

Enhancement of Ti_3C_2 MXene Pseudocapacitance after Urea Intercalation Studied by Soft X-ray Absorption Spectroscopy

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Abstract

MXenes have shown outstanding properties due to their highly active hydrophilic surfaces coupled with high metallic conductivity. Many applications rely on the intercalation between $Ti_3C_2T_x$ (T_x describes the surface termination) flakes by ions or molecules, which in turn might alter the $Ti_3C_2T_x$ surface chemistry and electrochemical properties. In this work, we show that the capacitance, rate capability, and charge carrier kinetics in $Ti_3C_2T_x$ MXene electrodes are remarkably enhanced after urea intercalation ($u-Ti_3C_2T_x$). In particular, the areal capacitance increased to 1100 mF/cm^2 , which is a 56% higher than that of pristine $Ti_3C_2T_x$ electrodes. We attribute this dramatic improvement to changes in the $Ti_3C_2T_x$ surface chemistry upon urea intercalation. The oxidation state and the oxygen bonding of individual $Ti_3C_2T_x$ flakes before and after urea intercalation was probed by soft X-ray absorption spectroscopy (XAS) at the Ti L- and O K-edges with 30 nm spatial resolution in vacuum. After urea intercalation, a higher Ti oxidation state was observed across the entire flake compared to pristine $Ti_3C_2T_x$. Additionally, *in situ* XAS of $u-Ti_3C_2T_x$ aqueous dispersions revealed a higher Ti oxidation similar to dry samples, while for pristine $Ti_3C_2T_x$ the Ti atoms are significantly reduced in water compared to dry samples.

Introduction

Electrochemical energy storage (EES) systems with high capacitance, fast rate capabilities, and low-cost electrodes are urgently demanded as society transitions to sustainable energy technologies. MXenes are a class of 2D transition metal carbides, nitrides, and carbonitrides that are currently attracting considerable attention for EES purposes.^{1–6} MXenes combine high electrical conductivity with hydrophilic 2D lamellas, enabling the fast and reversible insertion of a variety of intercalants in organic or aqueous environments.^{7–9} Intercalation of MXenes

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3 was found to have an impact on their surface chemistry and was suggested as a strategy to
4 obtain higher pseudocapacitance performance.¹⁰ MXenes can be intercalated both chemically
5 and electrochemically by mono- and multivalent metal cations such as H⁺, Li⁺, Na⁺, K⁺, and
6 Mg²⁺, as well as by organic molecules such as hydrazine.^{3,11–13} Recently, an outstanding urea
7 adsorption capacity was demonstrated in Ti₃C₂T_x MXenes, suggesting that these materials
8 could be promising for use in wearable kidneys.¹⁴ Urea intercalation has also been applied as
9 a first step to generate nitrogen-doped Ti₃C₂T_x MXenes with improved capacitance in aqueous
10 electrolyte.¹⁵

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15 The MXene interlayer distance has been found to be directly proportional to the intercalant's
16 hydration size, and intercalation generally induces a larger spacing between the material
17 layers, as demonstrated by X-ray diffraction (XRD).¹⁶ Despite the relatively large size of urea
18 compared to the interlayer gallery of MXenes, the change in the interlayer distance after
19 intercalation is relatively small owing to the parallel orientation of urea molecules relative to
20 the MXene surface, regardless of the possible surface terminations, T_x.¹⁴ In another study, the
21 decomposition temperature of urea was shown to be reduced to ~60 °C when intercalated
22 into MXenes.¹⁷ The impact of urea intercalation on the surface chemistry of pristine Ti₃C₂T_x
23 MXene and on the electrolyte's ion transportation mechanism remains largely unexplored,
24 while they represent a cornerstone in pseudocapacitance performance.

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31 Soft X-ray Absorption Spectroscopy (XAS)^{1,6,18} is an element-selective technique that is very
32 sensitive to surface chemistry. In particular, the characterization of transition metal L-edges is
33 very sensitive to the metal chemical environment and has been used to distinguish the various
34 Ti oxide species.^{19,20} While previous XAS reports on Ti₃C₂T_x MXenes at the Ti K-edge have
35 shown changes of Ti oxidation state during cycling in different conditions,^{1,6} Ti L-edge can
36 provide further information on the nature of the chemical bonds between Ti atoms and
37 surface groups due to its higher sensitivity to metal-ligand coordination.²¹ However, the
38 shorter penetration depth of soft X-rays makes *in situ* experiments on thick electrodes much
39 more complicated at the Ti L-edge compared to the Ti K-edge. Furthermore XAS can be
40 acquired using X-ray Photoemission Electron Microscopy (X-PEEM) to provide XA spectra with
41 30 nm spatial resolution in vacuum.²² Pristine Ti₃C₂T_x MXenes have also been found to be
42 sensitive to oxidation due to a charge transfer that can take place between surface O and Ti
43 atoms.^{23,24} The high chemical sensitivity of XAS at the Ti L-edge can also be employed *in situ*
44 in aqueous environments using flow cells with thin X-ray transparent membranes.²⁰ Probing
45 the MXene Ti chemical environment in different environments is important as electrochemical
46 reactions take place in aqueous media. Nevertheless, XAS in the soft X-ray range has not been
47 applied on MXene so far.

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56 In this work, we characterized the electrochemical performance of pristine and urea-
57 intercalated Ti₃C₂T_x (u-Ti₃C₂T_x) MXene electrodes and correlated it to the nature of Ti-O
58 bonding probed in vacuum and in water using XAS at the Ti L- and O K-edges. Spatially-resolved
59 oxidation over individual Ti₃C₂T_x MXene flakes was characterized by X-PEEM. In addition, *in*
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situ XAS was performed on aqueous dispersions of MXenes to observe the effect of solvation on MXene electronic structure. The u-Ti₃C₂T_x MXenes were characterized under similar conditions and demonstrated a significantly higher Ti oxidation state and capacitance compared to the pristine Ti₃C₂T_x MXene. The u-Ti₃C₂T_x-based electrode exhibits enhanced capacitance performance and rate capabilities over pristine Ti₃C₂T_x electrodes, the origin of which will be discussed based on XAS characterization in this work.

