

## Studying of 2D Titanium Carbide Structure by Raman Spectroscopy after Heat Treatment in Argon and Hydrogen Atmospheres

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### Abstract

Herein we show the effect of heat treatment of two dimensional layered titanium carbide structure ( $Ti_3C_2T_x$ ), so called MXene. As prepared MXene has functional groups -OH, -F, -Cl. In order to remove the functional groups we heat treated the MXene in Ar (with 0.01%  $O_2$ ) and  $H_2$  (with 0.01%  $H_2O$ ) atmospheres. We discovered the significant decrease in the amount of functional groups (-F and -Cl) and increase in the -O content, which refers to the oxidation of the material. Also we determined the optimal regime for Raman spectroscopy in order to avoid any changes in the structure of the material. We revealed that titanium carbide changes its structure at 700 °C and 900 °C into two different titanium dioxide modifications like rutile and anatase in Ar (with 0.01%  $O_2$ ) atmosphere. Also there are small changes occurred in  $Ti_3C_2T_x$  structure and formation of amorphous carbon after 700 °C treatment in  $H_2$  (with 0.01%  $H_2O$ ) atmosphere and formation of  $TiO_2$  (rutile) at 900 °C. Energy-dispersive X-ray spectroscopy (EDX) revealed the reduction of functional groups at 700 °C in both atmospheres and total disappearance of -F and -Cl and increasing the oxygen at 900 °C. The huge increase of oxygen by atomic percent, can be explained by the initial oxygen content in argon and hydrogen gases.

### 1. Introduction

The 2D materials attract a great interest since the discovery of graphene, because of their unique electrical and mechanical properties [1]. Recently, the new class of 2D materials, so called MXene, based on transition metal carbides and nitrides, has also attract the attention of the scientists, in particular due to its high specific surface and attractive physical properties [2]. MXenes are produced by selective etching of “A” element from MAX phase, which has more than 60 members [3]. MXene has a general formula  $M_{n+1}X_nT$ , where “M” stands for early transitional metal, “X” is carbon and/or nitrogen, “T” is a surface termination and  $n = 1, 2$  or 3. MXene has good electrical conductivity and hydrophilic properties [4], which makes it possible to use in energy storage devices [5]. It also has promising performance as an electrode material in electrochemical capacitors [6]. By sonication process it is possible to separate the layered structured

MXene ( $Ti_3C_2$ ) into individual sheets. Freestanding “paper” of  $Ti_3C_2$  has been produced by vacuum filtration and by rolling processes, which can be used as an electrode for supercapacitors and other energy storage devices because it has high volumetric capacitance [7].

After selective etching of “A” element from MAX phase, the material has a surface terminations (typically -O, -OH, -F) as a product from chemical process between the material and etchant [8]. It is been reported by density functional theory (DFT) calculations that pure MXene has higher theoretical capacitance in Li-ion batteries than those which has surface terminations [9–10]. It was shown that heat treatment of MXene can tune the surface termination in this material and can improve the volumetric capacitance [11–12]. The  $TiO_2/C$  composite (the composite based on  $TiO_2$  particles in amorphous carbon matrix) shows a good performance as an electrode material for Li-ion battery anodes. Transmission electron microscopy (TEM)

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shows the formation of  $\text{TiO}_2$  nanocrystals (rutile or anatase) are formed depending on temperature, annealing rate and time [13]. There is also report about hydrothermal treatment of  $\text{Ti}_3\text{C}_2\text{T}_x$  which is resulted in hybrid  $\text{TiO}_2$  and  $\text{Ti}_3\text{C}_2$  structure with good photocatalytic properties. The produced  $\text{TiO}_2$  structure depends on temperature and time of hydrothermal treatment [14].

In this work we showed the effect of heat treatment on  $\text{Ti}_3\text{C}_2\text{T}_x$  in two different types of gasses like argon and hydrogen. It was experimentally determined that at  $700\text{ }^\circ\text{C}$  in argon and hydrogen environments the functional groups of MXene starts to intensively reduce from the structure comparing to  $500\text{ }^\circ\text{C}$ . The samples were treated at  $700\text{ }^\circ\text{C}$  and  $900\text{ }^\circ\text{C}$ . Using Raman spectroscopy we discovered the oxidation process and formation of titanium oxide in the structure of MXene. Also there was a significant reduction of functional groups, which was determined by EDX (Energy-Dispersive X-ray spectroscopy) analysis.

