Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for

Ambient Oxidation of Ti_3C_2 MXene Initialized by Atomic Defects

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KEYWORDS: MXene, atomic defects, mechanism of oxidation, oxide nucleation and growth, materials stability, aberration corrected scanning transmission electron microscopy

Content: Supplementary Figures S1 to S8 and Tables S1-S3.

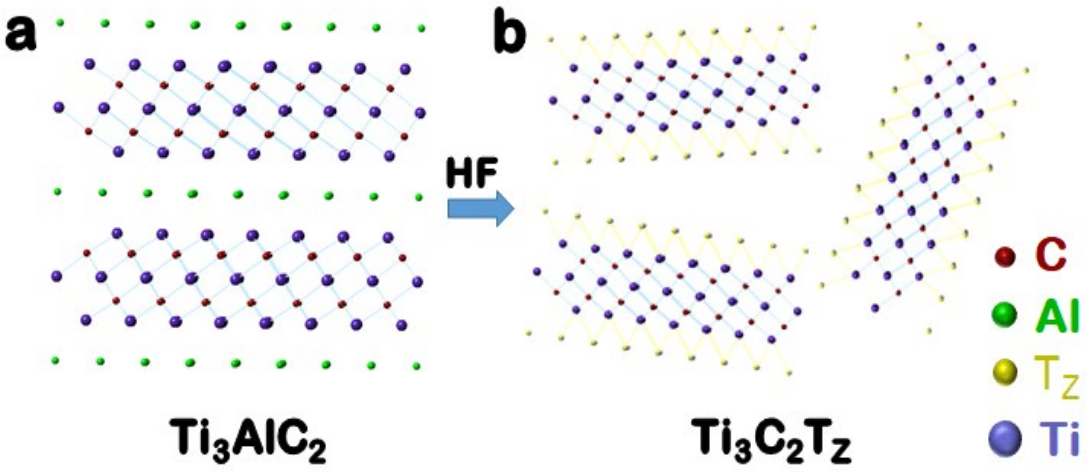

Figure S1. Schematic diagram of MXenes synthesis. (a) The layered-structured MAX phases (Ti_3AlC_2) and (b) the MXene ($Ti_3C_2T_Z$) obtained by selective etching Al atoms in the MAX phases with HF.

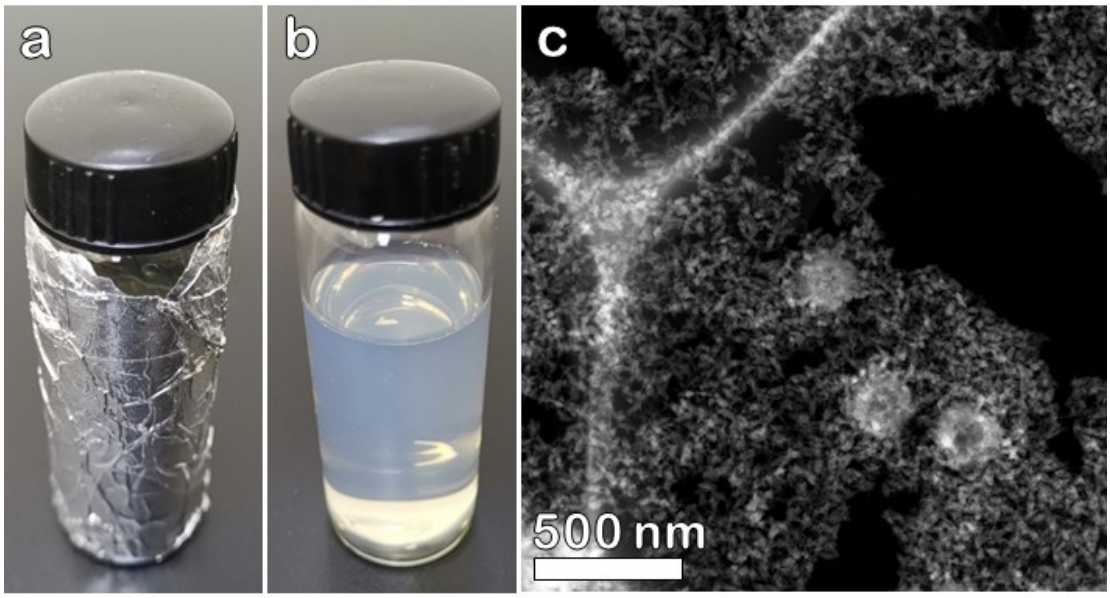

Figure S2. (a) The fresh $Ti_3C_2T_Z$ colloidal solution wrapped with tin foil and (b) the aged solution for 20 days at room temperature. (c) Corresponding HAADF-STEM image from (b).