Experimental section

Materials: Ti₃C₂T_x MXenes were synthesized from the respective precursor Ti₃AlC₂. To make Ti₃C₂T_x, 1 g of Ti₃AlC₂ (<37 μm particle size) powder was added into 10 mL of 10% hydrofluoric acid (50%, Fisher Scientific) solution for 2 min. The solution was stirred for 24 h at 35 °C. The obtained multilayered Ti₃C₂T_x was repeatedly washed with deionized water, followed by centrifugation and decantation until the pH of the suspension reached ~6. After the final centrifugation, the sediment of each Ti₃C₂T_x MXene was collected via vacuum-assisted filtration, and the obtained Ti₃C₂T_x powder was kept under vacuum at room temperature to prevent any deterioration due to oxidation. To study the impact of urea intercalation on the Ti₃C₂T_x MXene, the adsorption of urea was performed in aqueous solution with an initial urea concentration of 5 g/dL at room temperature. 2 g of MXene (Ti₃C₂T_x) powder was added to 50 mL of aqueous urea solution and mixed by hand for approximately 6 min, followed by shaking at 150 rpm for an hour. Afterwards, the Ti₃C₂T_x/urea suspension was centrifuged at 1000 rpm for 2 min. Both the precipitate and supernatant were reserved for analysis. The resulting u-Ti₃C₂T_x precipitate and the pristine Ti₃C₂T_x precipitate were dried via vacuum-assisted filtration and used for XRD analysis. Both samples were also vacuum annealed at 110 °C for 12 hours (marked as @ 110 °C) to remove any intercalated water prior to performing XRD analysis. For other experiments than XRD, the samples were not annealed prior characterization.

Thermogravimetric analysis-mass spectrometry (TG-MS): TG-MS measurements were carried out using a TA Instruments thermal analyzer (SDT Q 650, Discovery Series) equipped with a Mass Spectrometer (110/220V) from room temperature to 1000°C with a heating rate of 10 °C/min under a constant helium flow 100 mL/min. The gas products that evolved during heating were determined by MS and mass/charge (m/z) evolution profiles as a function of temperature were obtained. The ion current was normalized by the corresponding initial weight of the materials loaded for TG-MS analysis.

X-PEEM and TEY-XAS measurements in vacuum: All sample preparation and thin film processing for synchrotron measurements were carried out in the chemistry laboratory at the Energy Materials *In situ* Laboratory Berlin (EMIL), jointly operated by Helmholtz-Zentrum Berlin für Materialien and Energie, GmbH (HZB) and the Max-Planck Society. Solid samples were spin coated in air on conductive Si substrates to obtain isolated multi-layer single flakes of pristine Ti₃C₂T_x, u-Ti₃C₂T_x, and a thin TiO₂ nanoparticle film. In order to mimic the studied bulk like sample, we have investigated the oxidation state of Ti atoms of relatively thick flake with more or less the same flake size. Please note that this is quite difficult with XPEEM

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3 technique as it took hours just to find a good candidate flake. The samples were characterized
4 by XAS using Partial Electron Yield (PEY) mode with the X-PEEM endstation at the UE-49-PGM-
5 A beamline of the synchrotron light source BESSY II operated by HZB. Anatase TiO₂
6 nanoparticles (PL-TiO, Plasmachem, GmbH) have an average particle size of 4–8 nm and were
7 stabilized by a 10 wt% nitric acid (HNO₃) solution. Drop cast films on conductive Si substrates
8 for all samples were dried in air first and then measured in Total Electron Yield (TEY) mode
9 under vacuum conditions at the U49-2_PGM1 beamline of BESSY II using the LiXEdrom
10 endstation.
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16 ***In situ XAS measurements in water:*** Experiments were conducted at the U49-2_PGM1
17 undulator beamline of BESSY II using the LiXEdrom endstation. Pure water, dispersed
18 multilayered Ti₃C₂T_x, u-Ti₃C₂T_x, and 1M urea in water samples were characterized using a
19 membrane-based flow cell using Total Fluorescence Yield (TFY) recorded with a XUV-100
20 silicon photodiode (AMS Technologies). 50 nm thick silicon nitride membranes (Plano GmbH)
21 with a window size of 0.5mm x 0.5mm were used to isolate the liquid from the vacuum
22 chamber (10⁻⁶ mbar range), which is required for soft XAS measurements. To have a constant
23 flow during the experiments enabling efficient sample renewal during measurement, a Legato
24 270 syringe pump (KD Scientific Inc.) was operated in push-pull mode with a flow rate of 1
25 mL/min. After characterization of each sample, the flow cell was flushed with deionized water
26 and reference spectra were acquired again at the O K-edge to validate that no sample
27 contamination was left in the cell.
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33 The energy of the O K-edge was calibrated to the water pre-edge at 535.0 eV. For clarity, the
34 intensity of the O K edge XA spectra was normalized to the intensities before and after the
35 water main edge. The Ti L-edge was normalized to the dried Ti₃C₂T_x MXene L₃ (t_{2g}) peak at
36 458.1 eV.
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40 ***Electrochemical measurements:***

