

Colloidal Properties and Stability of 2D Ti₃C₂ and Ti₂C MXenes in Water

A. Rozmysłowska^{1,*}, T. Wojciechowski¹, W. Ziemkowska¹, L. Chlubny², A. Olszyna¹, S. Poźniak¹, K. Tomkiewicz¹, A. M. Jastrzębska¹

¹ Warsaw University of Technology, Faculty of Materials Science and Engineering, 02-507 Warsaw, Woloska 141, Poland

² AGH University of Science and Technology, Faculty of Materials Science and Ceramics, 30-059 Krakow, Mickiewicza 30, Poland

*E-mail: anita.rozmyslowska@gmail.com

Received: 29 May 2018 / Accepted: 27 July 2018 / Published: 1 October 2018

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 Ti₃C₂ and Ti₂C 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 Ti₃C₂ and Ti₂C stabilities from pH 4 to 10. The type of water environment also affects the stability of Ti₃C₂ and Ti₂C due to electrical double layer compression. The aggregation and stabilities of Ti₃C₂ and Ti₂C in the aquatic systems followed colloidal theories, even though Ti₃C₂ and Ti₂C flakes shape is not spherical. The presence of NaCl stabilized more the 2D Ti₃C₂ than the 2D Ti₂C. Dispersions prepared when using tap water were more stable in the case of Ti₂C compared to the NaCl solution. The opposite effect was found for Ti₃C₂. This may be due to the binding capacity of Ca²⁺ ions with hydroxyl and carbonyl functional groups whose amounts vary on the surface of Ti₃C₂ and Ti₂C. In general, our study demonstrates that the 2D flakes of Ti₃C₂ MXenes are highly stable in NaCl, although they settle more quickly in tap water. The 2D flakes of Ti₂C MXenes are more stable in distilled water and less stable in the physiological NaCl solution.

Keywords: 2D Ti₃C₂, 2D Ti₂C, 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_2C 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 self-propagating 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 $50\text{ cm}^3/1\text{ g}$. 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 $50\text{ cm}^3/1\text{ g}$ 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 ($V=f(p/p^0)$ 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 ($-195.8\text{ }^\circ\text{C}$). Before the measurements the expanded 2D sheets of Ti_3C_2 and Ti_2C MXenes were degassed under vacuum at $300\text{ }^\circ\text{C}$ for 24 h. The adsorption–desorption isotherms were recorded in whole range of relative pressure p/p^0 . 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 $5 \cdot 10^{-4} \text{ g/cm}^3$ 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

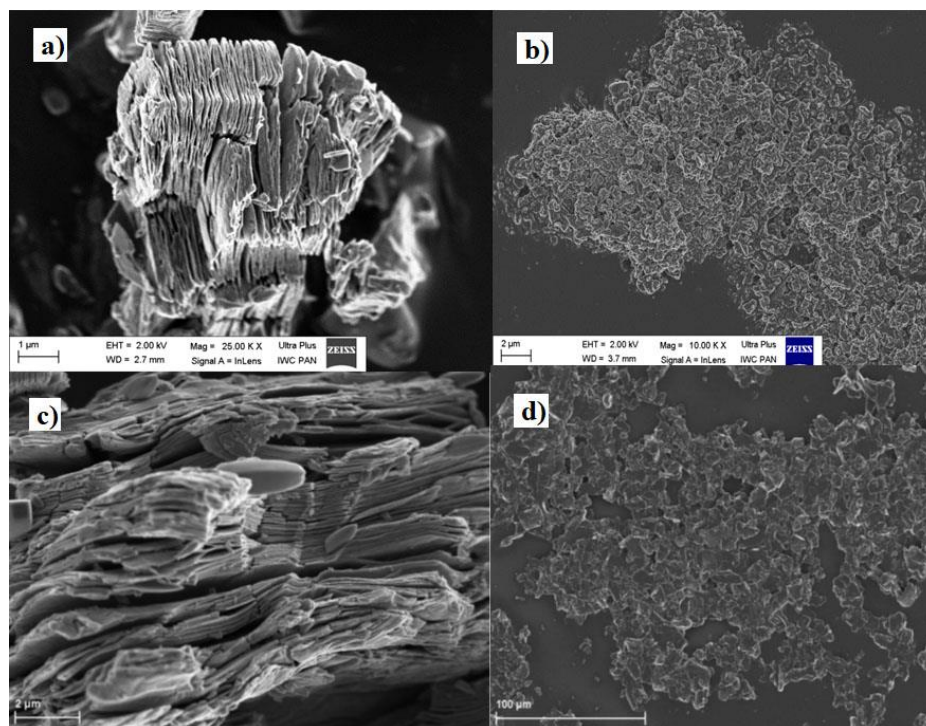


Figure 1. SEM images obtained for the expanded Ti_3C_2 MXene a), delaminated 2D sheets of Ti_3C_2 MXene b), expanded Ti_2C MXene c), and delaminated 2D sheets of Ti_2C MXene d).

