

Supporting Information for

Stability of $Ti_3C_2T_x$ MXenes in Engineered Environments

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Measuring the oxidized film's composition. Based on XPS and EDS analysis the solid reaction products (other than the comparatively small amount of Ti^{4+} released in solution) consist of a mixture of unreacted Ti_3C_2 , TiO_2 , and amorphous/graphitic carbon (C). If we describe the fractional concentrations of Ti_3C_2 , TiO_2 , and amorphous/graphitic carbon (C) in the reaction product as [MXene], [TiO_2], and [C] respectively, then;

$$[MXene] + [TiO_2] + [C] = 1 \quad (I)$$

After 1 day of exposure to chlorine:

- (1) XPS depth profiling data shows that some graphitic or amorphous carbon is formed and a small amount of $Ti_3C_2T_x$ remains. Based on peak fitting the C 1s region (Figure S8D) the overall % MXene is determined to be ≈ 0.35 . Based on the of the Ti_3C_2 stoichiometry of the MXene this means that:

$$[MXene]:[C] = 0.54 \quad (II)$$

- (2) EDS analysis indicates that the O:C ratio in the film is about 2.55. The oxygen signal arises exclusively from TiO_2 , while the C signal comes from both Ti_3C_2 and the amorphous/graphitic carbon formed. Consequently, we can write:

$$([TiO_2]/2) / (([MXene]/2) + [C]) = 2.55 \quad (III)$$

In this way, we can write three simultaneous equations with three unknowns and thereby solve for [MXene], [TiO_2], and [C]. Solving these three simultaneous equations allows us to determine that the approximate composition of the oxidized film after 1 day of chlorine exposure to be:

$$(Ti_3C_2)_{0.07}(TiO_2)_{0.80}C_{0.13}$$

Reaction	E° / V
$Cl_2 (g) + 2e^- \rightleftharpoons 2Cl^-$	1.36
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.77
$O_2 (g) + 2H_2O (l) + 4e^- \rightleftharpoons 4OH^-$	0.40

Table S1. The oxidative potentials of the oxidants present in three engineered environments present in this study.¹

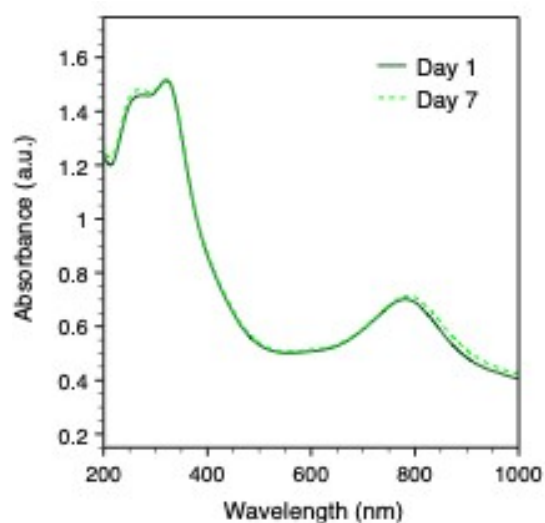


Figure S1. Stability of $Ti_3C_2T_x$ colloidal suspensions ($25 \text{ mg}\cdot\text{L}^{-1}$) at pH 6 over time. UV-vis spectra of $Ti_3C_2T_x$ suspended without chlorine for 1 day and 7 days. Samples were kept open to air at room temperature throughout the experimental timeframe.