41 - *MXene and activated carbon (AC) electrode films*

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43 Multilayer powders of Ti₃C₂T_x or u-Ti₃C₂T_x were mixed with polytetrafluoroethylene (60 wt.%
44 in water, Sigma Aldrich) to form a weight ratio of 95:5 for the working electrode films.
45 Similarly, activated carbon (AC) films were prepared by mixing 5 wt.% polytetrafluoroethylene
46 (60 wt.% in water, Sigma Aldrich) with 95 wt.% YP50 (Kuraray, Japan). Electrodes were formed
47 by rolling the mixtures into 100 μm thick films followed by drying in a vacuum oven at 70 °C
48 overnight.
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52 The electrochemical tests (cyclic voltammetry, galvanostatic charge-discharge,
53 electrochemical impedance spectra) were conducted at room temperature using a VMP3
54 electrochemical workstation (BioLogic, France). Cyclic voltammograms (CV) were recorded
55 using a VMP3 at scan rates ranging from 5-100 mV/s after pre-cycling electrodes at 5 mV/s for
56 50 cycles. Electrochemical impedance spectroscopy (EIS) measurements were performed in
57 the frequency range from 100 kHz to 0.1 Hz at open circuit potential by applying a small
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3 sinusoidal potential signal with an amplitude of 10 mV. The 3-electrode measurements were
4 performed in 1M H₂SO₄ electrolyte, in which Ti₃C₂T_x and u-Ti₃C₂T_x electrodes were employed
5 as the working electrodes with over-capacitive activated carbon and Ag/AgCl as the counter
6 and reference electrodes, respectively. Gravimetric, areal, and volumetric capacitances were
7 calculated based on the weight, area, and volume of the active materials, respectively.
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10 - Calculations

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12 The gravimetric specific capacitance, C_m (F/g), of the electrode materials was calculated from
13 the CV curves by integrating the discharge portion according to the following equation:
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$$C_m = \frac{1}{vmv} \int idV$$
 where i is the current (mA), V is the potential window (V), v is the scan
17 rate (mV/s), and m is the mass of the active material (mg).
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20 Areal capacitance values (F/cm²) C_A were estimated by multiplying the gravimetric capacitance
21 with the areal mass loading (~ 20 mg/cm²) of the working electrodes.
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$$23 C_A = C_m * \text{mass loading}$$

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25 Volumetric capacitance (F/cm³) values were estimated by normalizing the areal capacitance
26 with the thickness (100 μm) of the working electrodes
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$$28 C_V = C_A / \text{thickness}$$

31 Results and Discussion

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33 Ti₃C₂T_x MXenes were synthesized via the 10 wt.% hydrofluoric acid (HF) selective etching
34 method²⁵ and urea intercalation was performed according to previously published methods
35 (see SI for details).²⁵ **Figure 1a** illustrates a schematic of the urea intercalation in Ti₃C₂T_x
36 MXenes. The orientation of urea molecules in the gallery of the MXene flakes shown in Figure
37 1a is based on our previous computational calculations.¹⁴ XRD patterns of the as-synthesized
38 pristine Ti₃C₂T_x and the u-Ti₃C₂T_x at room temperature are shown in **Figure 1b**. The u-Ti₃C₂T_x
39 sample shows a 002 diffraction peak at 7° 2θ (corresponding to a c lattice parameter of 25.3
40 Å), which corresponds well with the c lattice parameter expected for urea intercalated in a
41 planar orientation as shown in **Figure 1a**.¹⁴ However, a similar spacing was also observed for
42 the pristine MXene as a result of water intercalation.²⁶ We therefore performed vacuum
43 annealing at 110 °C to remove intercalated water molecules in both samples. The 002 peak
44 shifted to 8.6° 2θ and 6.4° 2θ for pristine Ti₃C₂T_x and the u-Ti₃C₂T_x, corresponding to c lattice
45 parameters of ~20.6 and ~27.6 Å, respectively. The interlayer spacing of pristine Ti₃C₂T_x clearly
46 decreases upon water desorption, which is not observed for u-Ti₃C₂T_x. This indicates that the
47 large interlayer spacing for u-Ti₃C₂T_x at room temperature is not due to water intercalation.
48 The difference in spacing between the two annealed MXene samples (~3.5 Å) is similar to that
49 of a previously reported change in kaolinite interlayer spacing after urea intercalation.²⁷
50 To shed light on the nature of the intercalated species, TG-MS measurements were performed
51 (**Figure 1c**). Our results show decomposition products from urea starting from 130 °C,
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representing a ~ 3.4 wt.% loss, demonstrating that urea was present in the $u\text{-Ti}_3\text{C}_2\text{T}_x$ at room temperature. The TG-MS results also show that the interlayer water that exists in pristine $\text{Ti}_3\text{C}_2\text{T}_x$ was largely replaced by urea molecules due to the difference in water weight loss from 2% for pristine $\text{Ti}_3\text{C}_2\text{T}_x$ to $<0.2\%$ in $u\text{-Ti}_3\text{C}_2\text{T}_x$. As the sample environment was dissimilar during the XRD and TG-MS measurements, there is a possibility that urea had already decomposed prior to the XRD measurements performed at 110°C in vacuum, as has been suggested in a previous study.¹⁷ This will be studied in detail in future work. Irrespective of the urea stability at high temperature, both XRD and TG-MS measurements demonstrate that urea was intercalated in $u\text{-Ti}_3\text{C}_2\text{T}_x$ at room temperature.