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.

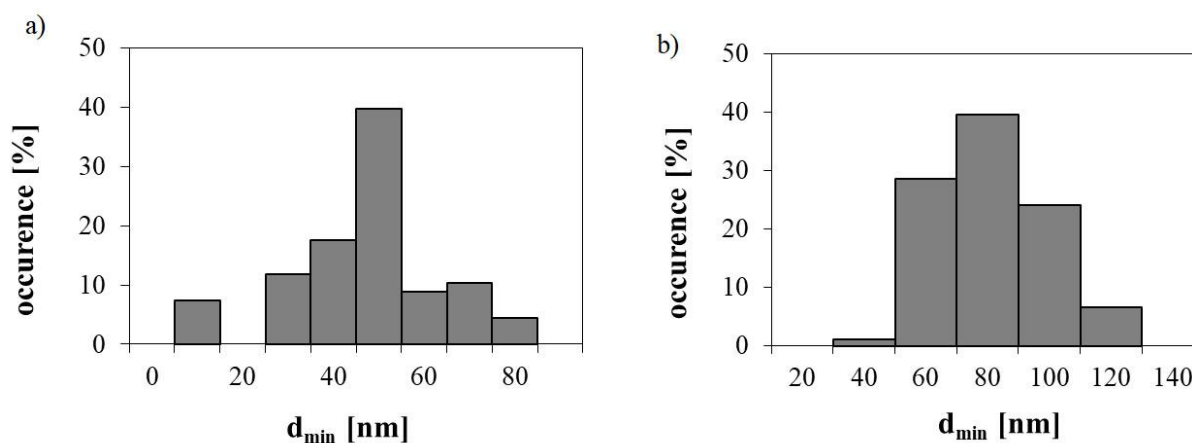


Figure 2. The distributions of the average thickness of the expanded 2D sheets of Ti_3C_2 a) and Ti_2C b), determined on basis of SEM micrograph.

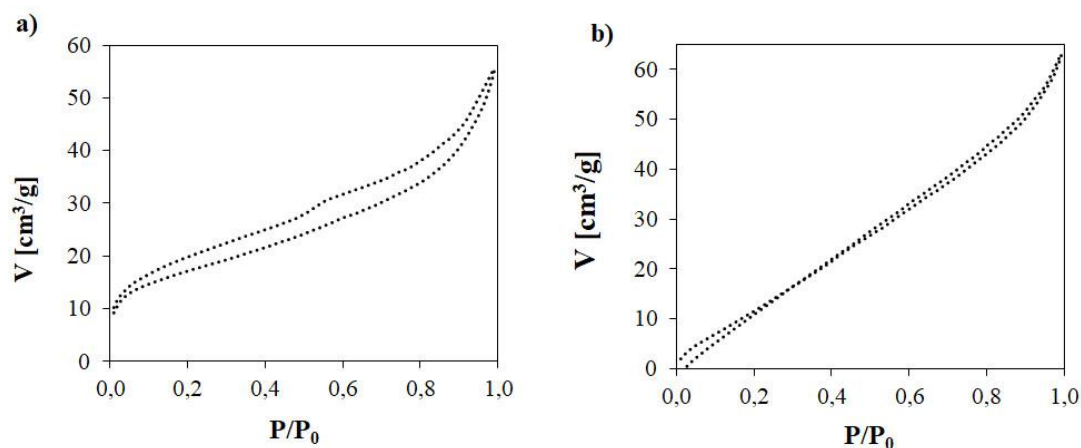


Figure 3. Isotherms of physical sorption of nitrogen on the surface of the 2D flakes of Ti_3C_2 a) and Ti_2C b) MXenes phases.

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.

