Remarkable differences in the voltammetric response towards hydrogen peroxide, oxygen and Ru(NH₃)₆³⁺ of electrode interfaces modified with HF or LiF-HCl etched Ti₃C₂Tₓ MXene

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Abstract
An electrochemical study was performed on the behavior of Ti₃C₂Tₓ MXenes prepared by using either HF (MXene1) or LiF/HCl as etchants (MXene2). The use of two redox probes indicates the presence of a higher negative charge density on MXene2 in comparison to MXene1. The characterization of two nanomaterials shows that titanium and fluoride are present higher by one order of magnitude at the interface of MXene2, compared to MXene1. The high Ti and F content is accompanied by a 82-fold larger (249 μA·cm⁻² vs. 5.64 μA·cm⁻²) anodic peak at the peak potential near 0.4 V (vs. Ag/AgCl). Similarly, the peak current on MXene2 is 317-fold higher for the oxygen reduction at pH 7.0 (at a voltage of −0.84 V) and 215-fold higher for the reduction of H₂O₂ at −0.89 V, when compared to MXene1.

Keywords MXene · Ti₃C₂Tₓ · Electrocatalysis · Electrochemistry · H₂O₂ reduction · Oxygen reduction reactions · Redox stability

Introduction
MXenes are so-called 2D nanomaterials that have rapidly become an attractive research subject due to their unique properties with employment in numerous applications [1–13]. MXenes are prepared from MAX phases by a selective etching of the A layers [14] with a final interfacial termination by -F and -OH/=O functional groups depending on synthesis conditions [15, 16].

Etching of MAX phases by HF has been initially widely used to produce Ti₃C₂Tₓ MXene [17, 18]. The process however requires handling noxious HF, what is not a green and sustainable way for producing MXene. Alternative etching ways were seeking such as (NH₄HF₂) salt-based approach [19] and subsequently a combination of LiF and HCl (making HF in-situ) was introduced [20]. Presence of Li⁺ ions in the LiF-HCl etchant has a significant effect on the properties of

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MXene. While, a lattice c parameter of HF-produced Ti$_3$C$_2$Tx was 20 Å, in case of LiF-HCl protocol, it increased to a value of ~40 Å. Thus, Li$^+$ ions and water molecules were intercalated and thus no other intercalants are needed to make stable MXene sheets. As a result, the obtained Ti$_3$C$_2$T_x MXene flakes are larger with much lower density of defects and at the same time with higher yield of dispersed MXene flakes [21]. Thus, LiF-HCl etchant is recommended to be applied when high electrical conductivity, larger flake sizes, and high mechanical stability are desired, and HF would be more suitable for preparing Ti$_3$C$_2$T_x with smaller or more defective flakes [21, 22]. Several techniques were applied to study differences in the composition of Ti$_3$C$_2$T_x MXene produced either by HF or LiF-HCl method including $^1$H, $^{13}$C and $^{19}$F NMR, SEM, XRD, EDS techniques [23] from an application for Li-ion batteries point of view. Similar techniques have been applied also to study differences in the properties of Ti$_3$C$_2$T_x MXene prepared using an original “clay” method [20] and a new MILD method based on higher concentration of LiF and HCl not requiring sonication [24]. The first study describing differences in the electrochemical behavior of Ti$_3$C$_2$T_x MXene prepared either by a “clay” or a MILD method was recently published [25].

MXene-modified interfaces besides energy storage applications [26] as batteries or supercapacitors can be effectively applied as electrochemical sensors and biosensors [14]. The differences in the electrochemical behavior of Ti$_3$C$_2$T_x MXene prepared using HF or LiF/HCl as etchants are described here for the first time. Besides electrochemical examination of two types of Ti$_3$C$_2$T_x MXene materials, a battery of techniques was applied, as well, with a conclusion that the amount of Ti and F present on the surface of Ti$_3$C$_2$T_x MXene most likely plays a cardinal role in the electrochemical properties of this nanomaterial.

Materials and methods

This section is part of the ESM file.