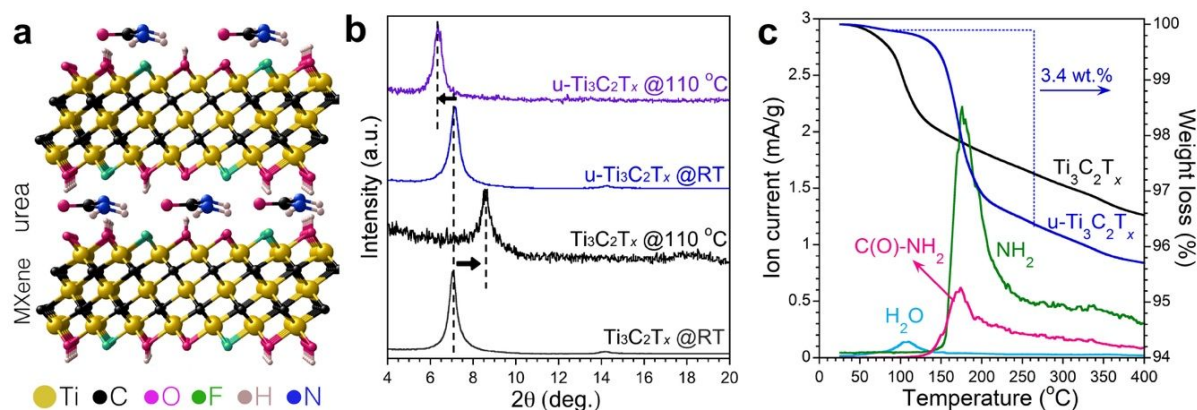


Figure 1. (a) Schematic of urea adsorption on $\text{Ti}_3\text{C}_2\text{T}_x$ from an aqueous urea solution. (b) X-ray diffraction patterns of the as-synthesized $\text{Ti}_3\text{C}_2\text{T}_x$ powder at room temperature ($\text{Ti}_3\text{C}_2\text{T}_x$ @RT) and after annealing at 110°C ($\text{Ti}_3\text{C}_2\text{T}_x$ @ 110°C), $\text{Ti}_3\text{C}_2\text{T}_x$ after urea adsorption at room temperature ($u\text{-Ti}_3\text{C}_2\text{T}_x$ @RT) and after annealing at 110°C ($u\text{-Ti}_3\text{C}_2\text{T}_x$ @ 110°C). The arrows show the change in position of the 002 diffraction peaks after vacuum annealing at 110°C . (c) Thermogravimetric analysis for pristine $\text{Ti}_3\text{C}_2\text{T}_x$ and $u\text{-Ti}_3\text{C}_2\text{T}_x$, and mass spectrometry from the $u\text{-Ti}_3\text{C}_2\text{T}_x$.

The electrochemical behavior of $\text{Ti}_3\text{C}_2\text{T}_x$ and $u\text{-Ti}_3\text{C}_2\text{T}_x$ MXenes was investigated using three-electrode cells assembled in 1M H_2SO_4 electrolyte (see SI). **Figure 2a** shows typical cyclic voltammograms of $u\text{-Ti}_3\text{C}_2\text{T}_x$ and $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes at a scan rate of 5 mV/s. The broad redox envelop is more prominent in the case of $u\text{-Ti}_3\text{C}_2\text{T}_x$ compared to $\text{Ti}_3\text{C}_2\text{T}_x$, which can be attributed to the increased accessibility of protons and hydronium ions within the MXene galleries after the intercalation of urea molecules. Interestingly, there is a small reduction peak at -0.51 V (vs. Ag/AgCl) for the $u\text{-Ti}_3\text{C}_2\text{T}_x$ electrode, which is absent in the case of $\text{Ti}_3\text{C}_2\text{T}_x$. This is probably due to the protonation of urea molecules at low scan rates, as a reduction peak at high scan rates (>20 mV/s) is absent, as shown in **Figure S2**. The areal (volumetric) capacitance of $u\text{-Ti}_3\text{C}_2\text{T}_x$ increases dramatically, and is found to be 1100 mF/cm² (110 F/cm³), which is 56% higher compared to pristine $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes. Please note that the volumetric capacitance of $u\text{-Ti}_3\text{C}_2\text{T}_x$ electrodes (ultrathick electrodes, ~ 100 μm at mass loading of 20 mg/cm²) should not be compared with the few micron thick MXene electrodes ($\sim 1\text{-}5$ μm at mass loading of $1\text{-}3$ mg/cm²) reported by Lukatskaya et al.²⁸ as the investigated electrode here is powder-based rather than a freestanding film electrode. Optimization of the electrode capacitance in terms of absolute numbers is currently in progress.

The rate retention capability of $u\text{-Ti}_3\text{C}_2\text{T}_x$ is superior relative to $\text{Ti}_3\text{C}_2\text{T}_x$ as shown in **Figure 2b**. These findings corroborate with the measured XRD, where the enlarged interlayer spacing of $u\text{-Ti}_3\text{C}_2\text{T}_x$ provides not only a greater number of electrochemically active sites, but also facilitates much faster diffusion of electrolyte ions relative to $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes. Likewise, charge-discharge profiles at a current density of 1.5 A/g reveal higher capacitance for $u\text{-Ti}_3\text{C}_2\text{T}_x$ relative to $\text{Ti}_3\text{C}_2\text{T}_x$, as illustrated in **Figure 2c**. Importantly, the $u\text{-Ti}_3\text{C}_2\text{T}_x$ electrode exhibits superior ion transport kinetics relative to $\text{Ti}_3\text{C}_2\text{T}_x$. Figure 4d shows the electrochemical impedance data of $\text{Ti}_3\text{C}_2\text{T}_x$ and $u\text{-Ti}_3\text{C}_2\text{T}_x$ MXenes which supports the good capacitive and rate performance of urea intercalated $\text{Ti}_3\text{C}_2\text{T}_x$. The inset in **Figure 2d** highlights the absence of a semi-circle and 45° line in the high frequency region for the $u\text{-Ti}_3\text{C}_2\text{T}_x$ electrode, indicating a more efficient mass diffusion.

