

RADICAL-BASED TUNING THE SURFACE FUNCTIONALITY OF MXENE

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Abstract

The family of MAX phases and their derivative MXenes are continuously growing in terms of both crystalline and composition varieties. MXenes are a new family of two-dimensional (2D) transition metal carbides, carbonitrides and nitrides, with a general formula $Mn+1AX_n$, where $n = 1-3$, M denotes a transition metal, A is an element such as aluminum or silicon, and X is either carbon or nitrogen. Considering the various elemental composition possibilities, surface functional tunability, various magnetic orders, and large spin-orbit coupling, MXene can truly be considered as multifunctional materials that can be used to realize highly correlated phenomena. However, a change in surface chemical groups can significantly alter the properties and functionality of MXene flakes and may even damage the flakes. In this paper, we propose the possibility of using soft, chemical transformation to tune the MXene surface chemistry and termination. We used fluorinated and brominated substituents for MXenes grafting and subsequent analysis of the surface composition of the MXene flakes indicated a decrease in oxygen and a simultaneous increase in fluorine and bromine surface concentrations. The ability to graft organic groups with various substituents to the surface of the flakes opens up new possibilities for their application. The presence of fluorinated groups on the surface makes it hydrophobic, which allows the creation of water-repellent flakes, and prevents rapid oxidation by atmospheric oxygen and related formation of titanium oxide on the surface.

Keywords: Chemical transformation, MXene, Surface grafting, Tuned functionalization

1. INTRODUCTION

Creation and study of two-dimensional (2D) materials is a young and very promising area of modern materials science [1-4]. These materials are very thin (often less than one nm), so they can be used to create layered heterostructures that are used in modern electronics, from transistors to sensors, solar cells and LEDs [5-10]. The most famous two-dimensional material is graphene, its discovery in 2010 was awarded the Nobel Prize in physics [11]. Graphene possesses high values of electrical and thermal conductivity and is sufficiently strong in tensile strength [12-15]. At the same time, it forms folds and is unstable as a separate free-hanging film [16,17]. Discovered in 2011, the MXene have surpassed graphene in both electrical characteristics and manufacturability [18,19]. MXene exhibits conductivity superior to graphene coating. In addition, MXene combines many characteristics, including high shielding efficiency, low density, low thickness, high flexibility and ease of processing [20-22]. So, it is a great candidate for numerous applications, such as transparent conductive coatings, protective layers, and electrochemically-active supports [23, 24].

It has been proven that the surface chemistry of Mxene affects its conductive properties, which can be controlled and even rearranged. However, methods of modifying the surface chemistry of MXene flakes often damage the MXene structure.

In this contribution, we propose a new approach for modifying a new and interesting class of 2D materials – Mxenes with formula Ti_3AlC_2 . Our approach is based on the surface modification under attack by highly reactive radicals.

2. EXPERIMENTAL

2.1. Materials

3,5-Bis(trifluoromethyl)phenyl-boronic acid ($\geq 95\%$), 1-iodo-3,5-bis(trifluoromethyl)benzene (98%), boron trifluoride diethyl etherate (99%), 3-Chloroperbenzoic acid ($\leq 77\%$), methanol and were purchased from Sigma-Aldrich. Powder of titanium (99%), aluminum (99.5%) and graphite (99%) were purchased from Alfa Aesar. All reagents were used without further purification. Throughout the all experiments deionized water was used. Ti_3AlC_2 MAX phase and Mxene flakes were prepared according to [25,26, 27].

2.2. Preparation of Ti_3AlC_2 MAX phase

Ti_3AlC_2 MAX phase was performed by the procedure described in [25]. Powders of titanium, aluminum and graphite were mixed in molar ratio 3.00:1.10:1.88 with zirconia balls (diameter 3 mm) by ball milling at 60 rpm during 3 hours in a plastic jar. The mixed powders were putted into alumina boat and transferred to a tube furnace (4016T, Clasic CZ). Before synthesis, vacuum pumping was carried out twice to a pressure of 2 mbar, followed by a purge with argon. The MAX phase synthesis was accomplished by heating the mixture at $10^\circ\text{C}/\text{min}$ to 1550°C in argon atmosphere followed by 2 hours holding period at 1550°C and cooling down to room temperature at $10^\circ\text{C}/\text{min}$.