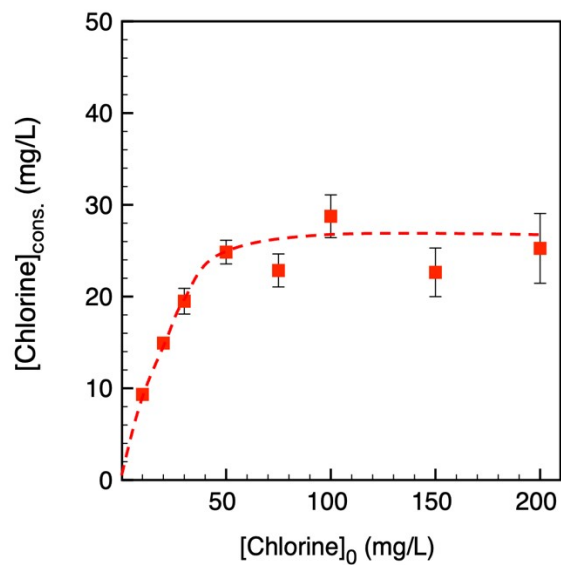


Figure S2. Concentration of free chlorine consumed throughout the reaction with $\text{Ti}_3\text{C}_2\text{T}_x$ ($25 \text{ mg}\cdot\text{L}^{-1}$) at pH 6 as a function of initial free chlorine concentration. Samples were kept open to air at room temperature throughout the experimental timeframe.

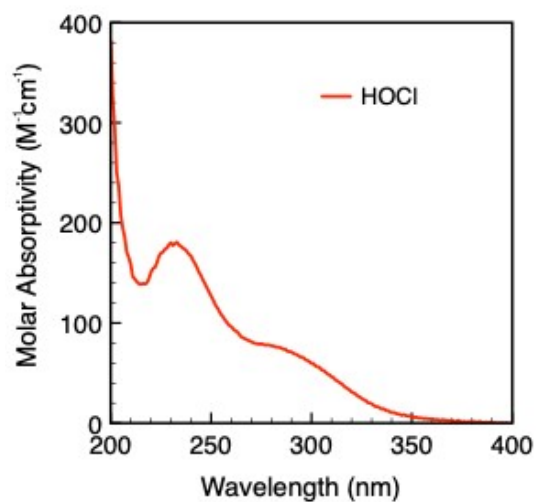


Figure S3. The molar absorptivity of HOCl as a function of wavelength determined from reference 2. Molar extinction coefficients of HOCl: $\epsilon_{\text{max},235} = 98 - 101 \text{ M}^{-1} \text{ cm}^{-1,2}$

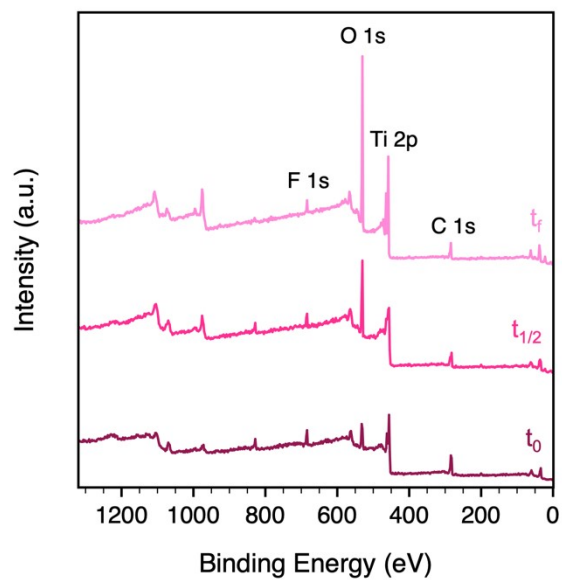


Figure S4. XPS survey spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ before and after exposure to $50 \text{ mg}\cdot\text{L}^{-1}$ free chlorine at pH 6 at varying exposure times: t_0 , $t_{1/2}$, and t_f , correspond with exposure times resulting in $[\text{MXene}]/[\text{MXene}]_0 = 1.00$, 0.50 , and ≤ 0.05 , respectively.