Results and discussion

Extensive spectroscopic analysis of both MXene samples showed successful preparation of MXene from MAX phase using both routes as determined by X-ray photoelectron spectroscopy (XPS) analysis (Figs. S1-S3, Table S1), Raman spectrum analysis (Fig. S4), particle size analysis (Fig. S5) and Time-of-Flight (TOF) Secondary Ion Mass Spectrometry (SIMS) (Figs. S9-S17).

Atomic force microscopy of MXene1 and MXene2

The size of MXene flakes was visualised by AFM. The results indicate that MXene2 contains larger particles compared to MXene1 (Fig. S8). The results obtained by AFM are in a good agreement with the size of MXene flakes observed by DLS imaging as shown in Fig. S5. The intensity distribution reveals a Z-average of 132 nm and a polydispersity index of 0.366, with two peaks located at 121 nm (92.7%), and 28.8 nm (7.3%) for MXene1. In contrast, for MXene2 the following parameters were obtained: a Z-average of 178 nm, a polydispersity index of 0.379 with two peaks located at 189 nm (93.6%), and 2.6 μm (6.4%).

Electrochemical characterization of MXene1 and MXene2

Redox behavior in the plain electrolyte under N$_2$ atmosphere

We investigated electrochemical performance of MXene1 and MXene2 in aqueous solutions by CV. Quite stable electrochemical behavior of both types of Ti$_3$C$_2$T_x MXenes in the cathodic potential window for GCE/MXene1 (Fig. 1a) and for GCE/MXene2 is observed (Fig. 1c).

In case of MXene1, a drop of a current density from 111 μA·cm$^{-2}$ to 79 μA·cm$^{-2}$ at −0.75 V i.e. drop to 71% of the original value in 10 scans in the cathodic potential window 0 V → −1 V was observed (Fig. 1a). In the anodic potential window (0 V → 1 V) two peaks were observed at a potential of 0.39 V and 0.60 V. The peak current at 0.39 V sharply decreased and after 3 scans it was stable (4.7 μA·cm$^{-2}$ → 1.6 μA·cm$^{-2}$, i.e. drop to 34% of the original value) (Fig. 1b). Electrical investigation of GCE/MXene2 in a plain electrolyte proved presence of high anodic current of 16.5 μA (249 μA·cm$^{-2}$) at +0.39 V in the 1st CV scan (Fig. 1d), while under the same conditions an anodic current of 0.30 μA (5.64 μA·cm$^{-2}$) (Fig. 1b) was observed for GCE/MXene1. After background subtraction, there is 82-fold increase in the current density on GCE/MXene2 in comparison to GCE/MXene1.

In case of MXene1, a drop of a current density from 196 μA·cm$^{-2}$ to 142 μA·cm$^{-2}$ at −0.8 V i.e. drop to 72% of the original value in 10 scans was observed, while scanning the potential in the cathodic potential window 0 V → −1 V (Fig. 1c). In the anodic potential window (0 V → 1 V) only one dominant peak at a potential of 0.38 V was seen. The peak current at 0.38 V sharply decreased and after 3 scans it was stable (253 μA·cm$^{-2}$ → 1.8 μA·cm$^{-2}$, i.e. drop to 0.7% of the original value) (Fig. 1d). There is also difference between redox behavior of MXene2 and MXene1, since at GCE/MXene2 an anodic peak at a potential of ~0.95 V is present (Fig. 1c).
Thus, it can be concluded that the electrochemical stability for both types of MXene is very similar in the cathodic potential window with a striking difference of the electrochemical stability and behavior in the anodic potential window. The anodic oxidation of both MXene types is an irreversible process, and the oxidation peak disappears after 3 CV cycles.

**Electrochemical behavior using electrochemical redox probes**

The Ti$_3$C$_2$T$_X$ MXene is not stable in an anodic potential window required to study redox behavior of an inner-sphere electrochemical redox probe - ferricyanide/ferricyanide [25, 27]. Therefore, the redox behavior of an outer-sphere electrochemical redox probe Ru(NH$_3$)$_6$Cl$_3$ was studied. This redox probe was also used for calculation of an electrochemically active surface area.