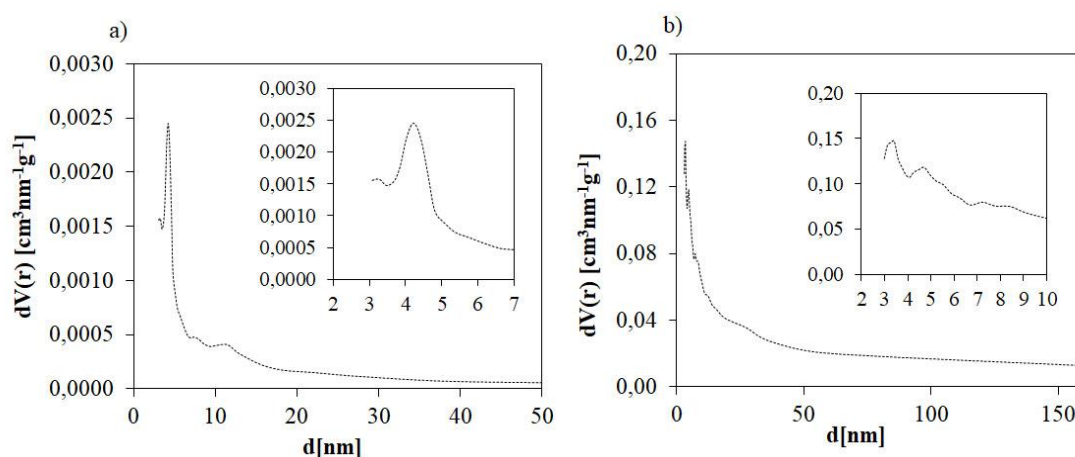


Figure 4. Distributions of the pore diameters obtained using the BJH method for the 2D flakes of Ti_3C_2 a) and Ti_2C b).

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_3C_2 and Ti_2C MXenes.

	S_{BET} [m^2/g]	V_{pores} [cm^3/g]	D_{pores} [nm]
Ti_2C	69,11	0,094	3,12
Ti_3C_2	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 $5 \cdot 10^{-4} \text{ g/cm}^3$. 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.

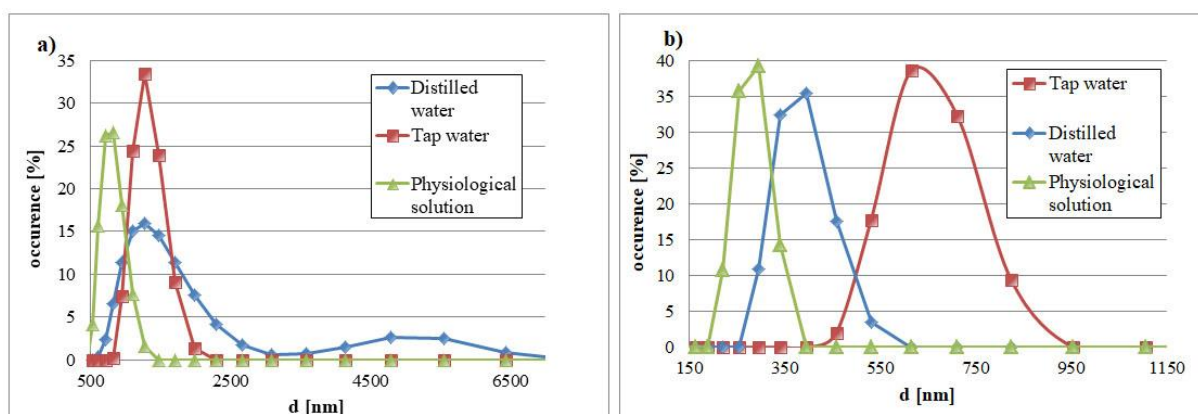


Figure 5. DLS analysis of dispersions of 2D sheets of Ti_3C_2 a) and Ti_2C b) MXene in a water solution (distilled water, tap water and physiological NaCl solution of 0.9%).

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_2C	-4.43 mV	-13.96 mV	-8.12 mV
Ti_3C_2	-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 $5 \cdot 10^{-4} \text{ g/cm}^3$. The measurements for the particle size distribution as a function of pH is presented in Fig. 6.