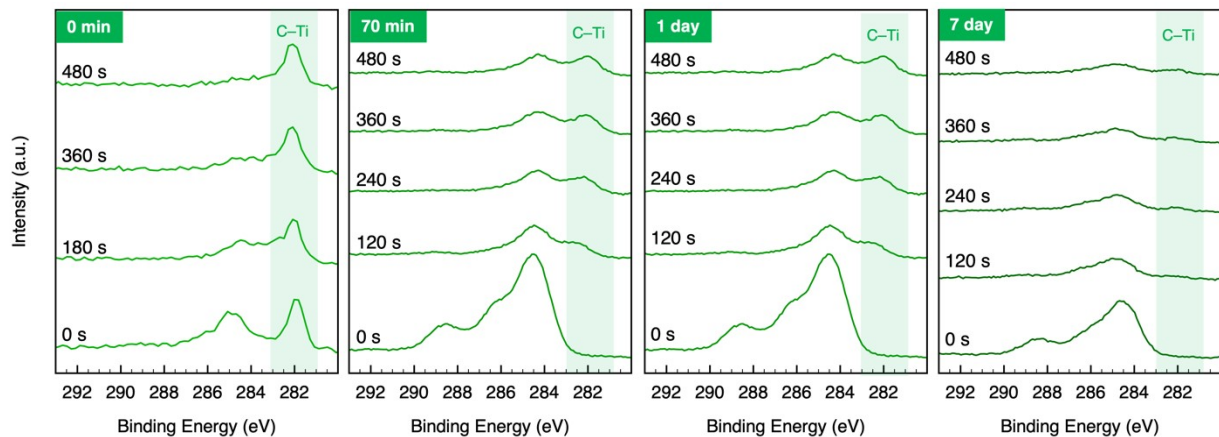


Figure S5. XPS depth profiles of C 1s region for $\text{Ti}_3\text{C}_2\text{T}_x$ before and after exposure to $50 \text{ mg}\cdot\text{L}^{-1}$ free chlorine at pH 6 after varying exposure times. The depth profile in the Ti 2p region did not show distinct peak shape change throughout the etching process except for the appearance of a lower binding energy peak around 455.4 eV which was attributed to reduced titanium produced by ion-irradiation (Figure S6).

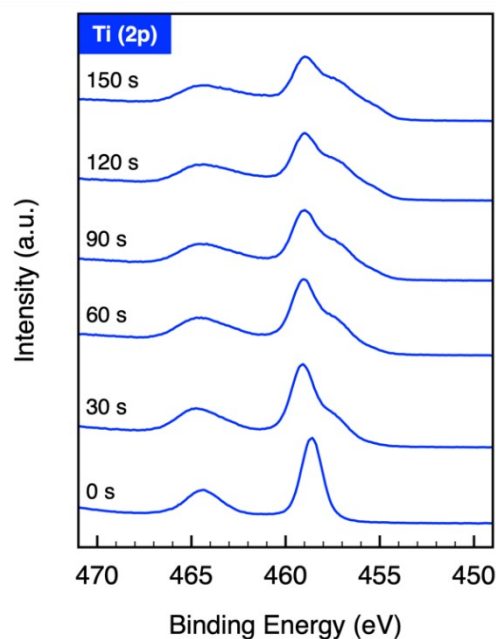


Figure S6. XPS depth profile of Ti 2p region for $\text{Ti}_3\text{C}_2\text{T}_x$ after 70 min of exposure to $50 \text{ mg}\cdot\text{L}^{-1}$ free chlorine at pH 6.