Preparation of MXenes flakes

Ti_3C_2 MXene was synthesized using the MILD method described in [26]. Before selective etching of aluminum from Ti_3AlC_2 MAX phase, the MAX phase ceramics were crushed by mortar and pestle and sieved to separate the particles of size below $45\ \mu\text{m}$. The etchant was prepared by dissolving 300 mg of LiF (99.98 % metals basis, Alfa Aesar) in 6 mL of 6M HCl in the plastic centrifuge tube. Then, the 300 mg of sieved MAX phase powder (particle size below $45\ \mu\text{m}$) was added to prepared etchant and stirred at 22°C for 24 hours. After etching, the MXene were washed several times until the pH of the supernatant reached 5.5. Delamination of MXene flakes was carried out by hand shaking of the sample (15 mL DI water in 50 mL plastic test tube) for 5 min followed by 15 min of centrifugation at 3500 rpm to precipitate and separate the non-delaminated MXene.

Surface grafting and MXene thin film preparation

The colloidal suspension of MXene flakes (2 mL, 5 g/L) was mixed with a 1 mL of a radical source (1 mM solution) in a 9:1 water/methanol mixture and activated under the continuous mixing for different time intervals. After the modification, the MXene flakes were collected by centrifugation (15 min, 5000 rpm) and 3x subsequently washed by water and a methanol. For coating preparation, the purified MXene flakes were dispersed (1 g/L) in water/methanol mixture (1:1 ratio) and sprayed on previously cleaned glass or silicon surfaces using home-made equipment.

2.3. Measurement techniques

For the characterization of the solutions, the UV/Vis/NIR spectroscopy technique was used in the spectral range 300-1000 nm, scanning rate $480\ \text{nm}\ \text{min}^{-1}$, data collection interval 1 nm. The solutions were measured in 1 cm quartz cells.

TEM images were obtained on a JEOL JEM-1010 transmission electron microscope with a SIS MegaView III digital camera.

Fourier transform infrared (FTIR)–attenuated total reflection (ATR) spectra were recorded using a Nicolet 6700 spectrometer (Thermo Scientific, France) with a Smart ATR accessory device (1000 scans and 4 cm⁻¹ resolution).

The crystal structure of Ti₃AlC₂ MAX phase and Ti₃C₂ MXene phase were characterized by X-ray diffractometer (Empyrean, Malvern Panalytical) using Cu K α radiation (photon energy – 8.04 keV, wavelength $\lambda = 1.54151 \text{ \AA}$, U = 45 kV, I = 30 mA) in grazing incidence X-ray diffraction mode and in 2 θ - θ mode. The incident angle was 0.85 corresponding to ~10 mm of sample irradiation.

X-ray photoelectron spectroscopy (XPS) was performed using an Omicron Nanotechnology ESCAProbeP spectrometer fitted with a monochromated Al K alpha X-ray source at 1486.7 eV. MXene flake samples were deposited on Si wafers, the analyzed area had dimensions of 2×3 mm².

3. RESULTS AND DISCUSSION

The schematic representation of main experimental concept is given in **Figure 1**. The MXene flakes were dispersed in an aqueous methanol solution containing radical source and then activated by external triggering. Excitation of the surface MXene increases the energy of electrons on the surface, which in turn leads to homolytic of radical source and the appearance of reactive radicals. The created radicals were then grafted to the MXene surface. Moreover, simultaneous triggering and radical grafting can result in substitution of terminated groups on flake surface, leading to pronounced modification of MXene surface composition.

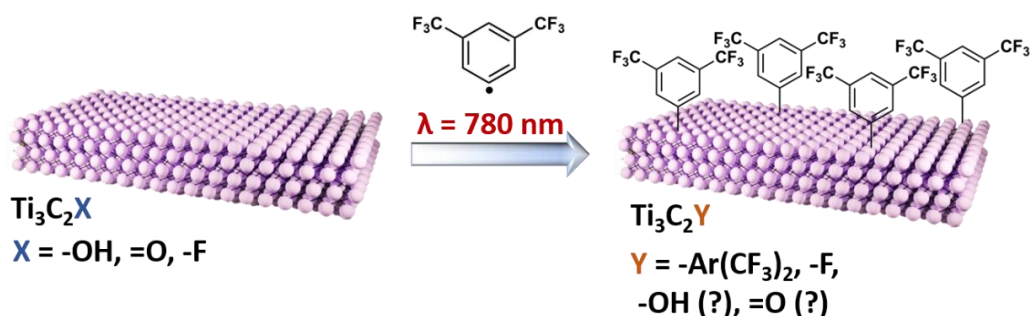


Figure 1 Schematic representation of proposed experimental concept

UV/Vis spectra of pristine MXenes in the water/methanol solution (**Figure 2A** – insert) were measured to determine the wavelength position of MXene absorption band. Next, the UV spectra were measured after different modification times (**Figure 2A**). We can observe that the absorption peak gradually shifts to the blue region with increasing modification time. After 3 hours of modification, the peak shift no longer occurred. The grafting of MXene flakes surface was further confirmed by IR measurements. IR spectra are presented in the **Figure 2B**. Pristine MXene contains peaks at 1740 (C=O), 1408 (O-H), and 595 (Ti-O) cm⁻¹ related to terminated oxidized groups. After radical grafting the appearance of new, well pronounced absorption bands on modified flakes indicate the presence of grafted chemical moieties.

