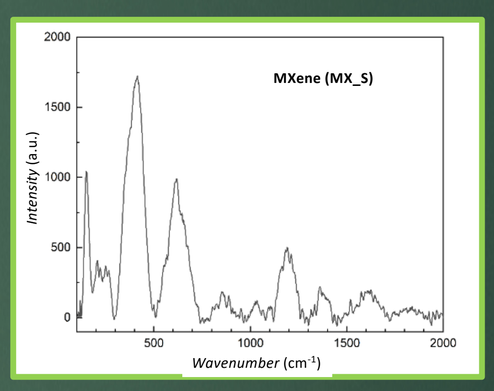


Figure 4. Raman spectrum of MX_S.

The PL (photoluminescence) peak at around 630 cm^{-1} suggests the presence of TiO_2 which is in accordance with UV/Vis and FTIR results. Broad peaks were observed in the range of 700–2000 cm^{-1} indicating the presence of carbon and disorder in the samples.

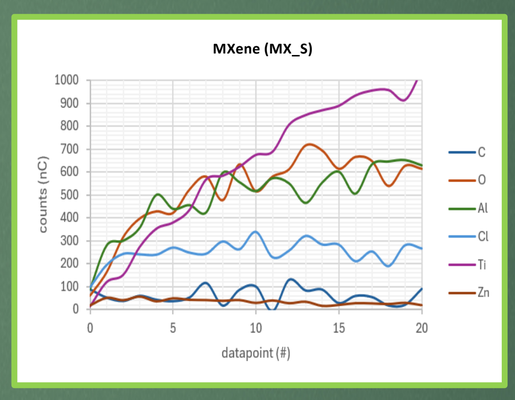
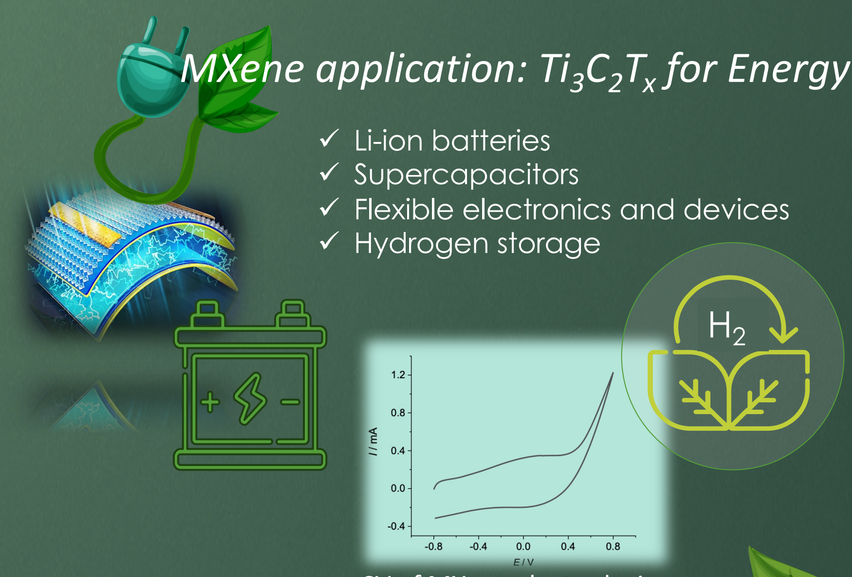


Figure 5. Depth profile of MXene executed with low energy ion scattering spectroscopy (LEIS)

Fig. 5 illustrates the depth profile for the MXene MX_S. Depth profiles profiling provides information about the elemental composition of the observed compound as well as its depth distribution of atoms on the outermost surface layer. Datapoint represents the distance of the surface of the material into its bulk.

In the outermost atomic layer observed data confirms the gradually increase of titanium content towards the bulk with the highest concentration observed.

There is depletion of oxygen at one point (x-axis #10), indicating oxide layer formation (corraborated with UV/Vis, FTIR and Raman results). Depth profile confirms etching occured on the surface with a few nanometers of aluminium being etched.



CV of MXene electrode in 0.1 mol dm^{-3} KCl at 50 mV s^{-1}