Supplementary Information:

Process Safety Analysis for $Ti_3C_2T_x$ MXene Synthesis and Processing

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SECTION S1

In this section, we have listed the assumptions used in computing the Dow Fire and Explosion Index (Dow F&EI) shown in **Figure 5b**.

Assumptions:
- Moderate exotherms for etching (equivalent to that of an oxidation reaction)
- Adequate ventilation (reaction done inside hood)
- Adequate access to laboratory in case of emergency (at least two clear doorways and easy access to fire extinguisher)
- Spills are contained (doesn't spread to other experiments or equipment)
- No air sensitive material used
- H_2 released could make the environment flammable
- MAX phase particle size is < 75 micron
- No over pressure (done at atmospheric condition)
- Minor leaks
- Agitation failure could lead to bad consequences
- No flammable liquid/gas/solids in use or stored for the process
- Reaction conditions are same for all 6 methods
- In terms of toxicity, HF of concentrations >10 wt.% have same amount of toxicity

Tables S1 through S6 shows the values assigned for each category for the 6 etching methods available in literature. The Dow F&EI used in this study is adapted from Jensen et al. which is modified for laboratory processes (Dow 1994, Jensen 1994).

S1. $Ti_3C_2X_n$ synthesis using HF (> 10 wt. %)

		Nh	**Nf**	**Nr**	**MF**
HF	**10 wt. %**	**4**	**0**	**1**	**14**
Material Factor (MF)					14
General process hazard factors					
Penalty factor description		**Value/range**			**Value**
Base penalty factor		1			1
Exothermic chemical reactions		0.30 to 1.25			0.5
Endothermic chemical reactions		0.20 to 0.40			0
Handling and transfer of materials		0.25 to 1.05			0.5
Indoor and otherwise enclosed facility		0.25 to 0.90			0.3
Access to facility		0.20 to 0.35			0
Liquid drainage from area		0.25 to 0.50			0
Total (F1)					2.3
Special process hazards factor					
Penalty factor description		**Value/range**			**Value**
Base penalty factor		1			1
Toxicity of material used		0.20 to 0.80			0.8
Operation of sub-atmospheric pressure		0.5			0
Operation in/or near flammable range		0.30 to 0.80			0.3
Dust explosion hazard		0.25 to 2.00			2
Operating pressure		0.16 to 1.50			0
Low temperature operation		0.20 to 0.30			0
Quantity of flammable or unstable material		0.12 to 4.00			0
Corrosion		0.10 to 0.75			0.2
Leakage		0.10 to 1.50			0.1
Use of direct fired equipment		0.00 to 1.00			0
Hot oil exchange system		0.15 to 1.15			0
Rotating equipment		0.5			0.5
Total (F2)					4.9
Process Unit Hazards Factors, F3					11.27
Fire and Explosion Index (F&EI)					157.78

S2. $Ti_3C_2X_n$ synthesis using LiF and HCl

		Nh	Nf	Nr	MF
LiF		2	0	0	1
HCl		**3**	**0**	**1**	**14**

Material Factor (MF)			14
General process hazard factors			
Penalty factor description	**Value/range**		**Value**
Base penalty factor	1		1
Exothermic chemical reactions	0.30 to 1.25		0.5
Endothermic chemical reactions	0.20 to 0.40		0
Handling and transfer of materials	0.25 to 1.05		0.5
Indoor and otherwise enclosed facility	0.25 to 0.90		0.3
Access to facility	0.20 to 0.35		0
Liquid drainage from area	0.25 to 0.50		0
Total (F1)			2.3
Special process hazards factor			
Penalty factor description	**Value/range**		**Value**
Base penalty factor	1		1
Toxicity of material used	0.20 to 0.80		0.6
Operation of sub-atmospheric pressure	0.5		0
Operation in/or near flammable range	0.30 to 0.80		0.3
Dust explosion hazard	0.25 to 2.00		2
Operating pressure	0.16 to 1.50		0
Low temperature operation	0.20 to 0.30		0
Quantity of flammable or unstable material	0.12 to 4.00		0
Corrosion	0.10 to 0.75		0.2
Leakage	0.10 to 1.50		0.1
Use of direct fired equipment	0.00 to 1.00		0
Hot oil exchange system	0.15 to 1.15		0
Rotating equipment	0.5		0.5
Total (F2)			4.7
Process Unit Hazards Factors, F3			10.81
Fire and Explosion Index (F&EI)			151.34