The intensity of characteristic band, located at 1275 cm⁻¹ (C-F stretch in -CF₃), is plotted against the time of radicals grafting in **Figure 2B** insert. Given dependency corresponds well with UV/Vis results – apparent increase of band intensity during the first 30 min of triggering and it's saturation after 3 hours of reaction. So, results of UV/Vis and IR spectroscopy indicate that radicals grafting of MXene flakes mainly occurs at the initial stages of triggering and is further enhanced under the prolongation of triggering time up to 3 hours.

In addition, the structure and crystallinity of MXene flakes were evaluated by TEM and XRD, XPS measurements before and after radicals grafting. TEM analysis confirm the preservation of flake structure during the grafting. Results of XPS and XRD analysis are in a good agreement and approve the successful grafting of organic radicals to the surface of MXene.

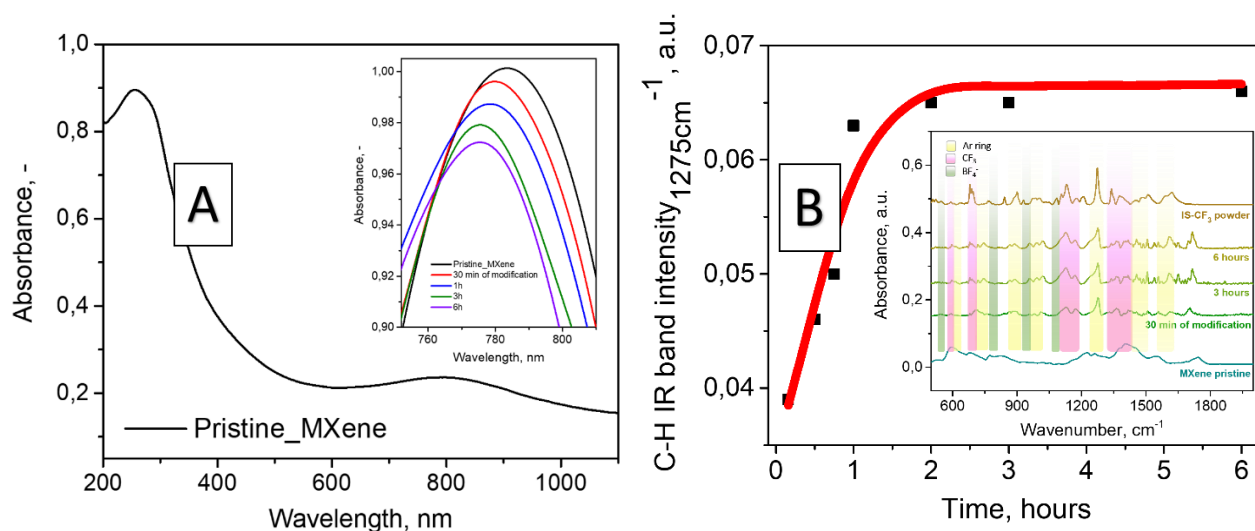


Figure 2 (A) UV/Vis absorption spectrum of MXene after different time of grafting (insert shows the full UV/Vis absorption spectrum of pristine flakes suspension); (B) IR spectra, measured on MXene flakes after the different time of radicals grafting (insert show the time dependent changes of characteristic (1275cm⁻¹) IR band intensity)

4. CONCLUSION

A surface modification of MXene flakes under radical attack has been proposed. The mixture of flakes with the radical source was activated for different times. As a result of chemical bond homolysis the active radicals appear, attack the MXene surface and change the chemical composition of the surface terminated groups. Due to the high MXene catalytic potential the proposed experimental route is very simple and does not require high-energy cleaning of the flake surface. As a model example the fluor-substituted radicals were used, resulting in hydrophobization of MXene flakes surface. The proposed method provides the creation of conductive, superhydrophobic and water-repellent coatings with improved resistance of MXene to oxidation.

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