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# Colloidal Properties and Stability of 2D $Ti_3C_2$ and $Ti_2C$ MX enes in Water

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While MXenes have been utilized in many applications, their surface properties in water systems are still unexplored, especially in the aspect of colloidal properties, which highly limits their practical use. In this study, the colloidal properties and stabilities of 2D Ti<sub>3</sub>C<sub>2</sub> and Ti<sub>2</sub>C MXenes were investigated using time-resolved dynamic light scattering and zeta potential over a wide range of waters (deionized water, tap water and physiological NaCl solution of 0.9%) relevant to natural and engineered systems. Our results indicate that pH has a significant influence on  $Ti_3C_2$  and  $Ti_2C$  stabilities from pH 4 to 10. The type of water environment also affects the stability of  $Ti_3C_2$  and  $Ti_2C$  due to electrical double layer compression. The aggregation and stabilities of  $Ti_3C_2$  and  $Ti_2C$  in the aquatic systems followed colloidal theories, even though Ti<sub>3</sub>C<sub>2</sub> and Ti<sub>2</sub>C flakes shape is not spherical. The presence of NaCl stabilized more the 2D Ti<sub>3</sub>C<sub>2</sub> than the 2D Ti<sub>2</sub>C. Dispersions prepared when using tap water were more stable in the case of  $Ti_2C$  compared to the NaCl solution. The opposite effect was found for  $Ti_3C_2$ . This may be due to the binding capacity of  $Ca^{2+}$  ions with hydroxyl and carbonyl functional groups whose amounts vary on the surface of Ti<sub>3</sub>C<sub>2</sub> and Ti<sub>2</sub>C. In general, our study demonstrates that the 2D flakes of Ti<sub>3</sub>C<sub>2</sub> MXenes are highly stable in NaCl, although they settle more quickly in tap water. The 2D flakes of Ti<sub>2</sub>C MXenes are more stable in distilled water and less stable in the physiological NaCl solution.

Keywords: 2D Ti<sub>3</sub>C<sub>2</sub>, 2D Ti<sub>2</sub>C, MXenes, dynamic light scattering, zeta potential, stability, safety

#### **1. INTRODUCTION**

Advances in nanomaterial technologies, nowadays, provide many opportunities for the development of new types of biomaterials, innovative treatments in the area of nanomedicine [1,2] as

well as water treatment [3]. As a result, the development of new two-dimensional (2D) materials with unique bioactivity is now one of the fastest growing fields of nanoscience [4].

Recently, a new class of 2D nanomaterials has been introduced; MXenes. They are of the formula  $M_{n+1}X_n$ , where M denotes a transition metal and X stands for C and/or N. They are obtained by the selective etching of the A atom from the ceramic MAX phases which results in MXene, also called layered early-transition-metal carbides and nitrides [4-7].

MXenes have been utilized in many applications that require the use of an aqueous environment. Furthermore, studies on the biological properties of MXenes materials were published. They describe the possibility of  $Ti_3C_2$  phase application in water treatment [8-10], surface modification with enzymes [11,12], as well as the toxicity of  $Ti_3C_2$  MXene against bacteria cells [13,14] and the lack of toxicity of  $Ti_2C$  MXene [15]. There are also several reports on the potential biomedical applications of this material [16], also in the area of photothermal therapy [17-19]. A potential usage of MXenes for the combined photothermal and photoacoustic imaging of cancer cells was also reported [20].

An interesting problem, although not yet fully covered in the literature, is the influence of a water environment resulting in a specific zeta potential on MXenes stability, which is equally important for their potential use in both water treatment and nanomedicine. In case of MXenes, our research group was the first to carry out adsorption studies of bacteria cells on the surface of the expanded Ti<sub>2</sub>C structure, using zeta potential [15]. We have shown that the role of pH and the influence of electrostatic interactions are important in such studies. Literature data also indicates that the zeta potential and dynamic light scattering (DLS) methods are effective analytical tools to study the colloidal properties of 2D materials and the influence of surface-oxidation layer on stability in water [21-28].

It is clear that MXenes have found their place in many applications. However, their surface properties in water systems are still unexplored, especially in the aspect of colloidal properties, which highly limits their applications in practical use.

In this work, for the first time, we present a systematic, comparative, in-depth study on the colloidal properties and stabilities of 2D flakes of MXenes from the Ti-C system, using time-resolved dynamic light scattering and zeta potential over a wide range of waters (deionized water, tap water and physiological NaCl solution of 0.9%), relevant to natural and engineered systems. 2D Flakes of  $Ti_3C_2$  and  $Ti_2C$  were selected for this study from a large group of MXene phases as promising in the context of potential applications.