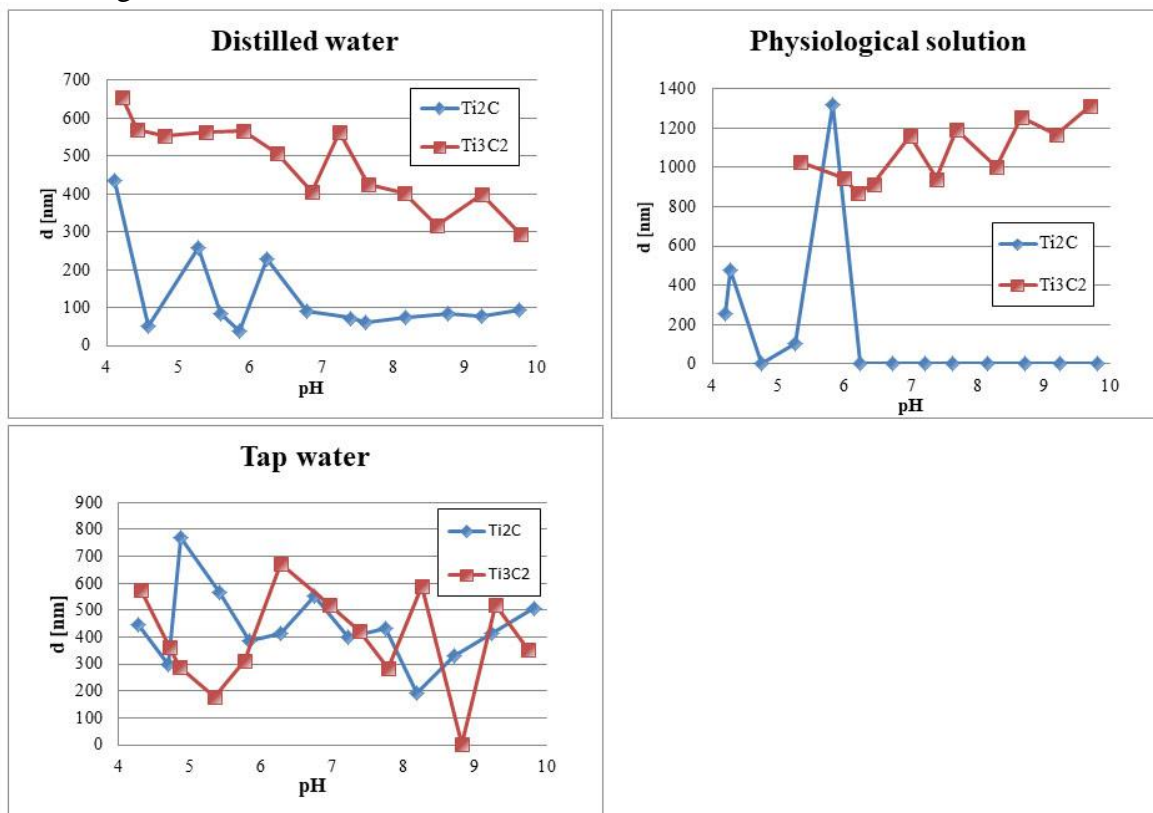


Figure 6. The results of DLS analysis of dispersions of 2D sheets of Ti_3C_2 and Ti_2C MXene in distilled water a), physiological NaCl solution of 0.9% b), and tap water c), with different pH.

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: Cl^- , 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. Alhabeab *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 varied within -13 mV, and for Ti_2C -17 mV. The Ti_2C colloid in the physiological solution was unstable at pH 4-8.5, but after exceeding pH 8.5 dropped rapidly to value -25 mV. In the case of Ti_3C_2 zeta potential the whole range of measured pH was stable at ca. -20 mV.