From the slope of a linear plot of $i_p$ vs. $v^{1/2}$ for the cathodic part of the CV for GCE/MXene1 and GCE/MXene2 in 5 mM Ru(NH$_3$)$_6$Cl$_3$ (inset figures in Fig. S6), the electroactive surface area was calculated as follows: (5.27 ± 0.07) mm$^2$ for GCE, (5.32 ± 0.08) mm$^2$ for GCE/MXene1 and (6.62 ± 0.08) mm$^2$ for GCE/MXene2. This really suggests that MXene2 is much better delaminated compared to MXene1 with a higher electrochemical/interfacial surface area of the nanomaterial exposed to the electrolyte.

There is a striking difference in the electrochemical behavior of Ru(NH$_3$)$_6$Cl$_3$ between GCE/MXene1 and GCE/MXene2 (Table S1 and S2; Fig. 2). An anodic peak potential for Ru(NH$_3$)$_6$Cl$_3$ at both GCE/MXene1 and GCE/MXene2

![Figure 1: CVs of GCE/MXene1 showing 10 consecutive scans run in two potential windows (a) from −1 V to 0 V, (b) from 0 V to 1 V. CVs of GCE/MXene2 showing 10 consecutive scans run in two potential windows (c) from −1 V to 0 V, (d) from 0 V to 1 V, at a sweep rate of 100 mV s$^{-1}$ in 0.1 M PB pH 7.0](image-url)

![Figure 2: Redox behavior of 5 mM Ru(NH$_3$)$_6$Cl$_3$ in 1 M KCl depending on the potential scan rate showing dependence of $E_{pc}$ (a), $E_{pa}$ (b), $\Delta E_p$ and (c), and a ratio of $i_{pc}$ / $i_{pa}$ (d) on a scan rate for GCE/MXene1 and GCE/MXene2. A scan rate was varied from 0.1 V s$^{-1}$ to 0.8 V s$^{-1}$](image-url)
does not change with an increased scanning rate and remains constant at a value of \(-139\) mV (Table S1 and S2, Fig. 2b). A cathodic peak potential remains stable only for GCE/MXene1 with a value of \(-213\) mV (Table S1, Fig. 2a), while for GCE/MXene2 it increases from \(-215\) mV to \(-225\) mV with an increasing scan rate from 0.1 V·s\(^{-1}\) to 0.8 V·s\(^{-1}\) (Table S2, Fig. 2a). Moreover, there is a change of the \(E_{pc}\) vs. \(v\) is linear with a slope of \(-0.0188\) V / (V·s\(^{-1}\)) for GCE/MXene2 within the interval of scan rates from 0.2 V·s\(^{-1}\) to 0.7 V·s\(^{-1}\) (Fig. 2a). At the same time there is also a linear dependence of \(\Delta E\) vs. \(v\) with a slope of \(-0.0181\) V / (V·s\(^{-1}\)) for GCE/MXene2 within the interval of scan rates from 0.2 V·s\(^{-1}\) to 0.7 V·s\(^{-1}\) (Fig. 2c).

Besides differences in the electrochemical behavior of Ru(NH\(_3\))\(_6\)Cl\(_3\) between GCE/MXene1 and GCE/MXene2, when a peak potential is taken into account, there are also significant differences, when peak current is considered. For GCE/MXene1, the value of \(i_{pc}/i_{pa}\) increased from 1.26 (0.1 V·s\(^{-1}\)) to a value of 1.08 (0.8 V·s\(^{-1}\)) (Fig. 2d). For GCE/MXene2, after an initial drop from a value of 1.24 to 1.20 (0.1 V·s\(^{-1}\) → 0.2 V·s\(^{-1}\)) there is an increase in the value of \(i_{pc}/i_{pa}\) from a value of 1.20 to a value of 1.32 (0.2 V·s\(^{-1}\) → 0.8 V·s\(^{-1}\)) (Fig. 2d). Interestingly, GCE modified by both nanomaterials exhibits the same initial \(i_{pc}/i_{pa}\) of 1.24–1.25 at a low potential scan rate of 0.1 V·s\(^{-1}\) (Fig. 2d).