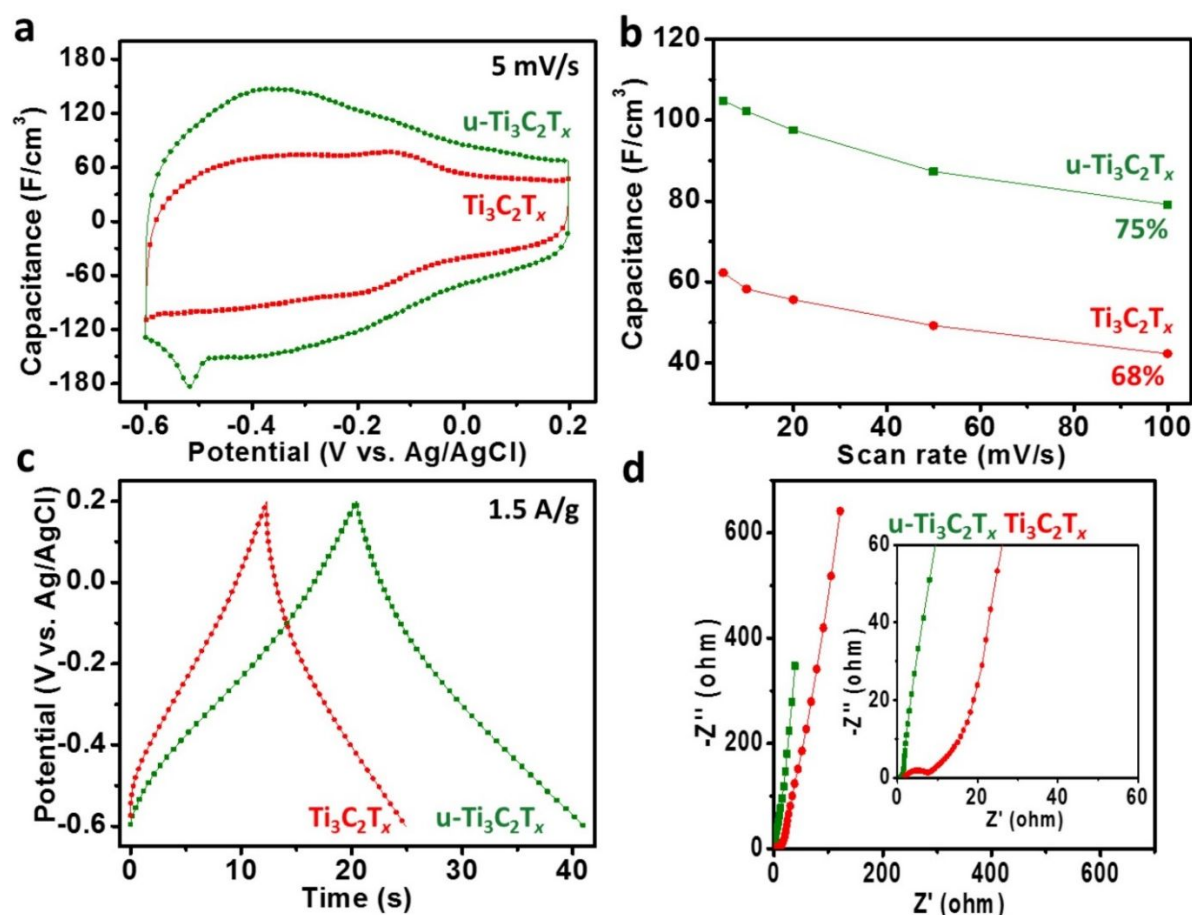


Figure 2. Comparison of the electrochemical performance between $\text{Ti}_3\text{C}_2\text{T}_x$ and $u\text{-Ti}_3\text{C}_2\text{T}_x$ electrodes in 1M H_2SO_4 electrolyte. (a) Cyclic voltammograms at 5 mV/s. (b) Volumetric capacitance versus scan rate shows 75% retention in $u\text{-Ti}_3\text{C}_2\text{T}_x$ relative to 68% for $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes at 100mV/s scan rate. (c) Galvanostatic charge-discharge profiles at a current density of 1.5 A/g, (d) Electrochemical impedance spectra of MXene electrodes at various frequency regimes.

The oxidation state of the Ti atoms in $\text{Ti}_3\text{C}_2\text{T}_x$ constitutes a key element in the electrochemical performance. To investigate the oxidation state of the Ti atoms, the XAS technique was applied before and after urea intercalation in different environments. **Figure 3a** shows X-PEEM images taken in vacuum at the Ti L-edge of individual $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes before and after urea intercalation. The flakes were found to be a few micrometers in diameter, with sharp edges. The yellow and green marked areas in **Figure 3a** serve to highlight the specific regions

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3 denoted as center and edge, respectively, from which XA spectra of the Ti L-edge were
4 extracted from the spectral images. The Ti L-edge is related to the excitation of Ti $2P_{3/2}$ (L_3 -
5 edge) and Ti $2P_{1/2}$ (L_2 -edge) core levels to an unoccupied Ti 3d state. Due to the ligand field
6 induced by binding with oxygen, the Ti L_3 and L_2 edges are each split into two sub peaks,
7 corresponding to electronic states with t_{2g} and e_g symmetries. The e_g band is known to be
8 highly sensitive to the local environment because the Ti e_g orbitals point directly to the 2p
9 orbitals of the surrounding O atoms.^{29,30}

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11 For the $Ti_3C_2T_x$ MXene flake, the splitting of the L_3 edge into t_{2g} and e_g sub-bands was observed
12 at each location on the flake but is more defined at the edge. The onset of the Ti L-edge, shown
13 in **Figure 3b**, also varies between the edge and the center of the flake and is used to estimate
14 the Ti oxidation state. The onset energy shifts from 454.6 eV at the center compared to 455.0
15 eV at the edge of the flake, corresponding to an estimated oxidation state slightly higher than
16 Ti^{3+} at the center while the edge position is relatively close to Ti^{4+} (see **Figure S3a**).

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18 For the u- $Ti_3C_2T_x$ MXene flake, the X-PEEM-based XAS reveals that the L_3 feature splits into
19 two pronounced sub-bands corresponding to the t_{2g} and e_g peaks. The pre-edge onset energy
20 of 455.8 eV is independent of location on the u- $Ti_3C_2T_x$ flake and corresponds to a large
21 Ti^{4+} contribution. The Ti atoms are in a significantly higher state of oxidation relative to the
22 pristine $Ti_3C_2T_x$ MXene flake and are homogeneously oxidized over the entire flake.