#### 2. EXPERIMENTS

#### 2.1. Synthesis procedure of delaminated 2D sheets of $Ti_2C$ and $Ti_3C_2$ MXenes

 $Ti_3C_2$  and  $Ti_2C$  were synthesized using the  $Ti_3AlC_2$  and  $Ti_2AlC$  MAX phase. The selfpropagating high-temperature synthesis (SHS) with a local ignition system was used for manufacturing the MAX phase material. The black powders of MAX phases were immersed in a 48% solution of hydrofluoric acid (HF, Sigma-Aldrich) for 24 h at room temperature. The resulting suspensions were allowed to sediment and after discarding the supernatant, were washed with deionized water and technical grade ethanol (four times each). The solid products of expanded  $Ti_3C_2$  and  $Ti_2C$  were dried overnight at room temperature.

In our studies a modified delamination process was carried out in comparison with other studies [29]. In the first step the sample was subjected to ultrasound under inert gas (argon) flow using high – energy probe sonication Vibra Cell VCX750, 20 kHz, Sonics & Materials Inc. The dispersing medium was hexane with a ratio of 50 cm<sup>3</sup>/1 g. The process was carried out for 3 h in an ice bath with the periodical mode of sonication (1 s/1 s) and together with 520 Watt power. In the next step the powder was sedimented and hexane was removed as the supernatant, the powder was then dried at room temperature. In the next step of the process, dry isopropanol was used as a dispersant together in the same ratio of 50 cm<sup>3</sup>/1 g dispersion. The sonication process was repeated as previously, except the process was conducted for 2 h. The obtained mixture was centrifuged at 2500 rpm for 2 min. The supernatant was then collected and centrifuged at 4500 rpm for 10 min. The sediment of 2D MXene sheets was collected after discarding the supernatant and dried for 6 h at room temperature.

#### 2.2. Characterization of materials

The morphologies of the expanded and delaminated  $Ti_3C_2$  and  $Ti_2C$  MXene were examined using scanning electron microscope (SEM-LEO 1530, Zeiss, USA). The powder samples were directly deposited on the surface of a conductive carbon tape. Next, samples were coated with a thin carbon layer. The morphology of each sample was investigated at an accelerating voltage of 2.0 kV.

The quantitative analysis was made on the basis of SEM photos in the NIS Elements BR 3.2 program by NIKON. The grain boundaries were manually corrected to create binary images that could be used for further analysis, i.e. the automatic determination of the quantitative values sought for the morphology characterization of the MXene flakes.

The specific surface area of the expanded  $Ti_2C$  and  $Ti_3C_2 2D$  sheets was examined based on the isotherms of the physical nitrogen sorption (V=f(p/p<sup>0</sup>) i.e. the relative volume of the adsorbed nitrogen as a function of nitrogen relative pressure). The measurements were carried out using Quadrasorb-SI equipment (Quantachrome Instruments, USA) in a liquid nitrogen bath (-195.8 °C). Before the measurements the expanded 2D sheets of  $Ti_3C_2$  and  $Ti_2C$  MXenes were degassed under vacuum at 300 °C for 24 h. The adsorption–desorption isotherms were recorded in whole range of relative pressure p/p°. The specific surface area  $S_{BET}$  was determined using the Brunauer, Emmett, Teller method, and the total volume of the pores  $V_{BJH}$  was calculated using Barret, Joyner, Halenda method.

The size distributions of the expanded 2D sheets of  $Ti_2C$  and  $Ti_3C_2$  were obtained using Dynamic Light Scattering (DLS) method. The measurement were investigated using the NANO ZS ZEN3500 analyzer equipped with a back-scattered light detector operating at a 173° angle. The Zetasizer Nano ZS apparatus was also used for analyzing the stability of the MXene suspensions in different media. The environments in which the measurements were carried out were distilled water, tap water and physiological NaCl solution of 0.9%. The concentration of the tested samples was  $5 \cdot 10^{-4}$   $g/cm^3$ . The studies were carried out at 25 °C and were repeated 3 times. Before the measurements, each sample was homogenized for 30 sec using mild sonication.

The Zetasizer Nano ZS apparatus was also used for analyzing the stability of the MXene suspensions in different media. The zeta potential was investigated using Smoluchowski's formula. The concentrations of the analyzed suspensions were the same as in the initial DLS studies. The zeta potential studies were carried out at 25 °C, and were repeated 10 times. The results were expressed as the mean value of zeta potential  $\pm$  SD.