Possibly, the irreversibility of the redox behavior on GCE/MXene1 and GCE/MXene2 is caused by different affinity of Ru\(^{2+}\) and Ru\(^{3+}\) species towards both MXene nanomaterials (initial \(i_{pc}/i_{pa}\) far from an ideal value of 1.00 i.e. 1.24–1.25).

Electrochemical impedance spectroscopy (EIS) using 5 mM ferricyanide/ferrocyanide solution in 0.1 M PB pH 7.0 showed that interfacial charge transfer resistance \(R_{ct}\) is higher for GCE/MXene2 (5.0 ± 0.2 kΩ) compared to GCE/MXene1 (2.6 ± 0.3 kΩ) (Fig. S7), what can suggest higher density of negatively charged species present on the surface of GCE/MXene2 compared to GCE/MXene1. The plain GCE exhibited \(R_{ct} = (164 ± 36)\) Ω.

We can conclude from the electrochemical investigations using two redox probes that most likely GCE/MXene2 has a higher density of a negative charge on the surface compared to GCE/MXene1, as judged by the use of a ferricyanide/ferrocyanide as a redox couple. A higher density of a negative interfacial charge on GCE/MXene2 compared to GCE/MXene1 is consistent with a redox behavior of a redox probe Ru(NH\(_3\))\(_6\)Cl\(_3\), since a higher density of negative charge on GCE/MXene2 will have a higher affinity towards Ru\(^{3+}\) redox species over Ru\(^{2+}\) redox species. Thus, GCE/MXene2 will pre-concentrate Ru\(^{3+}\) over Ru\(^{2+}\), a feature, which is more obvious at high scan rates, not allowing Ru\(^{3+}\) species to be diluted in the bulk of the electrolyte.

Oxygen reduction reaction (ORR)

Naturally abundant 2D materials are investigated for their exceptional electrocatalytic properties as in energy-related reactions including hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR), oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) or promising energy conversion process, carbon dioxide reduction reaction (CO\(_2\)RR). ORR presents a pertinent reaction in the majority of energy conversion and storage devices; for example, in fuel cells and rechargeable metal-air batteries. ORR progresses via a direct four-electron pathway or a two-step two-electron process that produces a H\(_2\)O\(_2\) intermediate [28].

The electrocatalytic activity of MXene1 and MXene2 towards ORR in alkaline, neutral and acidic media was also studied and can be seen in Fig. 3.

In the alkaline electrolyte (0.1 M NaOH) ORR on GCE, GCE/MXene1 and GCE/MXene2 is very similar (a potential at which ORR starts and a current density) (Fig. 3a-c), when subtracted CVs are considered (Fig. 3e). This really indicates that very high pH does not keep Ti\(_3\)C\(_2\)TX MXene in an active state and that at alkaline pH Ti\(_3\)C\(_2\)TX MXene is not electrochemically stable. The same conclusion was recently made by Nayak et al. [25].

At neutral pH, the situation is completely different for GCE/MXene1 and for GCE/MXene2. ORR starts at a potential of \(-131\) mV on GCE (Fig. 3d), at a potential of \(-190\) mV at GCE/MXene1 (Fig. 3d) and at a potential of \(-100\) mV at GCE/MXene2 (Fig. 3e). ORR exhibits a maximal current density of 147 μA·cm\(^{-2}\) at a potential of \(-698\) mV on GCE, a maximal current density of 157 μA·cm\(^{-2}\) at a potential of \(-674\) mV on GCE/MXene1 and a maximal current density of 1270 μA·cm\(^{-2}\) at a potential of \(-840\) mV on GCE/MXene2. This really means that GCE/MXene1 exhibits ORR parameters very similar to GCE (Fig. 3d, f) and that MXene prepared by HF etching does not exhibit significant intrinsic ORR capabilities. At neutral pH, there is only a mild intrinsic ORR on GCE/MXene1 (\(J_{ORR/GCE/MXene1} - J_{ORR/GCE} = 3.6\) μA·cm\(^{-2}\)) read at \(-840\) mV, compared to intrinsic ORR on GCE/MXene2 (\(J_{ORR/GCE/MXene2} - J_{ORR/GCE} = 1270\) μA·cm\(^{-2}\)). Thus, it is concluded that there is 317-fold higher intrinsic ORR on GCE/MXene2 in comparison to intrinsic ORR on GCE/MXene1 at pH 7 (Fig. 3f).