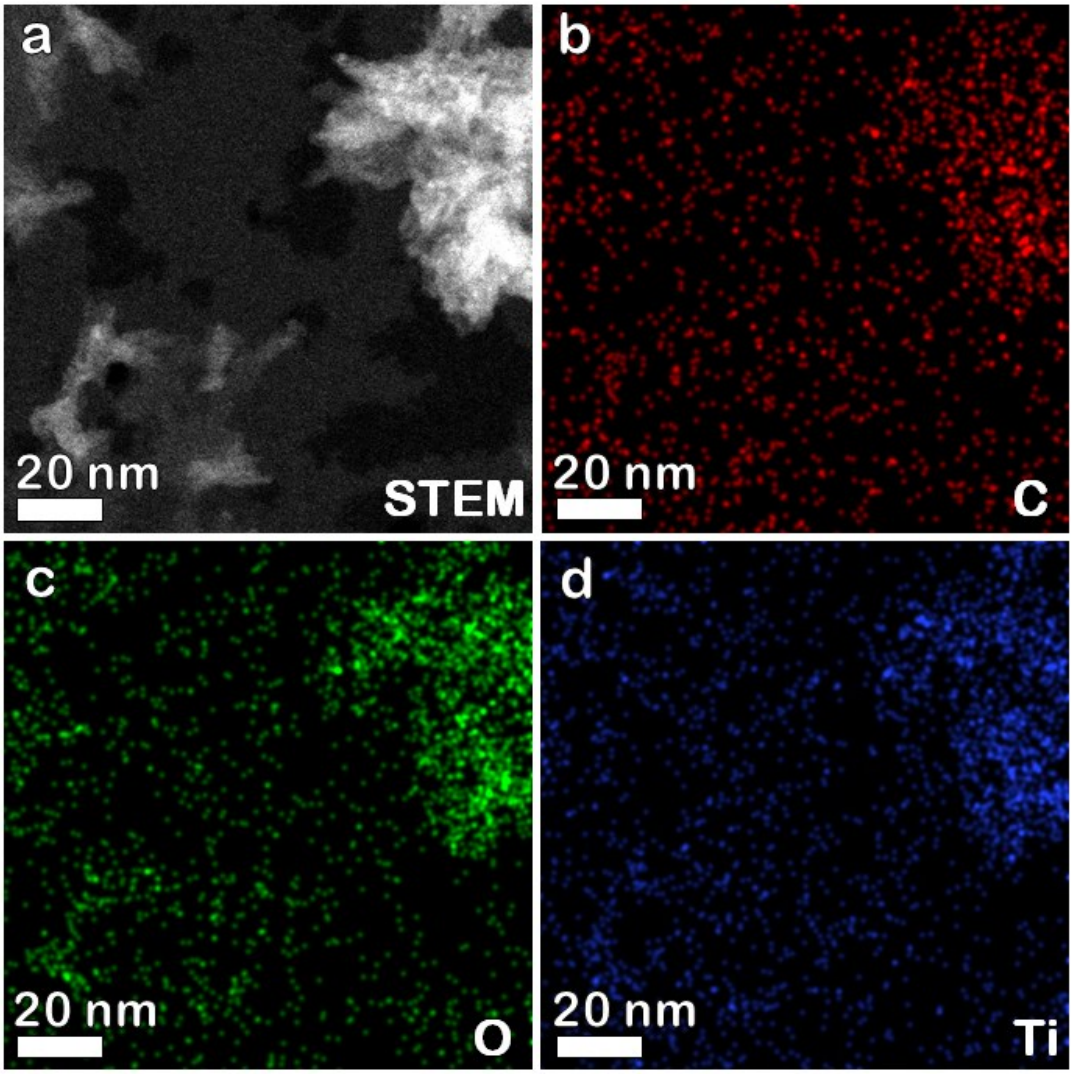

Figure S3. (a) HAADF-STEM image at low magnification, (b-d) Corresponding EDS elemental maps of the whole area in (c), C shown in red, O in green and Ti in blue.