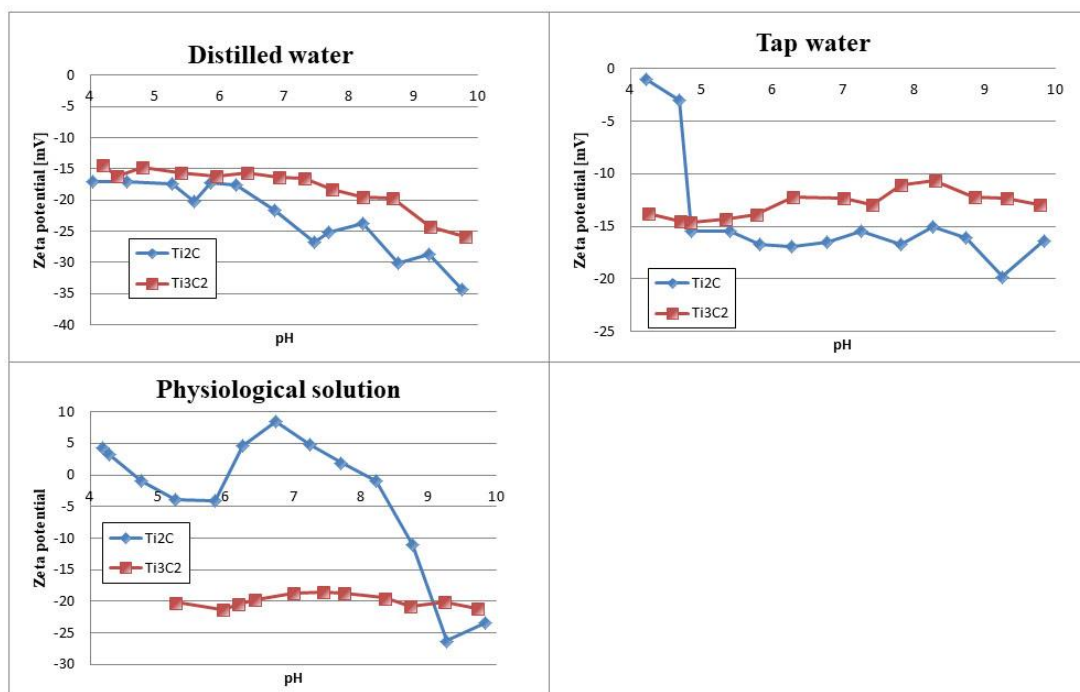


Figure 7. The results of zeta potential analysis of dispersions of 2D sheets of Ti_3C_2 and Ti_2C MXene in distilled water a), physiological solution b) and tap water c) in a function of pH.

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.

ACKNOWLEDGEMENTS

The study was accomplished thanks to the funds allotted by the National Science Centre on basis of decision no. DEC-2017/26/E/ST8/01073, within the framework of the research project 'SONATA BIS 7' no. UMO-2017/26/E/ST8/01073.

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.

References

1. S. Vinogradov, S. Wei, *Nanomed.*, 7 (2012) 597.
2. V. C. Sanchez, A. Jachak, R. H. Hurt, A. B. Kane, *Chem. Res. Toxicol.*, 25 (2012) 15.
3. D. K. Tiwari, J. Behari, P. Sen, *World Appl. Sci. J.*, 3 (2008) 417.
4. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Sci.* 306 (2004) 666.
5. M. Naguib, O. Mashtalir, J. Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi, M. W. Barsoum, *ACS Nano*, 6 (2012) 1322.
6. M. Ghidui, M. R. Lukatskaya, M. Q. Zhao, Y. Gogotsi, M. W. Barsoum, *Nature*, 519 (2016) 78.
7. M. Naguib, V. N. Mochalin, M. W. Barsoum, Y. Gogotsi, *Adv. Mater.*, 26 (2014) 992.
8. G. R. Berdiyrov, M. E. Madjet, K. A. Mahmoud, *Appl. Phys. Lett.*, 108 (2016) 113110.
9. C. E. Ren, K. B. Hatzell, M. Alhabeab, Z. Ling, K.A. Mahmoud, Y. Gogotsi, *J. Phys. Chem. Lett.*, 6 (2015) 4026.