At an acidic pH, ORR starts at a potential of \(-198\) mV on GCE (Fig. 3g), at a potential of \(-105\) mV at GCE/MXene1 (Fig. 3g) and at a potential of \(-46\) mV at GCE/MXene2 (Fig. 3h). ORR exhibits a peak current density of 91 μA·cm\(^{-2}\) at a potential of \(-574\) mV on GCE, a peak current density of 196 μA·cm\(^{-2}\) at a potential of \(-640\) mV on GCE/MXene1 and a peak current density of 2270 μA·cm\(^{-2}\) at a potential of \(-671\) mV on GCE/MXene2. At an acidic pH, there is only a mild intrinsic ORR on GCE/MXene1 (\(J_{ORR/GCE/MXene1} - J_{ORR/GCE} = 81\) μA·cm\(^{-2}\)) read at \(-671\) mV, compared to intrinsic ORR on GCE/MXene2 (\(J_{ORR/GCE/MXene2} - J_{ORR/GCE} = 2160\) μA·cm\(^{-2}\)). Thus, there is 27-fold higher intrinsic ORR on GCE/MXene2 in comparison to intrinsic ORR on GCE/MXene1 at an acidic pH (0.1 M H\(_2\)SO\(_4\)) (Fig. 3i).
Electrochemical reduction of H$_2$O$_2$

The electrochemical determination is H$_2$O$_2$ is widely applied using various types of nanomaterials [29–31]. H$_2$O$_2$ reduction starts at a potential of $-224$ mV at GCE, at a potential of $-190$ mV at GCE/MXene1 and at a potential of $-140$ mV at GCE/MXene2 (Fig. 4). H$_2$O$_2$ reduction exhibits a peak current density of 87 $\mu$A cm$^{-2}$ at a potential of $-818$ mV on GCE, a peak current density of 107 $\mu$A cm$^{-2}$ at a potential of $-686$ mV on GCE/MXene1 and a peak current density of 2100 $\mu$A cm$^{-2}$ at a potential of $-894$ mV on GCE/MXene2. When H$_2$O$_2$ reduction is considered, there is only a mild intrinsic activity towards H$_2$O$_2$ reduction at a potential of $-894$ mV on GCE/MXene1 (i.e. $J_{GCE/MXene1} - J_{GCE}$) of 9.4 $\mu$A cm$^{-2}$, while on GCE/MXene2 the activity towards H$_2$O$_2$ reduction is 215-fold higher ($J_{GCE/MXene2} - J_{GCE} = 2020$ $\mu$A cm$^{-2}$).

TOF-SIMS analysis

The electrochemical behavior of MXene1 and MXene2 cannot be explained by any typical characterization techniques applied for that purpose (i.e. XPS, Raman spectroscopy, contact angle measurements) all provided in the ESM file. This is why for that purpose we tried to use TOF-SIMS method, which can determine interfacial composition of nanomaterial at the nanoscale.