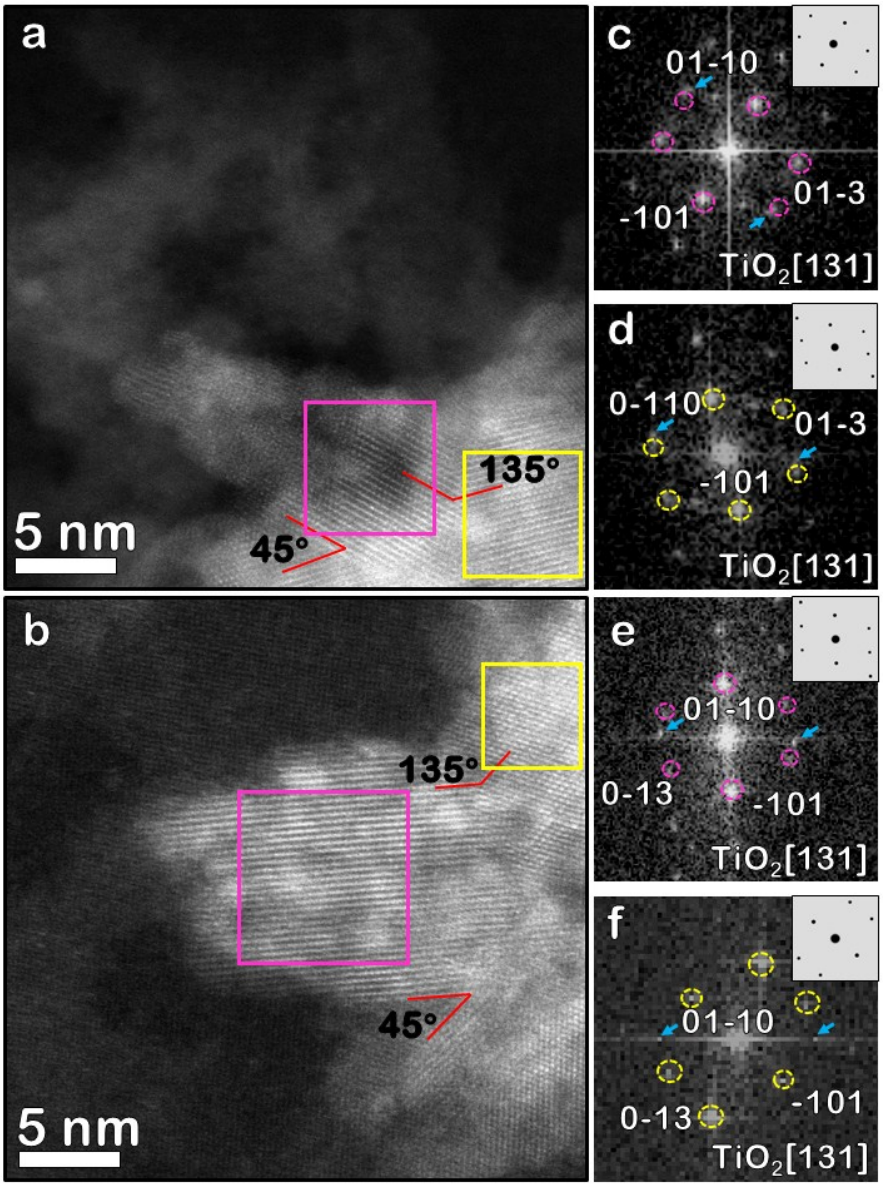

Figure S4. Phase identification of anatase TiO_2: (a-b) HAADF STEM images showing the formation of TiO_2 nanoparticles on the substrate of Ti_3C_2 MXene. (c-f) The FFT patterns of the area marked by (c) and (e) pink, (d) and (f) yellow box in (a) and (b), compared to the simulated diffractions as insets. The TiO_2 is identified as anatase phase. Additionally, the Ti_3C_2 diffraction spots marked by the blue arrows.