The zeta potential as a function of pH was also investigated. For this purpose 1 mL of solution containing  $5 \cdot 10^{-4}$  g/cm<sup>3</sup> MXene in different media (deionized water, tap water and physiological NaCl solution of 0.9%) was prepared. During the measurement the pH value was changed from 4 to 10 with step of 0.5 and tolerance 0.2. The titrants were 0.1M HCl and 0.1M NaOH.

The size distributions as a function of pH were also analyzed. The parameters were the same as in zeta potential measurements. The studies were carried out at 25 °C and repeated 3 times. The results were presented as the mean value of sheet diameter.

#### **3. RESULTS AND DISCUSSION**

3.1. Results of characterization



**Figure 1.** SEM images obtained for the expanded Ti<sub>3</sub>C<sub>2</sub> MXene a), delaminated 2D sheets of Ti<sub>3</sub>C<sub>2</sub> MXene b), expanded Ti<sub>2</sub>C MXene c), and delaminated 2D sheets of Ti<sub>2</sub>C MXene d).

Analysis of the morphology of the expanded and delaminated 2D sheets of  $Ti_3C_2$  and  $Ti_2C$  MXene were examined using scanning electron microscope (SEM). The SEM images of MXenes after

etching with concentrated hydrofluoric acid, but before receiving 2D flakes using sonication, are presented in Fig. 1a and 1c. The characteristic layered structure of MXenes is clearly visible. The structure resembles an open book and is caused by etching with concentrated HF acid to remove A compound from the structure of the MAX phase. The image shows each layer bearing sharp edges and connected to each other forming a compact structure of multi-layer MXenes with large narrow pores. In Fig. 1b and 1d MXenes after the delamination process are presented. These are 2D flakes that have an irregular shape and are presented in aggregates – agglomerates.

We also performed quantitative analysis of the expanded 2D sheets of  $Ti_3C_2$  and  $Ti_2C$ . The results are presented in Fig. 2.



**Figure 2.** The distributions of the average thickness of the expanded 2D sheets of Ti<sub>3</sub>C<sub>2</sub> a) and Ti<sub>2</sub>C b), determined on basis of SEM micrograph.



Figure 3. Isotherms of physical sorption of nitrogen on the surface of the 2D flakes of  $Ti_3C_2$  a) and  $Ti_2C$  b) MXenes phases.

Quantitative analysis showed that ca. 40% of the expanded MXene sheets had an average thickness of 50 nm for  $Ti_3C_2$  and 80 nm for  $Ti_2C$ . These studies confirmed that the analyzed MXenes are indeed two-dimensional materials, which complies with the literature data [30,31].

Analysis of the specific surface area and porosity of the delaminated 2D flakes of MXene was carried out using isotherms of the physical nitrogen sorption. The obtained isotherms are shown in Fig. 3. In both samples a hysteresis loop was observed, which indicates the occurrence of capillary condensation in the pores. The shape of these isotherms represents the presence of mainly slit pores in the tested materials. These kind of pores were also detected by other groups [32].

The pore size distributions for the delaminated 2D sheets of  $Ti_3C_2$  and  $Ti_2C$  are presented in Fig 4. The analyzed materials were characterized by the presence of mainly nanometric pores. In  $Ti_2C$ , pores were present primarily in two size ranges i.e.: 3-3.5 nm and 4.5-5 nm, whereas in the case of  $Ti_3C_2$  the average pore size was ca. 4 nm. The tested materials also contained larger pores. Their presence resulted from the natural tendency of MXenes to agglomerate.



Figure 4. Distributions of the pore diameters obtained using the BJH method for the 2D flakes of  $Ti_3C_2 a$ ) and  $Ti_2C b$ ).

Table 1 presents the results of the specific surface area analysis using BET method and the total volume of pores calculated using BJH method of delaminated 2D  $Ti_3C_2$  and  $Ti_2C$  flakes. We found that the specific surface area was only slightly higher for  $Ti_2C$  compared to  $Ti_3C_2$  i.e. 4%. The total volume of pores was higher for  $Ti_2C$ , differing by 50%. The average pore diameter for the delaminated  $Ti_3C_2$  was 4 nm, 0.88 nm higher than  $Ti_2C$ . The physical properties of the obtained 2D sheets of MXenes were also confirmed by other groups [33].