Secondary Ion Mass Spectrometry (SIMS) employing Time-of-Flight (TOF) analyzer is an analytical tool for examination of elemental/molecular composition of interfacial layers with high mass resolution on the order of 10,000 m/z, high lateral resolution of 100 nm, a depth resolution of 1 nm and with sensitivity down to ppm-ppb level [32]. The technique allows to acquire 2D map of the interface with a spatial distribution of selected ions [32].
SIMS spectra analysis confirmed that the fragmentation of MXene1 and MXene2 produced the following ions: C+, CH₃+, C₂H₅+, Ti+, C₄H₇+, TiO+ in a positive polarity and fragments O−, OH−, F− in a negative polarity. The main differences were in the intensity of particular fragments (Table 1), when the ratio MXene2/MXene1 was calculated (Table 1, last line). The highest differences between these two types of MXenes were observed for content of Ti+ (12.5-fold) and F− (39-fold) ions. This really means that although the average composition of both MXenes as determined by XPS (Table S1) is slightly different, interfacial composition of MXene1 is dramatically different from MXene2 as determined by TOF SIMS. Hence, it is concluded that differences in the interfacial density of various chemical species (Ti and F content) between these two types of MXenes are the reason for the dramatic differences in the electrochemical behavior of both MXenes. Moreover, 2D SIMS analysis also revealed that distribution of both ions Ti+ and F− is more homogeneous on MXene2 compared to MXene1 (Fig. S9). Further details regarding TOF SIMS analysis are provided in ESM (Figs. S10-S17).

**Conclusions**

The study revealed a striking difference in the electrochemical behavior of MXenes prepared either using HF (MXene1) or LiF/HCl (MXene2) etching routes. Electrochemical investigation of GCE/MXene2 in a plain electrolyte proved presence of a peak at potential of +0.39 V with 82-fold higher density on GCE/MXene2 in comparison to GCE/MXene1. Additional electrochemical experiments using two redox probes - outer one (Ru³⁺ complex for calculation of electrochemical surface area) and inner one (ferricyanide/ferrocyanide redox couple to investigate Rct) indicate higher negative charge on the surface MXene2 compared to MXene1. Finally, ORR at neutral pH was 317-fold more effective at GCE/MXene2 compared to MXene1 and significantly higher (215-fold) H₂O₂ reduction was observed on GCE/MXene2 in comparison to GCE/MXene1, as well.

Although traditional characterization techniques cannot explain such staggering difference in the electrochemical behavior for GCE/MXene2 in comparison to GCE/MXene1, TOF SIMS indicate significantly higher amount of Ti+ (12.5-fold) and F− (39-fold) ions on MXene2 compared to MXene1. This is why additional studies are needed to prove if there is a direct relationship between interfacial content of F− ions and electrochemical activity of MXenes.

Better understanding of electrochemical performance of MXenes is needed for further development of highly robust electrochemical catalytic and affinity-based biosensors.

### Table 1

Total ion normalized intensities values of MXene fragments

| Sample | C⁺ | CH₃⁺ | C₂H₅⁺ | Ti⁺ | C₄H₇⁺ | O⁻ | OH⁻ | F⁻ |
|--------|----|------|-------|-----|-------|----|-----|----|
| MXene1 | 6.58×10⁻⁵ | 2.06×10⁻³ | 1.97×10⁻² | 8.56×10⁻³ | 1.45×10⁻² | 2.36×10⁻¹ | 1.62×10⁻¹ | 5.7×10⁻³ |
| MXene2 | 2.50×10⁻⁴ | 4.72×10⁻³ | 9.07×10⁻³ | 1.07×10⁻¹ | 3.33×10⁻³ | 1.09×10⁻¹ | 7.35×10⁻² | 2.22×10⁻¹ |
| MX2/MX1 | 3.80 | 2.29 | 0.46 | 12.5 | 0.23 | 0.46 | 0.45 | 39.0 |