## 2. Experimental

$\text{Ti}_3\text{AlC}_2$  precursor (was synthesized in Drexel University) was characterized by XRD (X-ray Diffraction, Dron-7, Bourestnik) with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15406\text{ nm}$ ). The XRD spectrum is presented in Fig. 1. The  $\text{Ti}_3\text{C}_2\text{T}_x$  was prepared by chemical reaction in  $\text{LiF}:\text{HCl}$  aqueous solution [7, 15].  $\text{HCl}$  was added to distilled water to make 6 M solution (30 ml in total), after that 2 g of  $\text{LiF}$  was added to this solution. The mixture was stirred for several minutes, in order to dissolve the  $\text{LiF}$  in  $\text{HCl}$  solution. Two grams of  $\text{Ti}_3\text{AlC}_2$  was immersed to  $\text{LiF}+\text{HCl}$  solution. The mixture then stirred for 24 h at room temperature to etch the “Al” from

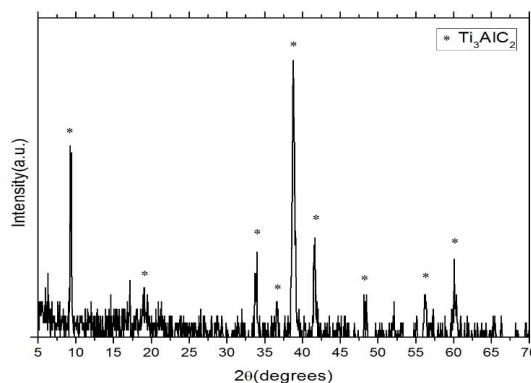


Fig. 1. XRD pattern of  $\text{Ti}_3\text{AlC}_2$  precursor.

$\text{Ti}_3\text{AlC}_2$ . After that the mixture was washed in distilled water using centrifuge (3500 rpm 30 min) several times (6–8) in order to wash out the acid from the mixture, until the pH is 6. The schematic diagram of etching process is represented in Fig. 2. First step is selective removal of “Al” from MAX phase and creation of the layered MXene structure. The second step represents formation of functional groups between MXene layers as a product of etching and washing process.

To prepare the freestanding  $\text{Ti}_3\text{C}_2\text{T}_x$  “paper”, the MXene was dispersed in distilled water (2 g per 500 ml) after that, the solution was passed through the membrane (3501 Coated PP, Celgard, USA) by vacuum filtration method.

As-prepared  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene freestanding “papers” firstly was treated in argon atmosphere in tube furnace at  $700\text{ }^\circ\text{C}$  for one hour and  $900\text{ }^\circ\text{C}$  for one hour, to prevent the oxidation process and to remove the  $-\text{Cl}$  and  $-\text{F}$  functional groups. The heating-cooling step was  $10\text{ }^\circ\text{C}$  per minute. After that, we did the same experiment in hydrogen atmosphere in order to remove oxygen.

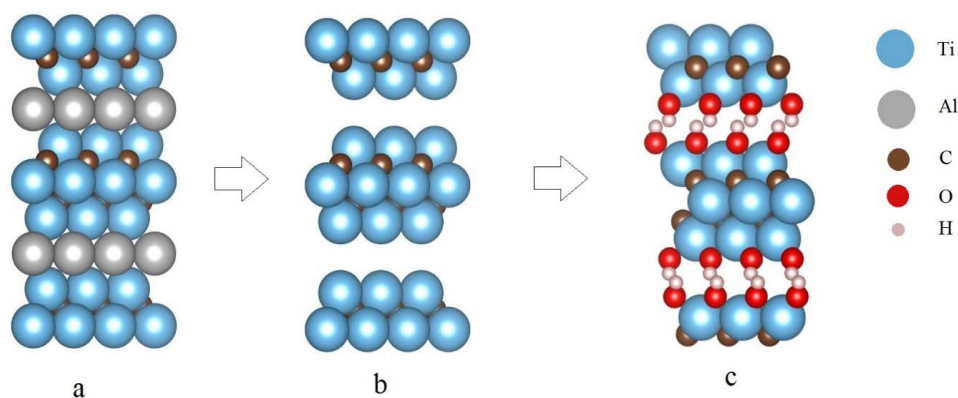


Fig. 2. Schematic illustration of etching process.  $\text{Ti}_3\text{AlC}_2$  precursor (a), selectively removing “Al” (b), and  $\text{Ti}_3\text{C}_2\text{T}_x$  with functional groups as a product of etching and washing process (c).