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24 The oxygen distribution and local bonding environment were also characterized by X-PEEM at
25 the O K-edge. To better visualize the oxygen distribution across the flake, X-PEEM difference
26 images are shown in **Figure 3c**. A higher contrast close to the flake edges demonstrates a
27 higher oxygen content in this region for the pristine MXene, while the oxygen content appears
28 more homogeneous after urea intercalation (see also **Figure S4**). **Figure S5** shows that the
29 oxygen content on pristine $Ti_3C_2T_x$ is mostly concentrated in the first few hundreds of
30 nanometers from the edge. **Figure 3d** shows a comparison of O K-edge XA spectra for pristine
31 $Ti_3C_2T_x$ and u- $Ti_3C_2T_x$ MXenes at the center and edge positions of the flakes. The O K-edge XAS
32 exhibit two main peaks in the energy range between 529.0-535.0 eV which originate from the
33 transitions between oxygen 1s and 2p states that are hybridized with empty Ti 3d orbitals.
34 Furthermore, the O K-edge spectra also show a second set of bands in the energy region from
35 537.0-546.0 eV, which can be assigned to transitions from O 2p states that are hybridized with
36 Ti 4s and 4p states.³¹ The MXene spectral features at 530.8 and 533.2 eV are assigned to the
37 t_{2g} and e_g orbitals, respectively. However, for the pristine $Ti_3C_2T_x$, the e_g peak intensity was
38 found to be relatively low in the center, suggesting a lower average oxidation state there
39 relative to the edges.

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41 After urea intercalation, the e_g peak at 533.2 eV becomes well-resolved, as shown in **Figure**
42 **3d**. The O K-edge spectra thus emphasize the similar oxidation state across the u- $Ti_3C_2T_x$
43 MXene flake, which agrees with the Ti L-edge results (see also **Figure S3b**). Note that the
44 contribution of intercalated urea is possibly appearing between 532.5 and 534.0 eV. The
45 features observed between 537.0-540.0 eV at the u- $Ti_3C_2T_x$ edge position are attributed to the
46 SiO_2 substrate (**Figure S6**).

The higher level of Ti oxidation state at the edges of the pristine $\text{Ti}_3\text{C}_2\text{T}_x$ MXene can probably be explained by its higher exposure to water molecules and oxygen from the ambient environment during aqueous dispersion and drying in air. Indeed, the oxidation proceeds faster at the edge positions of a $\text{Ti}_3\text{C}_2\text{T}_x$ flake relative to the basal plane, which has been found to eventually contribute to an overall decrease in conductivity of MXene electrodes.^{32–35}