Fig. 4 Representative blank-subtracted CV scans run at GCE, GCE/MXene1 and GCE/MXene2 in 1.5 mM H₂O₂ in 0.1 M PB pH 7.0 (a). The CV run in presence of H₂O₂ is subtracted from the CV run in plain buffer and for clarity only cathodic part of CV is shown (b). The experiments were run at a sweep rate of 100 mV·s⁻¹.
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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Zhao M-Q, Torelli M, Ren CE, Ghididiu M, Ling Z, Anasori B, Barsoum MW, Gogotsi Y (2016) 2D titanium carbide and transition metal oxides hybrid electrodes for Li-ion storage. Nano Energy 30: 603–613
2. Huang K, Li ZI, Lin J, Han G, Huang P (2018) Two-dimensional transition metal carbides and nitrides (MXenes) for biomedical applications. Chem Soc Rev 47:5109–5124
3. Sinha A, Dhanjai HM, Zhao YJ, Yang X, Chen X, Zeng GM, Zhou J, Wang X, Chew JW (2018) Jain, MXene: an emerging material for sensing and biosensing. Trends Anal Chem 105:424–435
4. Soleymaninia M, Shahbazi MA, Rafieerad AR, Maleki A, Amir A (2019) Promoting role of MXene Nanosheets in biomedical sciences: therapeutic and biosensing innovations. Adv Healthcare Mat 8:e1801137
5. Wang H, Wu Y, Yuan ZX, Zeng GM, Zhou J, Wang X, Chew JW (2018) Clay-inspired MXene-based electrochemical devices and photo-Electrocatalyst: state-of-the-art progresses and challenges. Adv Mater 30:e1704561
6. Zhang X, Zhang ZH, Zhou Z (2018) MXene-based materials for electrochemical energy storage. J Energy Chem 27:73–85
7. Luo Y, Tang L, Khan U, Yu Q, Cheng HM, Zou X, Liu B (2019) Morphology and surface chemistry engineering toward pH-universal catalysts for hydrogen evolution at high current density. Nat Commun 10:2690
8. Szuplewska A, Kulpińska D, Dybkó A, Jastrzębska AM, Wieczorecki T, Rozmysłowska A, Chudy M, Grabowska-Jadach I, Ziemkowska W, Brzózka Z, Ozłyna A (2019) 2D Ti₃Cₓ (MXene) as a novel highly efficient and selective agent for photothermal therapy. Mater Sci Eng C 98:874–886
9. Shi X, Wang H, Xie X, Xue Q, Zhang J, Kang S, Wang C, Liang J, Chen Y (2019) Bioinspired ultra-sensitive and stretchable MXene-based strain sensor via nacre-mimetic microscale “brick-and-mortar” architecture. ACS Nano 13:649–659
10. Muckley ES, Naguib M, Ivanov IN (2018) Multi-modal, ultra-sensitive, wide-range humidity sensing with Ti₂Cₓ film. Nanoscale 10: 21689–21695
11. Li T, Chen L, Yang X, Chen X, Zhang Z, Zhao T, Li X, Zhang J (2019) A flexible pressure sensor based on an MXene–textile network structure. J Mater Chem C 7:1022–1027
12. Liu J, Jiang X, Zhang R, Zhang Y, Wu L, Lu W, Li J, Li Y, Zhang H (2018) MXene-enabled electrochemical microfluidic biosensor: applications toward multicomponent continuous monitoring in whole blood. Adv Funct Mater 29:1807326
13. Shahzad F, Alhabeb M, Hatter CB, Anasori B, Man Hong S, Koo CM, Gogotsi Y (2016) Electromagnetic interference shielding with 2D transition metal carbides (MXenes). Science 353:1137
14. Lorencova L, Gajdosova V, Hroncekova S, Bertok T, Blahutova J, Vikartovska A, Parrakova L, Guneser P, Kasak P, Tkac J (2019) 2D MXenes as perspective immobilization platforms for Design of Electrochemical Nanobiosensors. Electroanalysis 31:1833–1844
15. Naguib M, Kurtoglu M, Presser V, Lu J, Niu J, Heon M, Hultman L, Gogotsi Y, Barsoum MW (2011) Two-dimensional nanocrystals produced by exfoliation of Ti₃AlC₂. Adv Mater 23:4248–4253