S3. $Ti_3C_2X_n$ synthesis using NH_4NF

		Nh	Nf	Nr	MF
NH_4NF		**3**	**0**	**1**	**14**

Material Factor (MF)		14
General process hazard factors		
Penalty factor description	**Value/range**	**Value**
Base penalty factor	1	1
Exothermic chemical reactions	0.30 to 1.25	0.5
Endothermic chemical reactions	0.20 to 0.40	0
Handling and transfer of materials	0.25 to 1.05	0.5
Indoor and otherwise enclosed facility	0.25 to 0.90	0.3
Access to facility	0.20 to 0.35	0
Liquid drainage from area	0.25 to 0.50	0
Total (F1)		2.3
Special process hazards factor		
Penalty factor description	**Value/range**	**Value**
Base penalty factor	1	1
Toxicity of material used	0.20 to 0.80	0.6
Operation of sub-atmospheric pressure	0.5	0
Operation in/or near flammable range	0.30 to 0.80	0.3
Dust explosion hazard	0.25 to 2.00	2
Operating pressure	0.16 to 1.50	0
Low temperature operation	0.20 to 0.30	0
Quantity of flammable or unstable material	0.12 to 4.00	0
Corrosion	0.10 to 0.75	0.2
Leakage	0.10 to 1.50	0.1
Use of direct fired equipment	0.00 to 1.00	0
Hot oil exchange system	0.15 to 1.15	0
Rotating equipment	0.5	0.5
Total (F2)		4.7
Process Unit Hazards Factors, F3		10.81
Fire and Explosion Index (F&EI)		151.34

S4. $Ti_3C_2X_n$ synthesis using FeF_3 and HCl

		Nh	Nf	Nr	MF
HCl		3	0	1	14
FeF3		**3**	**0**	**0**	**1**

Material Factor (MF)			14
General process hazard factors			
Penalty factor description	**Value/range**		**Value**
Base penalty factor	1		1
Exothermic chemical reactions	0.30 to 1.25		0.5
Endothermic chemical reactions	0.20 to 0.40		0
Handling and transfer of materials	0.25 to 1.05		0.5
Indoor and otherwise enclosed facility	0.25 to 0.90		0.3
Access to facility	0.20 to 0.35		0
Liquid drainage from area	0.25 to 0.50		0
Total (F1)			2.3
Special process hazards factor			
Penalty factor description	**Value/range**		**Value**
Base penalty factor	1		1
Toxicity of material used	0.20 to 0.80		0.6
Operation of sub-atmospheric pressure	0.5		0
Operation in/or near flammable range	0.30 to 0.80		0.3
Dust explosion hazard	0.25 to 2.00		2
Operating pressure	0.16 to 1.50		0
Low temperature operation	0.20 to 0.30		0
Quantity of flammable or unstable material	0.12 to 4.00		0
Corrosion	0.10 to 0.75		0.2
Leakage	0.10 to 1.50		0.1
Use of direct fired equipment	0.00 to 1.00		0
Hot oil exchange system	0.15 to 1.15		0
Rotating equipment	0.5		0.5
Total (F2)			4.7
Process Unit Hazards Factors, F3			10.81
Fire and Explosion Index (F&EI)			151.34