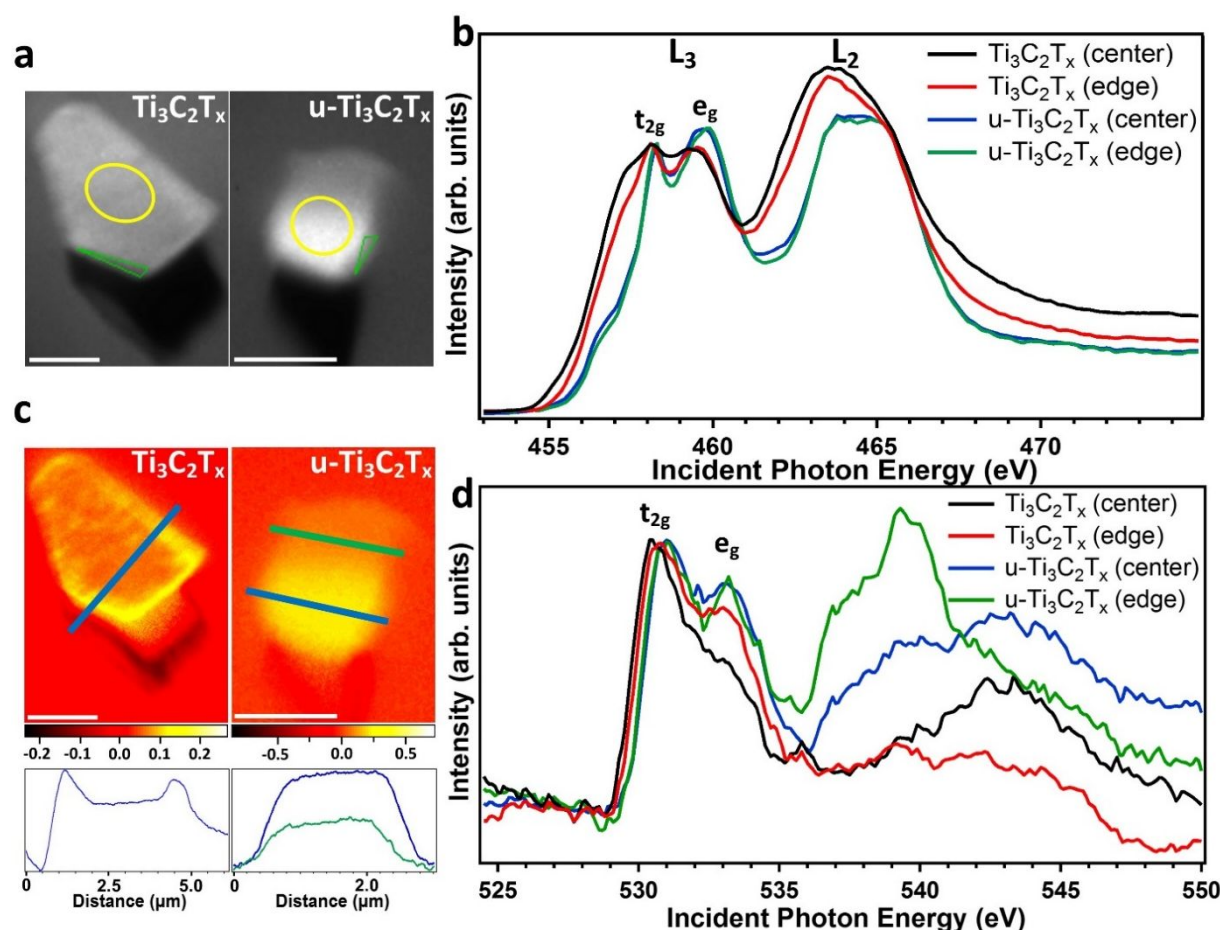


Figure 3. (a) X-PEEM micrographs at the Ti L-edge taken at an excitation energy of 463.9 eV (black and white) show individual flakes of pristine $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{u-Ti}_3\text{C}_2\text{T}_x$ MXenes (scale bar 2 μm). The regions labeled center and edge in (b, d) are highlighted in yellow and green, respectively. (b) X-PEEM Ti L-edge XA spectra of single flakes of pristine $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{u-Ti}_3\text{C}_2\text{T}_x$ MXenes. (c) Oxygen content distribution over individual MXene flakes obtained from the difference of averaged X-PEEM micrographs at the O K-edge in the t_{2g} and e_g region (530.0–534.5 eV) relative to the background (524.5–529.0 eV), the corresponding line profiles across the flake are shown underneath. (d) X-PEEM O K-edge XA spectra of pristine $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{u-Ti}_3\text{C}_2\text{T}_x$ MXene samples.

As the oxidation state of MXenes strongly influences their redox properties and despite a high Ti oxidation state (close to 4+) after urea intercalation, $\text{u-Ti}_3\text{C}_2\text{T}_x$ electrodes exhibit a reversible redox reaction as is evident from the broad redox profile shown earlier in **Figure 2a**. In order to estimate the origin of the increased Ti oxidation, *in situ* XAS measurements were also directly performed in water. The effect of aqueous solvation on the Ti oxidation state of the MXenes were monitored by comparing the Ti L-edge XA spectra of dried and dispersed pristine $\text{Ti}_3\text{C}_2\text{T}_x$ MXene multilayered powders (**Figure 4**). For the $\text{Ti}_3\text{C}_2\text{T}_x$ powder dried in air and then

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3 characterized under vacuum, the Ti L₃-edge includes a peak around 458.1 eV and a shoulder
4 at about 459.4 eV which confirms the coexistence of different Ti species, while the Ti L₂-edge
5 shows a single peak at about 463.4 eV. The XA spectra of the dried Ti₃C₂T_x MXene sample,
6 averaged over a large number of flakes, are very similar to the X-PEEM spectra recorded for
7 individual flakes. On the other hand, the dispersed Ti₃C₂T_x MXene shows no splitting of the Ti
8 L₃-edge into *t*_{2g} and *e*_g states, and a broad peak is detected at 457.4 eV. This new feature is
9 shifted by -0.7 eV compared to the maximum of the L₃ peaks of dried Ti₃C₂T_x sample, indicating
10 a lower level of the oxidation state. Estimation of the Ti oxidation state from the pre-edge
11 onset suggests a contribution from Ti²⁺ species for the dispersed sample (**Figure S 3b**).^{19,36}
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16 For u-Ti₃C₂T_x samples, the Ti L-edge XA spectra have similar profiles in both dry and solvated
17 environments, as depicted in **Figure 4**. The L_{2,3} edges split into two components separated by
18 about 5.4 eV. The Ti L₂-edge (462.3- 467.6 eV) features are broadened relative to the Ti L₃-
19 edge (457.3-461.3 eV) features, and are similar to previous reports on TiO₂ materials.²⁹ The *e*_g
20 peaks are broader than the *t*_{2g} peaks which can be attributed to a larger degree of
21 hybridization of the Ti *e*_g orbitals with O orbitals.³⁷ Unlike the pristine Ti₃C₂T_x MXenes, the
22 surface Ti atoms in both dried and solvated u-Ti₃C₂T_x MXenes have an averaged oxidation state
23 close to Ti⁴⁺, like in TiO₂. O K-edge XAS was also performed for Ti₃C₂T_x and u-Ti₃C₂T_x MXenes
24 dispersed in water, which supports the higher oxygen bonding to Ti atoms on u-Ti₃C₂T_x MXenes
25 (see **Figure S7**).
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31 These results demonstrate that the oxidation state of the Ti atoms of the pristine Ti₃C₂T_x
32 samples varies with the sample environment. The averaged Ti oxidation state of the dried
33 Ti₃C₂T_x MXene was found to be close to the Ti³⁺ species, similar to X-PEEM results. On the other
34 hand, dispersed Ti₃C₂T_x in water shows a significant contribution from Ti²⁺ species, which is
35 probably induced by a significant increase of hydroxyl groups at the MXene surface after
36 dispersion in water, inducing a reduction of Ti oxidation state. No clear *e*_g peak is observed at
37 the L₃-edges as opposed to the dry sample, showing that no Ti-O bonds with a strong σ-
38 character are detected in water. The same sample has been used for these experiments so
39 that pristine Ti₃C₂T_x MXene may be slightly oxidized upon drying in air.³² As a result, Ti₃C₂(OH)₂
40 terminations may change to Ti₃C₂O₂ terminations, resulting in an increase in the Ti oxidation
41 state to Ti³⁺.
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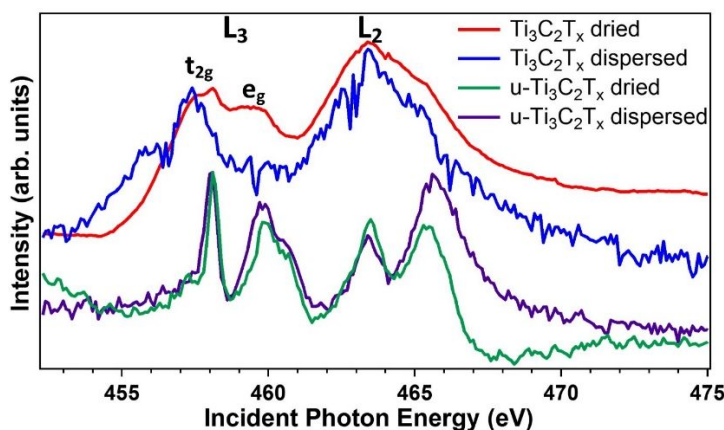