16. Eklund P, Rosen J, Persson POÅ (2017) Layered ternary MₓAlₓAx phases and their 2D derivative MXene: an overview from a thin-film perspective. J Phys D Appl Phys 50:113001
17. Lukatskaya MR, Mshashiril O, Ren CE, Dall’Agnese Y, Rozier P, Taberna PL, Naguib M, Simon P, Barsoum MW, Gogotsi Y (2013) Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide. Science 341:1502–1505
18. D.B. Xiong, X.F. Li, Z.M. Bai, S.G. Lu (2018) Recent advances in layered Ti₃C₂Tx MXene for electrochemical energy storage, Small, 14:1703419.
19. Halim J, Lukatskaya MR, Cook KM, Lu J, Smith CR, Näslund L-Å, May SJ, Hultman L, Gogotsi Y, Eklund P, Barsoum MW (2014) Transparent conductive two-dimensional titanium carbide epitaxial thin films. Chem Mater 26:2374–2381
20. Ghididiu M, Lukatskaya MR, Zhao M-Q, Gogotsi Y, Barsoum MW (2014) Conductive two-dimensional titanium carbide ‘clay’ with high volumetric capacitance. Nature 516:78
21. Xiong D, Li X, Bai Z, Lu S (2018) Recent advances in layered Ti₃C₂Tx MXene for electrochemical energy storage. Small 14: e1703419
22. Alhabeb M, Maleski K, Anasori B, Lelyukh P, Clark L, Sin S, Gogotsi Y (2017) Guidelines for synthesis and processing of two-dimensional titanium carbide (Ti₃C₂Tx MXene). Chem Mater 29: 7633–7644
23. Hope MA, Forse AC, Griffith KJ, Lukatskaya MR, Ghididiu M, Gogotsi Y, Grey CP (2016) NMR reveals the surface functionalisation of Ti₃C₂Tx MXene. Phys Chem Chem Phys 18:5099–5102
24. Lipatov A, Alhabeb M, Lukatskaya MR, Boson A, Gogotsi Y, Sinitskii A (2016) Effect of synthesis on quality, electronic properties and environmental stability of individual monolayer Ti₃C₂Tx MXene flakes. Advanced Electronic Materials 2: 1600255
25. Nayak P, Jiang Q, Mohanram R, Anjum D, Hedhili MN, Alshareef HN (2018) Inherent electrochemistry and charge transfer properties of few-layered two-dimensional Ti 3 C 2 T x MXene. Nanoscale 10:17030–17037
26. Anasori B, Lukatskaya MR, Gogotsi Y (2017) 2D metal carbides and nitrides (MXenes) for energy storage. Nature Reviews Materials 2:16098
27. Lorencova L, Bertok T, Dosekova E, Holazova A, Papcekova D, Vikartovska A, Sassinakova V, Filip J, Kasak P, Jerigova M, Velic D, Mahmoud KA, Tkac J (2017) Electrochemical performance of Ti₃C₂Tx MXene in aqueous media: towards ultrasensitive H₂O₂ sensing. Electrochem Acta 235:471–479
28. Chia X, Pumera M (2018) Characteristics and performance of two-dimensional materials for electrocatalysis. Nat Catalysis 1:909–921
29. Yang H, Wang Z, Zhou Q, Xu C, Hou J (2019) Nanoporous platinum-copper flowers for non-enzymatic sensitive detection of hydrogen peroxide and glucose at near-neutral pH values. Microchim Acta 186:631
30. Ma J, Bai W, Zheng J (2019) Non-enzymatic electrochemical hydrogen peroxide sensing using a nanocomposite prepared from
silver nanoparticles and copper (II)-porphyrin derived metal-organic framework nanosheets. Microchim Acta 186:482

31. Sivakumar M, Veeramani V, Chen S-M, Madhu R, Liu S-B (2019) Porous carbon-NiO nanocomposites for amperometric detection of hydrazine and hydrogen peroxide. Microchim Acta 186:59

32. Škantárová L, Oriňák A, Oriňáková R, Jerigová M, Stupavská M, Velič D (2013) Functional silver nanostructured surfaces applied in SERS and SIMS. Surf Interface Anal 45:1266–1272

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