S5. $Ti_3C_2X_n$ synthesis using HCl

		Nh	Nf	Nr	MF
HCl		3	0	1	14

Material Factor (MF)			14
General process hazard factors			
Penalty factor description	**Value/range**		**Value**
Base penalty factor	1		1
Exothermic chemical reactions	0.30 to 1.25		0
Endothermic chemical reactions	0.20 to 0.40		0
Handling and transfer of materials	0.25 to 1.05		0.5
Indoor and otherwise enclosed facility	0.25 to 0.90		0.3
Access to facility	0.20 to 0.35		0
Liquid drainage from area	0.25 to 0.50		0
Total (F1)			1.8
Special process hazards factor			
Penalty factor description	**Value/range**		**Value**
Base penalty factor	1		1
Toxicity of material used	0.20 to 0.80		0.6
Operation of sub-atmospheric pressure	0.5		0
Operation in/or near flammable range	0.30 to 0.80		0.3
Dust explosion hazard	0.25 to 2.00		2
Operating pressure	0.16 to 1.50		0
Low temperature operation	0.20 to 0.30		0
Quantity of flammable or unstable material	0.12 to 4.00		0
Corrosion	0.10 to 0.75		0.2
Leakage	0.10 to 1.50		0.1
Use of direct fired equipment	0.00 to 1.00		0
Hot oil exchange system	0.15 to 1.15		0
Rotating equipment	0.5		0.5
Total (F2)			4.7
Process Unit Hazards Factors, F3			8.46

S6. $Ti_3C_2X_n$ synthesis using NaOH

		Nh	Nf	Nr	MF
NaOH		3	0	1	14

Material Factor (MF)			14
General process hazard factors			
Penalty factor description	**Value/range**		**Value**
Base penalty factor	1		1
Exothermic chemical reactions	0.30 to 1.25		0
Endothermic chemical reactions	0.20 to 0.40		0
Handling and transfer of materials	0.25 to 1.05		0.5
Indoor and otherwise enclosed facility	0.25 to 0.90		0.3
Access to facility	0.20 to 0.35		0
Liquid drainage from area	0.25 to 0.50		0
Total (F1)			1.8
Special process hazards factor			
Penalty factor description	**Value/range**		**Value**
Base penalty factor	1		1
Toxicity of material used	0.20 to 0.80		0.6
Operation of sub-atmospheric pressure	0.5		0
Operation in/or near flammable range	0.30 to 0.80		0.3
Dust explosion hazard	0.25 to 2.00		2
Operating pressure	0.16 to 1.50		0
Low temperature operation	0.20 to 0.30		0
Quantity of flammable or unstable material	0.12 to 4.00		0
Corrosion	0.10 to 0.75		0.2
Leakage	0.10 to 1.50		0.1
Use of direct fired equipment	0.00 to 1.00		0
Hot oil exchange system	0.15 to 1.15		0
Rotating equipment	0.5		0.5
Total (F2)			4.7
Process Unit Hazards Factors, F3			8.46
Fire and Explosion Index (F&EI)			118.44

SECTION S2

The gas generation calculation in **Figure 7** based on the proposed reaction pathway and synthesis recipe provided by Naguib et al. (Naguib, 2012). The reaction pathway is show below:

$$Ti_3AlC_2 + 3HF = AlF_3 + Ti_3C_2 + 3/2\ H_2$$
$$Ti_3C_2 + 2H_2O = Ti_3C_2(OH)_2 + H_2$$
$$Ti_3C_2 + 2HF = Ti_3C_2F_2 + H_2$$

Where, one mole Ti_3AlC_2 give 3.5 moles of H_2 gas. The calculation is done at isothermal condition at room temperature (~ 25C, 298 K). Following recipe is used for the gas volume calculations (Naguib, 2012): 30 mL of 6M HCl, to 2 gm of LiF, 3 gm of Ti_3AlC_2

The pressure generation accounts only in vapor space of the reactor. Therefore, the volume of the reactor mass is subtracted from the total vapor space available for gas accumulation.

References:

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3. M. Naguib, O. Mashtalir, J. Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi, and M. W. Barsoum, “Two-dimensional transition metal carbides,” ACS nano, vol. 6, no. 2, pp. 1322–1331, 2012.