Figure 4. Ti L-edge XA spectra of dried and dispersed pristine $\text{Ti}_3\text{C}_2\text{T}_x$ and $u\text{-Ti}_3\text{C}_2\text{T}_x$ MXenes. Dispersed samples in water were characterized by XAS in Total Fluorescence Yield (TFY) mode using a flow cell and dried samples in Total Electron Yield (TEY) mode in vacuum.

In contrast, Ti atoms of the $u\text{-Ti}_3\text{C}_2\text{T}_x$ MXene appear highly oxidized both in water and after drying with an estimated average Ti oxidation state very close to Ti^{4+} . It is worth noting that the higher Ti oxidation state does not mean that the MXene samples are transformed into TiO_2 as no signature from TiO_2 is evident by the full XRD pattern shown in **Figure S1**.

Shedding light on the difference in the MXene oxidation state and surface chemistry after urea intercalation requires a thorough understanding of the intercalation mechanism. The interlayer distance of the $\text{Ti}_3\text{C}_2\text{T}_x$ planes after urea intercalation is similar but results from different intercalated molecules (water or urea, **Figure 1b**), and thus less van der Waals and hydrogen bonding between the layers.³⁸ Owing to the size of urea, the urea molecules might occupy considerable space within the interlayer distances between the MXene sheets with a preference of parallel orientation to the MXene surface.¹⁴ The increased MXene interlayer spacing may facilitate the bonding of oxygen, possibly coming from urea molecules, to the Ti atoms, and thus a higher Ti oxidation state is observed. On the other hand, the strong interaction between urea molecules and the Ti atoms on the MXene surface¹⁴ would likely prevent hydroxylation of the surface Ti atoms upon dispersion in water. Higher oxidation occurs over the entire MXene flake for $u\text{-Ti}_3\text{C}_2\text{T}_x$, while only the edges are relatively oxidized in the pristine $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. The higher Ti oxidation of $u\text{-Ti}_3\text{C}_2\text{T}_x$ is apparently not reversible after dispersion in water. The higher oxidation of surface Ti atoms after urea intercalation is most probably related to the observed higher pseudocapacitance. The latter is in full agreement with previous work on $\text{TiO}_2\text{-Ti}_3\text{C}_2$ nanocomposites showing a capacitance about 54% higher relative to pristine $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes.³⁹ Furthermore, another study revealed that having more oxidized surface group in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene lead to enhanced electrochemical performance.⁴⁰

Conclusion

In summary, the areal capacitance of multilayered $u\text{-Ti}_3\text{C}_2\text{T}_x$ powder-based electrodes is found to be 1100 mF/cm^2 , reflecting a 56% increase compared to pristine $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes.

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3 Interestingly, the diffusion of the electrolyte ions in the presence of urea was observed to be
4 very fast. We have probed the chemical environment of Ti atoms of both pristine $Ti_3C_2T_x$ and
5 $u-Ti_3C_2T_x$ MXene samples through XAS-based characterization in vacuum and aqueous
6 dispersions. Despite the high observed Ti oxidation state (close to 4+), induced by covalent
7 bonding with oxygen atoms, reversible redox reactions have been shown in $u-Ti_3C_2T_x$
8 electrodes as is evident from the broad redox profile. This suggests that a higher metal
9 oxidation state constitutes an opportunity to enhance the electrochemical performance in
10 MXene-based electrodes. The XA spectra at the Ti L- and O K-edges show that the electronic
11 structure of $Ti_3C_2T_x$ is dramatically altered after urea intercalation. Using the high spatial
12 resolution of X-PEEM, a direct mapping of the electronic structure of Ti and O atoms over a
13 single $Ti_3C_2T_x$ flake demonstrated a higher oxidation at the edges compared to the basal plane
14 of the flake while a homogeneous oxidation was detected over the entire $u-Ti_3C_2T_x$ MXene
15 flake. Finally, *in situ* XAS measurements in water demonstrated that hydration is affecting the
16 chemical bonding of Ti atoms in pristine $Ti_3C_2T_x$ MXene. This work illustrates that soft X-ray
17 absorption spectroscopy is a powerful method to probe the electronic structure of transition
18 metal oxide surface of MXenes in various environments. It paves the way to further
19 investigations on MXene surface chemistry, especially after intercalation with various
20 compounds or cations.
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35 **Supporting Information Available:** Full XRD patterns, Scan-rate dependent cyclic
36 voltammograms, details on Ti oxidation state estimation, X-PEEM and *in situ* XAS at the O K
37 edge.
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43 Author contributions

44 The manuscript was written by A.A. with contributions from all coauthors. A.A. and T.P.
45 designed and conducted the XAS measurements, and A.A. performed the entire data analysis.
46 A.A., K.A.M., F.K., and S.R. planned the X-PEEM experiments. A.A., K.A.M., F.K., M.A.M and
47 S.R. performed the X-PEEM experiments. B.A. and M.S. conducted the material synthesis, XRD,
48 and TG-MS measurements. A.A., T.P. and S.R. planned the electrochemical performance
49 measurements and it was conducted by N.K. and A.A. S.R., Y.G., and T.P. supervised the
50 research.
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Conflict of Interest

The authors declare no conflict of interest.

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TOC Graphic