**Table 1.** Results of surface area analysis and porosity of 2D flakes of Ti<sub>3</sub>C<sub>2</sub> and Ti<sub>2</sub>C MXenes.

	$S_{BET} [m^2/g]$	V <sub>pores</sub> [cm <sup>3</sup> /g]	D <sub>pores</sub> [nm]
Ti <sub>2</sub> C	69,11	0,094	3,12
Ti <sub>3</sub> C <sub>2</sub>	66,34	0,063	4,00

In this work DLS studies of the expanded 2D sheets of  $Ti_3C_2$  and  $Ti_2C$  in various water environments (in distilled water, tap water and physiological NaCl solution of 0.9%) were also investigated. The colloid prepared for analysis had a concentration of  $5 \cdot 10^{-4}$  g/cm<sup>3</sup>. The results are presented in Fig. 5. The measurements show that the colloidal solutions of the 2D flakes of the  $Ti_2C$ MXene phase were composed of dispersed small flakes (ca. 300 nm) in the NaCl solution, while the largest (ca. 600 nm) were present in tap water. In the case of the colloidal solution of 2D flakes of  $Ti_3C_2$  MXene phase the smallest flakes (ca. 700 nm) were observed in the physiological NaCl solution, while the largest ones were present in distilled water (ca. 1500nm). In this medium a smaller peak was observed, which maximum was reached at a particle size of 5000 nm, indicating that the  $Ti_3C_2$  2D flakes in this solution are agglomerated.



Figure 5. DLS analysis of dispersions of 2D sheets of  $Ti_3C_2$  a) and  $Ti_2C$  b) MXene in a water solution (distilled water, tap water and physiological NaCl solution of 0.9%).

In parallel with the DLS particle size distribution study, zeta potential measurements were also performed for the delaminated 2D  $Ti_3C_2$  and  $Ti_2C$  flakes in various aqueous environments (in distilled water, in tap water and physiological NaCl solution of 0.9%). The test results are presented in Table 2.

**Table 2.** Results of zeta potential measurements particle size measurements for 2D flakes of  $Ti_3C_2$  and $Ti_2C$  MXene flakes in three different media.

Sample	Medium		
	Distilled water	Tap water	Physiological solution
Ti <sub>2</sub> C	-4.43 mV	-13.96 mV	-8.12 mV
Ti <sub>3</sub> C <sub>2</sub>	-10.40 mV	-14.19 mV	-17.72 mV

It can be concluded, from Table 2, that the  $Ti_2C$  colloid solution exhibited the highest stability in tap water, zeta potential -13.96 mV, and the lowest in distilled water. In the case of  $Ti_3C_2$  the highest stability was achieved in physiological NaCl solution of 0.9%, and the lowest in tap water. Our investigations show that the tested colloids tend to sediment and coagulate, which may cause difficulties from the point of view of further applications. A very important factor affecting the stability of particles in colloidal systems is the pH of the environment, therefore, we measured the particle size distribution and zeta potential as a function of pH in different water environments (in distilled water, tap water and physiological NaCl solution of 0.9%). The studies used the colloids of delaminated 2D sheets of  $Ti_3C_2$  and  $Ti_2C$  MXene with a concentration of  $5 \cdot 10^{-4}$  g/cm<sup>3</sup>. The measurements for the particle size distribution as a function of pH is presented in Fig. 6.



**Figure 6.** The results of DLS analysis of dispersions of 2D sheets of Ti<sub>3</sub>C<sub>2</sub> and Ti<sub>2</sub>C MXene in distilled water a), physiological NaCl solution of 0.9% b), and tap water c), with different pH.

Fig. 6 shows that the particle size distribution depends on the pH and type of the environment. In the case of colloids in distilled water particles, which are larger in diameter could be observed for  $Ti_3C_2$ . The particle size distribution for this compounds decreased linearly with the increasing pH of the environment. In the case of  $Ti_2C$  from pH 4 to 6.5 instability of the diameter of the particles can be observed, however after exceeding pH 6.5 the size was constant and stabilized at ca. 100 nm. In the case of tap water the environment instability of the particle size distribution was observed for the entire range of tested pH for both materials. This instability can be caused by the presence of various ions such as:  $CI^-$ ,  $F^-$ ,  $Mn^{2+}$  [34], which can adsorb on the MXenes surface. In the case of colloids in physiological NaCl solution of 0.9% for  $Ti_3C_2$  particle size distribution increased linearly with increasing pH and was ca. 1000-1400 nm. For  $Ti_2C$  at pH ca. 5.5 a clear peak is visible, which indicates the agglomeration of the molecules. After exceeding pH 6 the signals disappear due to sedimentation of the aggregated 2D flakes.