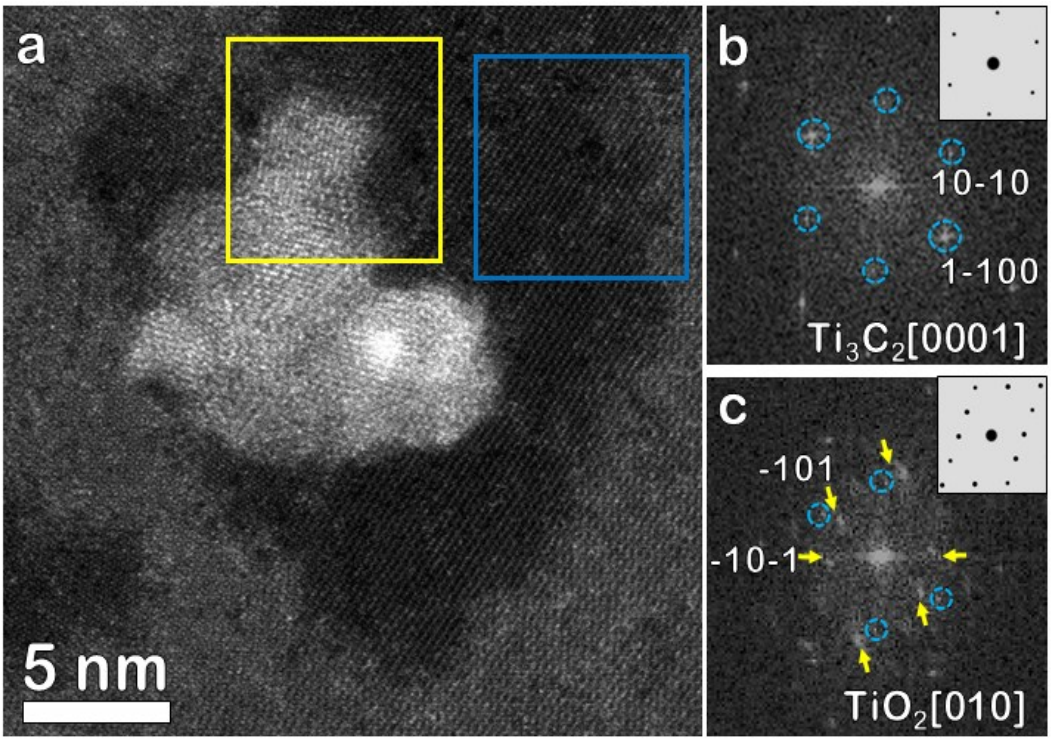

Figure S5. Other orientation relationship between anatase TiO_2 and Ti_3C_2 MXene. (a-b) HAADF STEM images showing the formation of TiO_2 nanoparticles on the substrate of Ti_3C_2 MXene. (b-c) The FFT patterns of the area marked by (b) blue, (c) pink box in (a), compared to the simulated diffractions as insets. The TiO_2 is identified as anatase phase along the [010] axis.

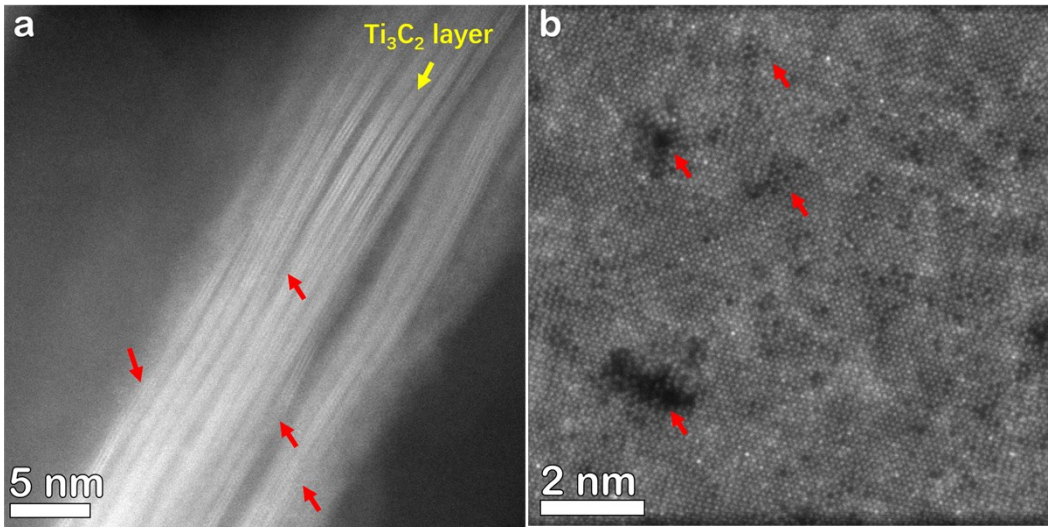

Figure S6 (a) A cross-sectional STEM image of an incomplete exfoliated Ti_3AlC_2 MAX phase, showing the generation of large amount of defects. (b) A plan-view STEM image showing the defects in the Ti_3C_2 MXene layer. The only defect found at atomic scale is the Ti-vacancy (or accumulation of many Ti-vacancies) as shown by the red arrowheads.