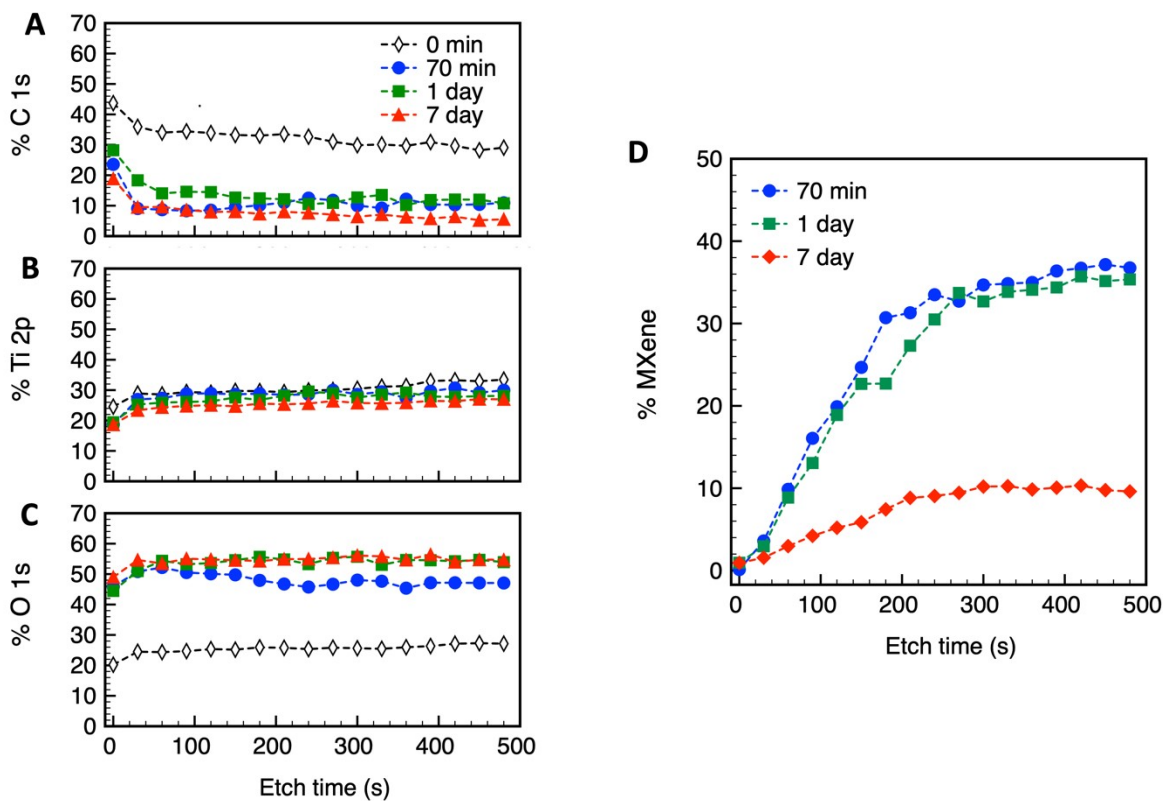


Figure S7. Approximate (A) C 1s, (B) Ti 2p, (C) O 1s and (D) $Ti_3C_2T_x$ atomic percentages for pristine and oxidized MXenes at varying chlorine exposure times based on XPS depth profile analysis.

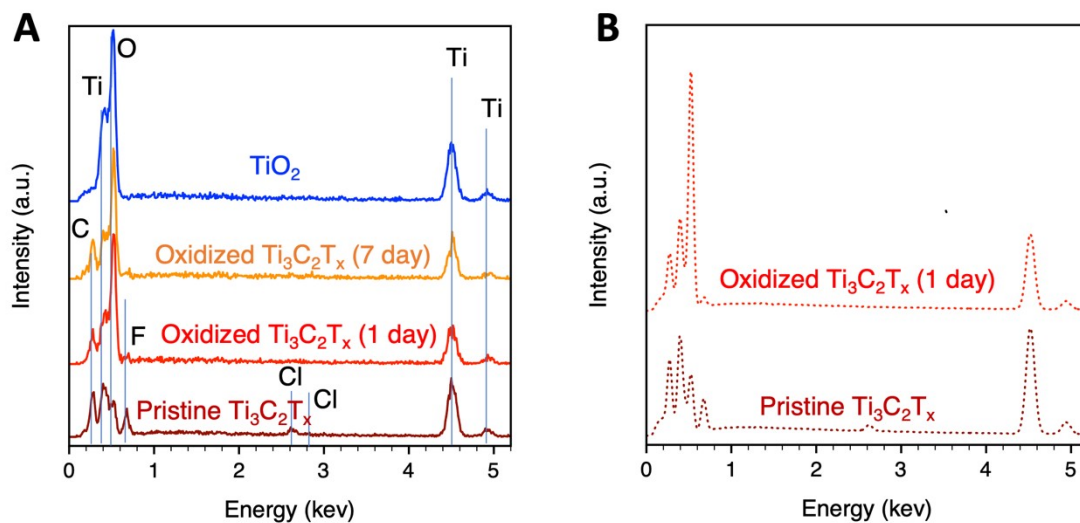


Figure S8. Full (A) experimental and (B) simulated EDS spectra of Ti₃C₂T_x before and after short (1 day) and long (7 day) exposure to 50 mg·L⁻¹ free chlorine at pH 6. For reference a TiO₂ (anatase) powder EDS spectra is also shown in A.