It should be additionally mentioned, that before our research there were a few reports on the zeta potential of not modified expanded  $Ti_3C_2$  in distilled water environment. Ren *et al.* [35] reported that the zeta potential of  $Ti_3C_2$  MXene was highly negative in high pH and reached even -39.5 mV. Ying *et al.* [http://sci-hub.tw/10.1021/am5074722] found that the zeta potential for  $Ti_3C_2$  at pH 7 was - 29 mV. Alhabeb *et al.* [36] contrary to our studies obtained  $Ti_3C_2$  from  $Ti_3AlC_2$  MXene. Zeta potential for this material reached ca. -50mV at pH 7. Research of Naguib *et al.* [37] show that MXenes of different structure are negatively charged in neutral environment. For  $Ti_3CN$  it was about -70 mV and for  $V_2C$  - about -50 mV. As can be seen, all these materials show stability in colloidal solutions. Lower stability was exhibited by the  $Ti_2C$  which zeta potential reached c.a. -15 mV [15].

It should be noted that all these measurements were made only in a distilled water environment. The only exception was tap water environment which was considered in work of Jastrzębska et al. [15]. However, there is no data on the behavior of MXenes in other water environments relevant to natural and engineered systems (i.e. physiological NaCl solution or tap water) in a function of pH. This is promising in the context of potential applications. The zeta potential measurements as a function of pH are presented in Fig. 7. We can deduce from Fig. 7 that the stability of the 2D sheets of  $Ti_3C_2$  and  $Ti_2C$  MXenes in distilled water increased linearly with increasing pH. The zeta potential changed for  $Ti_3C_2$  from ca. -15 mV, for pH 4, to -25 mV, for pH 10. In the case of  $Ti_2C$ , these values were ca. -15 mV, for pH 4, and -35 mV, for pH 10. As in the case of distilled water, the colloid with  $Ti_2C$  was more stable, but only after exceeding pH 5. The zeta potential value for  $Ti_3C_2$  zeta potential the whole range of measured pH was stable at ca. -20 mV.



**Figure 7.** The results of zeta potential analysis of dispersions of 2D sheets of Ti<sub>3</sub>C<sub>2</sub> and Ti<sub>2</sub>C MXene in distilled water a), physiological solution b) and tap water c) in a function of pH.

10846

# 4. SUMMARY

Our results indicate that pH has a significant influence on the stability of  $Ti_3C_2$  and  $Ti_2C$  from pH 4 to 10. However, the type of water environment had also a significant effect on  $Ti_3C_2$  and  $Ti_2C$  stabilities due to electrical double layer compression. The aggregation and stabilities of  $Ti_3C_2$  and  $Ti_2C$  in the aquatic systems followed colloidal theories, even though  $Ti_3C_2$  and  $Ti_2C$  flakes shape are not spherical. The presence of NaCl stabilized  $Ti_3C_2$  more significantly than  $Ti_2C$ . Dispersions in tap water were more stabilized in  $Ti_2C$  compared to the NaCl solution. The opposite effect was seen for  $Ti_3C_2$ . This may be due to the binding capacity of  $Ca^{2+}$  ions with hydroxyl and carbonyl functional groups whose percentage differs in  $Ti_3C_2$  and  $Ti_2C$ .

In general, our study demonstrates that the 2D flakes of MXenes from the Ti-C system are highly stable in distilled water. In physiological NaCl solution  $Ti_2C$  2D flakes of MXenes settled more quickly.

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## DECLARATION OF ABSENCE OF CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding publication of this manuscript.

# AUTHORS' CONTRIBUTIONS

A. Rozmysłowska collected the obtained results, prepared figures, tables and prepared the manuscript; carried out the analysis of the delamination process, analyzed morphology, physical properties and porous structure of the obtained materials as well as performed DLS and zeta potential analyses; T. Wojciechowski synthesized the expanded MXenes; W. Ziemkowska supervised MXenes preparation; L. Chlubny synthesized the MAX phase using SHS method; A. Olszyna revised the manuscript; S. Poźniak prepared the 2D  $Ti_3C_2$  samples; K. Tomkiewicz prepared the 2D  $Ti_2C$  samples; A.M. Jastrzębska supervised and coordinated the experiment. All the authors read and approved the manuscript.

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