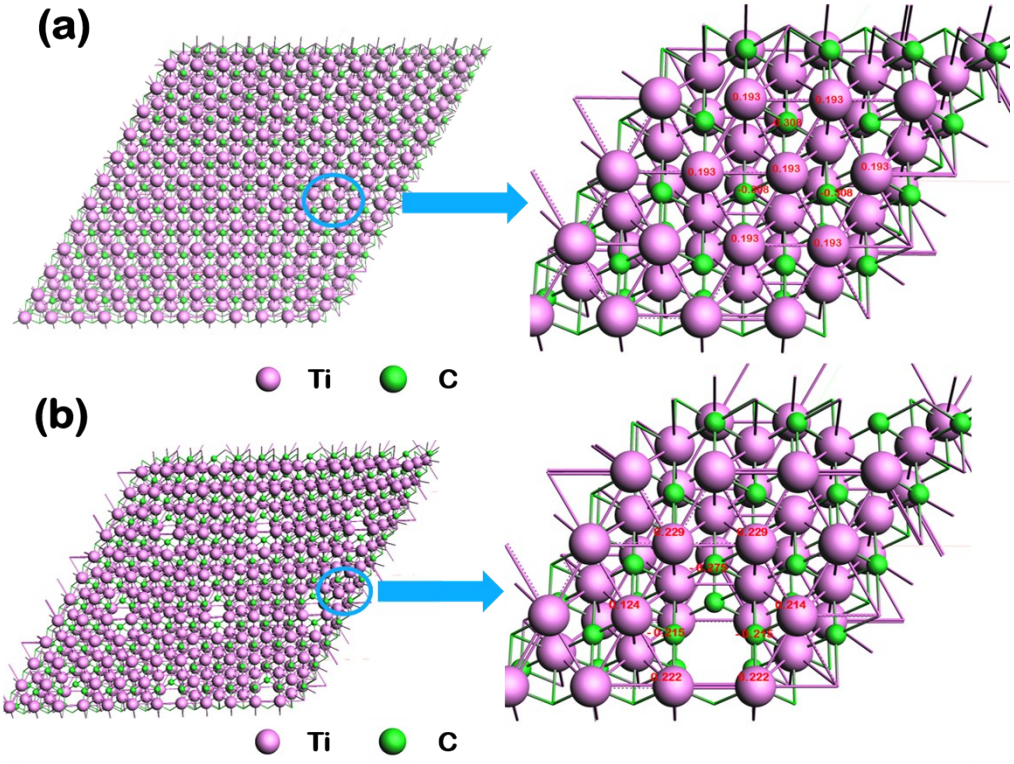

Figure S7 (a-b) Hirshfeld charge of intact Ti_3C_2 and Ti_3C_2 containing Ti-vacancies by ReaxFF calculation .

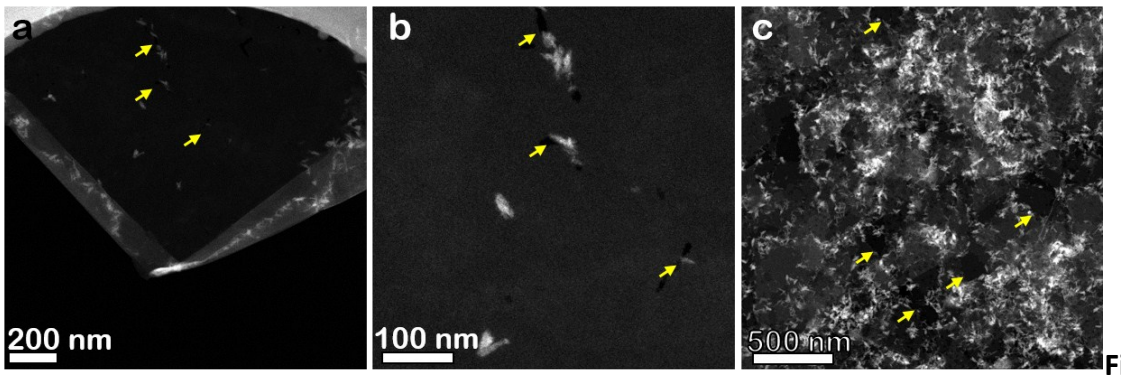

Figure S8 (a) A HAADF-STEM image showing the formation of TiO_2 nanoparticles (white contrast) along the edges and vertex of the Ti_3C_2 flake. (b) Inside the Ti_3C_2 layer, almost every nanoparticle is accompanied with a 'hole' nearby, which is a Ti-vacancy rich area. (c) With more and more TiO_2 nanoparticles appeared, there are more holes while the size of holes become large.