### 3. Results and Discussion

Pristine MXene was characterized by Raman spectroscopy (AFM-Raman instrument Solver Spectrum, NT-MDT). To take a spectrum we used blue laser with wavelength 473 nm and maximum laser power 35 mW and delaminated freestanding “paper” of  $\text{Ti}_3\text{C}_2\text{T}_x$ . With 2% of laser intensity we observed the spectrum of  $\text{Ti}_3\text{C}_2\text{T}_x$  with characteristic vibrational modes at 202, 380, 582, 624 and  $735\text{ cm}^{-1}$  [16]. The intensity of laser was increased in order to get good noise to peak ratio. With 10% of laser, we can obtain good spectrum of the sample without making any changes on it. Further the Raman spectra of annealed samples were taken using 10% of laser intensity. It was determined that with full power (100%) of laser the samples start to oxidize and changes its structure to anatase with amorphous carbon (Fig. 3). Anatase has characteristic peaks at 144, 197, 399, 519,  $639\text{ cm}^{-1}$  [17]. In our samples, we have peaks at 147, 198, 394, 515 and  $624\text{ cm}^{-1}$ , respectively.

Firstly, we processed the  $\text{Ti}_3\text{C}_2\text{T}_x$  in argon (with 0.01%  $\text{O}_2$ ) atmosphere. At  $700\text{ }^\circ\text{C}$  there is a transformation of  $\text{Ti}_3\text{C}_2\text{T}_x$  structure into  $\text{TiO}_2$  (anatase) with formation of amorphous carbon. At  $900\text{ }^\circ\text{C}$  the anatase transforms to rutile which has Raman bands at 235, 444 and  $607\text{ cm}^{-1}$  (Fig. 4).

Same pristine  $\text{Ti}_3\text{C}_2\text{T}_x$  was annealed under the same conditions in  $\text{H}_2$  (with 0.01%  $\text{H}_2\text{O}$ ) atmosphere. Raman spectrum shows a little change of MXene peaks and formation of amorphous carbon after heat treatment at  $700\text{ }^\circ\text{C}$ . Further heating at  $900\text{ }^\circ\text{C}$  leads to changes in the structure of the material and it transforms into  $\text{TiO}_2$  (rutile) with amor-

phous carbon (Fig. 5). It is evident by intensities of Raman peaks that the amount of oxygen in this structure is less than that at heat treatment in argon atmosphere at the same temperature. EDX analysis (FEI, Quanta 3D 200i) results also show that more carbon and less oxygen by At% occurs when heating at  $900\text{ }^\circ\text{C}$  in hydrogen atmosphere comparing to that after heating in argon atmosphere (Fig. 6). We presume that at  $900\text{ }^\circ\text{C}$  the some oxygen in hydrogen atmosphere make chemical bonding with hydrogen and separates from  $\text{Ti}_3\text{C}_2\text{T}_x$ . Heating at  $700\text{ }^\circ\text{C}$  in hydrogen and argon atmospheres also removes the  $-\text{F}$  and  $-\text{Cl}$  functional groups which are evident by EDX analysis. These functional groups are totally disappeared at  $900\text{ }^\circ\text{C}$  in both atmospheres. The high increase of oxygen by atomic percent, can be explained by the initial oxygen content in argon and hydrogen gases.

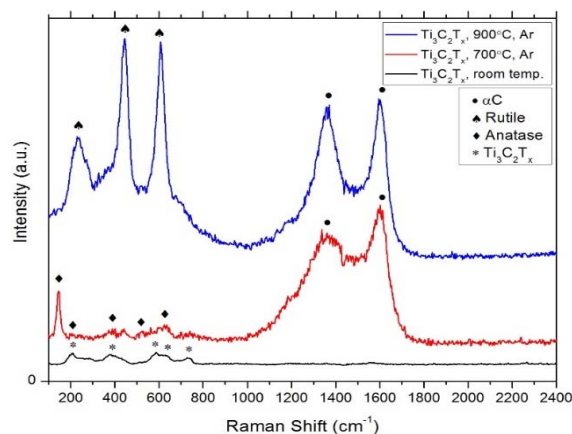


Fig. 4. Raman spectra of  $\text{Ti}_3\text{C}_2\text{T}_x$  after annealing in argon atmosphere.  $\text{Ti}_3\text{C}_2\text{T}_x$  changes its structure to anatase and rutile at  $700\text{ }^\circ\text{C}$  and  $900\text{ }^\circ\text{C}$  respectively.