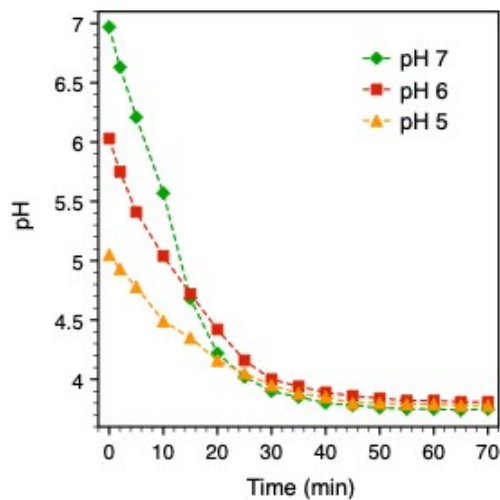


Figure S9. The decrease in pH of Ti₃C₂T_x colloidal suspensions (25 mg·L⁻¹) over time due reaction with free chlorine. Samples were prepared in DI water with 50 mg·L⁻¹ free chlorine at initial pH of 5, 6 or 7.

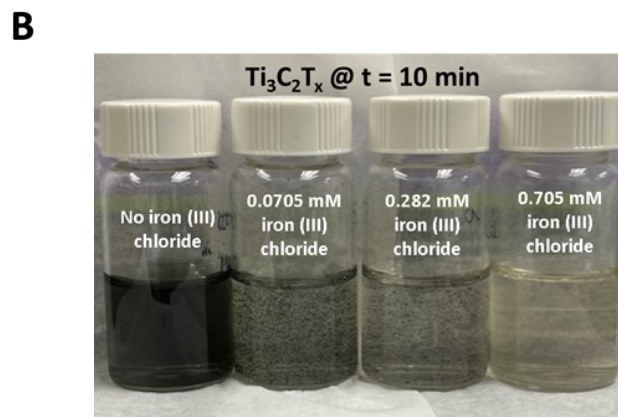
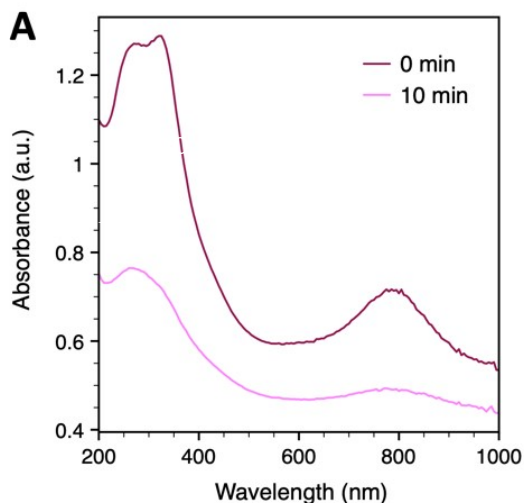


Figure S10. Reactivity of $\text{Ti}_3\text{C}_2\text{T}_x$ colloidal suspensions ($25 \text{ mg}\cdot\text{L}^{-1}$) with Fe(III) chloride. (A) UV-vis spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ suspended in water with $5 \text{ mg}\cdot\text{L}^{-1}$ free chlorine molar equivalent Fe(III) chloride ($7.05 \times 10^{-5} \text{ M}$ Fe(III) chloride) over the course of 10 minutes. There is a clear change in UV-vis spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ after 10 min of exposure. (B) Representative photographs of $\text{Ti}_3\text{C}_2\text{T}_x$ suspensions with 0 to $50 \text{ mg}\cdot\text{L}^{-1}$ free chlorine molar equivalent Fe(III) chloride after 10 minutes. All samples were kept open to air at room temperature throughout the experimental timeframe. At a higher concentration, $50 \text{ mg}\cdot\text{L}^{-1}$, the solution becomes colorless in 10 minutes, and the MXenes precipitate out.