Table S1: Ti_3C_2-O_2 Reactions (Molar Fraction of Ti_3C_2 from 0.000-1.000)

Molar Fraction	Reaction Equation	ΔG (kJ/mol)
0.000	$O_2 \rightarrow O_2$	0
0.167	$0.833\ O_2 + 0.167\ Ti_3C_2 \rightarrow 0.5\ TiO_2 + 0.333\ CO_2$	-627.1
0.250	$0.75\ O_2 + 0.25\ Ti_3C_2 \rightarrow 0.75\ TiO_2 + 0.5\ C$	-682.5
0.286	$0.714\ O_2 + 0.286\ Ti_3C_2 \rightarrow 0.286\ Ti_3O_5 + 0.571\ C$	-657.0
0.545	$0.455\ O_2 + 0.545\ Ti_3C_2 \rightarrow 0.182\ Ti_3O_5 + 1.091\ TiC$	-469.8
0.571	$0.429\ O_2 + 0.571\ Ti_3C_2 \rightarrow 0.286\ Ti_2O_3 + 1.143\ TiC$	-449.6
0.667	$0.333\ O_2 + 0.667\ Ti_3C_2 \rightarrow 1.333\ TiC + 0.667\ TiO$	-366.6
1.000	$Ti_3C_2 \rightarrow 0.333\ Ti_8C_5 + 0.333\ TiC$	-29.20

Table S2: TiC (Ti_3C_2 with large amount of ordered Ti-vacancies)-O_2 Reactions (Molar Fraction of TiC from 0.000-1.000)

Molar Fraction	Reaction Equation	ΔG (kJ/mol)
0.000	$O_2 \rightarrow O_2$	0
0.333	$0.667\ O_2 + 0.333\ TiC \rightarrow 0.333\ TiO_2 + 0.333\ CO_2$	-459.6
0.500	$0.5\ O_2 + 0.5\ TiC \rightarrow 0.5\ TiO_2 + 0.5\ C$	-431.3
0.545	$0.455\ O_2 + 0.545\ TiC \rightarrow 0.182\ Ti_3O_5 + 0.545\ C$	-392.3
1.000	$TiC \rightarrow TiC$	0

Table S3: Ti_3C_2-H_2O Reactions (Molar Fraction of Ti_3C_2 from 0.000-1.000)

Molar Fraction	Reaction Equation	ΔG (kJ/mol)
0.000	$H_2O \rightarrow H_2O$	0
0.143	$0.857\ H_2O + 0.143\ Ti_3C_2 \rightarrow 0.286\ H_4C + 0.429\ TiO_2 + 0.286\ H_2$	-96.90
0.176	$0.824\ H_2O + 0.176\ Ti_3C_2 \rightarrow 0.353\ H_4C + 0.118\ TiH_2 + 0.412\ TiO_2$	-114.5
0.186	$0.814\ H_2O + 0.186\ Ti_3C_2 \rightarrow 0.163\ Ti_3O_5 + 0.372\ H_4C + 0.07\ TiH_2$	-118.6
0.192	$0.808\ H_2O + 0.192\ Ti_3C_2 \rightarrow 0.269\ Ti_2O_3 + 0.385\ H_4C + 0.038\ TiH_2$	-119.7
0.625	$0.375\ H_2O + 0.625\ Ti_3C_2 \rightarrow 0.125\ Ti_2O_3 + 0.375\ TiH_2 + 1.25\ TiC$	-104.0
0.667	$0.333\ H_2O + 0.667\ Ti_3C_2 \rightarrow 0.333\ TiO + 0.333\ TiH_2 + 1.333\ TiC$	-100.9
0.750	$0.25\ H_2O + 0.75\ Ti_3C_2 \rightarrow$ 0.5 Ti2HC + 0.25 TiO + TiC	-90.11
1.000	$Ti_3C_2 \rightarrow 0.333\ Ti_8C_5 + 0.333\ TiC$	-29.20