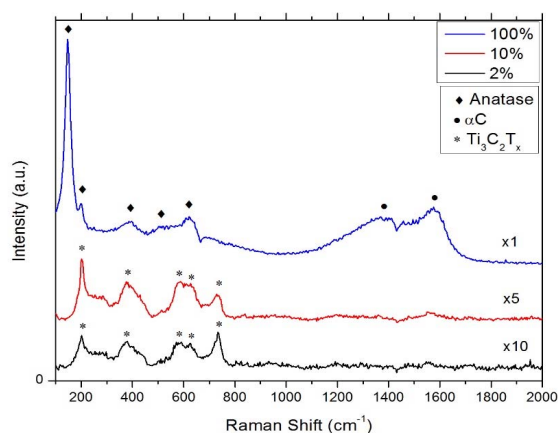


Fig. 3. Raman spectra of  $\text{Ti}_3\text{C}_2\text{T}_x$  with 2, 10 and 100% power of laser, showing the changing the structure to anatase with amorphous carbon when taking the spectra with full power of laser.

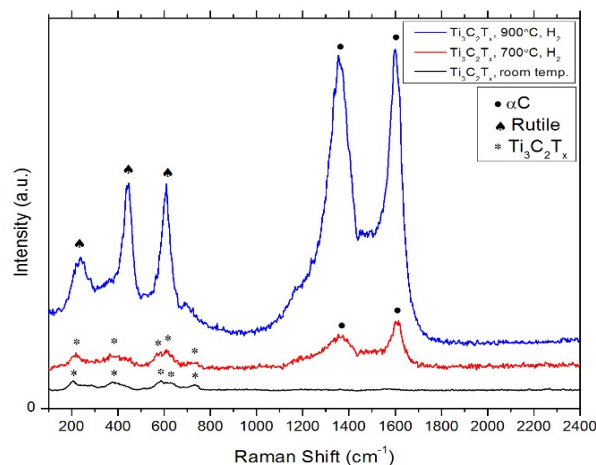


Fig. 5. Raman spectra of  $\text{Ti}_3\text{C}_2\text{T}_x$  after annealing in hydrogen atmosphere. There is a little change in structure of  $\text{Ti}_3\text{C}_2\text{T}_x$  with formation of amorphous carbon at  $700\text{ }^\circ\text{C}$  and formation of  $\text{TiO}_2$  (rutile) at  $900\text{ }^\circ\text{C}$ .

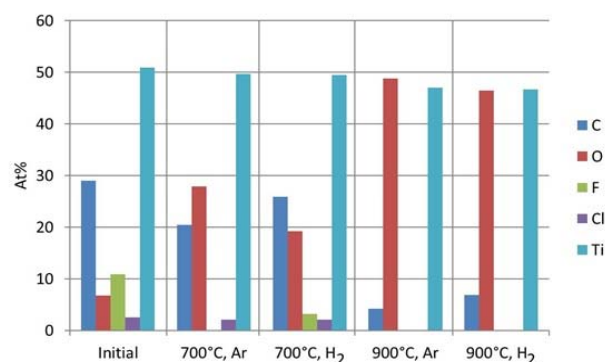


Fig. 6. Histogram shows the reduction of functional groups content in the  $Ti_3C_2T_x$  samples after heating in argon and hydrogen atmosphere.

#### 4. Conclusion

In this work, we demonstrated the oxidation process and removing the functional groups in 2D titanium carbide structure ( $Ti_3C_2T_x$ ). We determined the optimal regime for Raman spectroscopy in order to avoid any changes in the structure of the material. Annealing in argon atmosphere at 700 °C and 900 °C induces changes in structure of the material and it transforms into anatase and rutile, respectively. Annealing under the same conditions in hydrogen atmosphere leads to the reduction of functional groups without making significant changes in the structure of  $Ti_3C_2T_x$  at 700 °C and transformation to rutile at 900 °C.

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