10. M. Ghidui, J. Halim, S. Kota, D. Bish, Y. Gogotsi, M. W. Barsoum, *Chem. Mater.*, 28 (2016) 3507.
11. F. Wang, C. H. Yang, C. Y. Duan, D. Xiao, Y. Tang, J. F. Zhua, *J. Electrochem. Soc.*, 162 (2015) B16.
12. R. B. Rakhi, P. Nayuk, C. Xia, H. N. Alshareef, *Sci. Rep.*, 6 (2016) 36422.
13. K. Rasool, M. Helal, A. Ali, C. E. Ren, Y. Gogotsi, K. A. Mahmoud, *ACS Nano*, 10 (2016) 3674.
14. K. Rasool, K. A. Mahmoud, D. J. Johnson, M. Helal, G. R. Berdiyrov, Y. Gogotsi, *Sci. Rep.*, 7 (2017) 1598.
15. A. Jastrzębska, E. Karwowska, D. Basiak, A. Zawada, W. Ziemkowska, T. Wojciechowski, D. Jakubowska, A. Olszyna, *Int. J. Electrochem. Sci.*, 12 (2017) 2159.
16. A.M. Jastrzębska, A. Szuplewska, T. Wojciechowski, M. Chudy, W. Ziemkowska, L. Chlubny, A. Rozmysłowska, A. Olszyna, *J. Hazard. Mater.*, 339 (2017) 1.
17. H. Lin, X. Wang, L. Yu, Y. Chen, J. Shi, *Nano Lett.*, 17 (2017), 384.
18. C. Dai, H. Lin, G. Xu, Z. Liu, R. Wu, Y. Chen, *Chem. Mater.*, 29 (2017) 8637.
19. G. Liu, J. Zou, Q. Tang, X. Yang, Y. Zhang, Q. Zhang, W. Huang, P. Chen, J. Shao, X. Dong, *ACS Appl. Mater. Interfaces*, 9 (2017) 40077.
20. H. Lin, S. Gao, C. Dai, Y. Chen, J. Sh, *J. Am. Chem. Soc.*, 139 (2017) 16235.
21. A. M. Jastrzębska, J. Karcz, R. Letmanowski, D. Zabost, E. Ciecierska, E. Karwowska, M. Siekierski, A. Olszyna, *J. Alloy. Compd.*, 679 (2016) 470.
22. A. M. Jastrzębska, J. Karcz, E. Karwowska, A. Fiedorczuk, A. Olszyna, *J. Alloy. Compd.*, 724 (2017) 869.
23. A. M. Jastrzębska, J. Karcz, E. Karwowska, A. Fiedorczuk, A. Olszyna, *J. Nano Res.*, 47 (2017) 33.
24. A. M. Jastrzębska, A. Derecka, E. Karwowska, A. Płasek, T. Wojciechowski, W. Ziemkowska, A. Olszyna, *J. Nano Res.*, 47 (2017) 89.
25. A. M. Jastrzębska, J. Jureczko, J. Karcz, A. Kunicki, W. Ziemkowska, A. Olszyna, *Chem. Pap.*, 71 (2017) 579.
26. A. M. Jastrzębska, J. Karcz, E. Karwowska, A. Fiedorczuk, A. Olszyna, *Int. J. Appl. Ceram. Technol.*, 13 (2016) 856.
27. A. M. Jastrzębska, J. Karcz, R. Letmanowski, D. Zabost, E. Ciecierska, J. Zdunek, E. Karwowska, M. Siekierski, A. Olszyna, A. Kunicki, *Appl. Surf. Sci.*, 362 (2016) 577.
28. A. M. Jastrzębska, A. R. Olszyna, J. Jureczko, A. R. Kunicki, *Int. J. Appl. Ceram. Technol.*, 12 (2015) 522.
29. A. Lipatov, M. Alhabeab, M. R. Lukatskaya, A. Boson, Y. Gogotsi, A. Sinitskii, *Adv. Electron. Mater.*, 2 (2016), 1600255.
30. Z. Li, L. Wang, D. Sun, Y. Zhang, B. Liu, Q. Hu, A. Zhou, *Mater. Sci. Eng.: B*, 191 (2015) 33.
31. S. Zhao, W. Kang, J. Xue, *J. Phys. Chem. C*, 118 (2014) 14983.
32. M. Naguib, B. Dyatkin, V. Presser, P.-L. Taberna, P. Simon, M. W. Barsoum, Y. Gogotsi, *Electrochem. Commun.*, 16 (2012) 61.
33. L. Wu, X. Lu, Dhanjai, Z.-S. Wu, Y. Dong, X. Wang, S. Zheng, J. Chen, *Biosens. Bioelectron.*, 107 (2018) 69.
34. <https://www.mpwik.com.pl/view/jakosc-wody/centralny/2018&miesiac=kwiecien>
35. C. E. Ren, K. B. Hatzell, M. Alhabeab, Z. Ling, K. A. Mahmoud, Y. Gogotsi, *J. Phys. Chem. Lett.*, 6 (2015) 4026.
36. M. Alhabeab, K. Maleski, T. S. Mathis, A. Sarycheva, C. B. Hatter, S. Uzun, A. Levitt, Y. Gogotsi, *Angew. Chem. Int. Ed.*, 57 (2018) 5444.
37. M. Naguib, R. R. Unocic, B. L. Armstrong, J. Nanda, *Dalton Trans.*, 44 (2015) 9353.