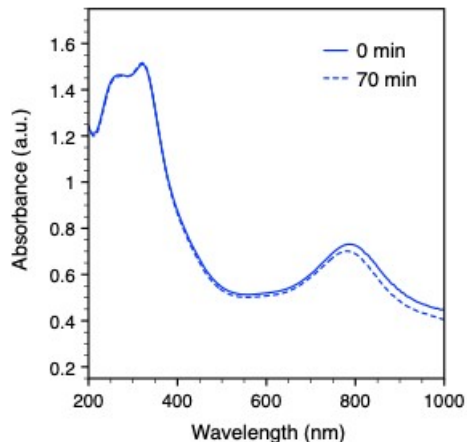


Figure S11. Reactivity of $\text{Ti}_3\text{C}_2\text{T}_x$ with saturated oxygen. UV-vis spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ ($25 \text{ mg}\cdot\text{L}^{-1}$) suspended in MQW with continuous bubbling of oxygen. The shape of the UV-Vis spectra did not change after 70 minutes of exposure to oxygen at room temperature, indicating that $\text{Ti}_3\text{C}_2\text{T}_x$ was inert in the less oxidizing environment represented by an oxygen saturated solution ($E_o = 0.40\text{V}$)

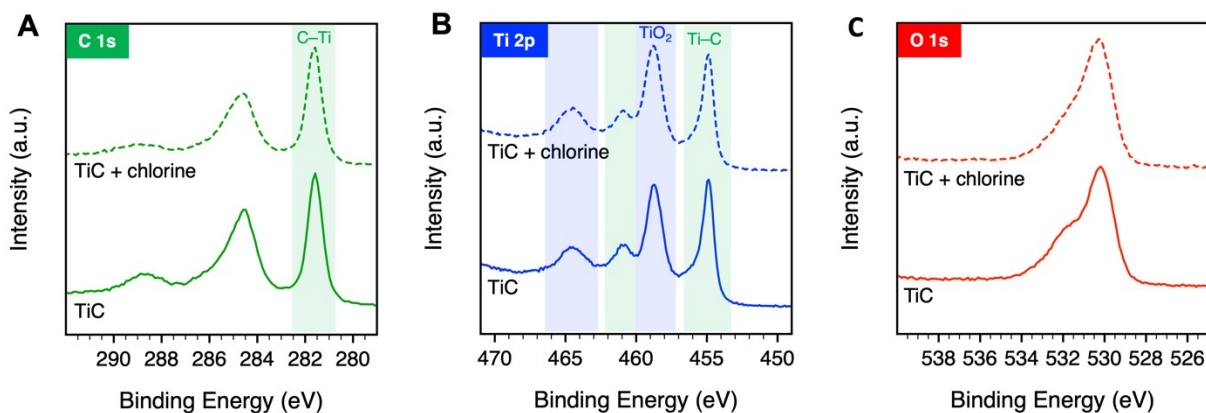


Figure S12. Reactivity of TiC with free chlorine. In these experiments, TiC suspended in phosphate buffer ($25 \text{ mg}\cdot\text{L}^{-1}$) at pH 6 was exposed to free chlorine ($50 \text{ mg}\cdot\text{L}^{-1}$) for up to 7 days. XPS spectra of (A) C 1s, (B) Ti 2p, and (C) O 1s regions of nanoscale TiC before and after exposure to $50 \text{ mg}\cdot\text{L}^{-1}$ free chlorine for one day at pH 6 are shown.

REFERENCES

- (1) Steven G. Bratsch. Standard Electrode Potentials and Temperature Coefficients in Water at 298.15K. *J. Phys. Chem. Ref. Data* **1989**, 18 (1).
- (2) Wang, D.; Bolton, J. R.; Hofmann, R. Medium Pressure UV Combined with Chlorine Advanced Oxidation for Trichloroethylene Destruction in a Model Water. *Water Res* **2012**, 4677–4686.