Supporting Information

Oxidation-resistant titanium carbide MXene film

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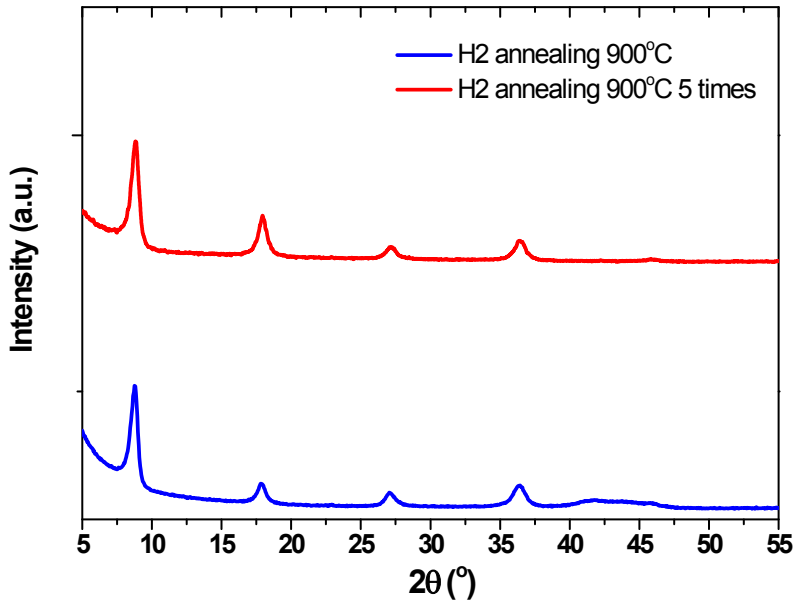

Figure S1. X-ray diffraction patterns of a Ti_3C_2 MXene film after annealing and after five repetitions of hydrogen annealing process.

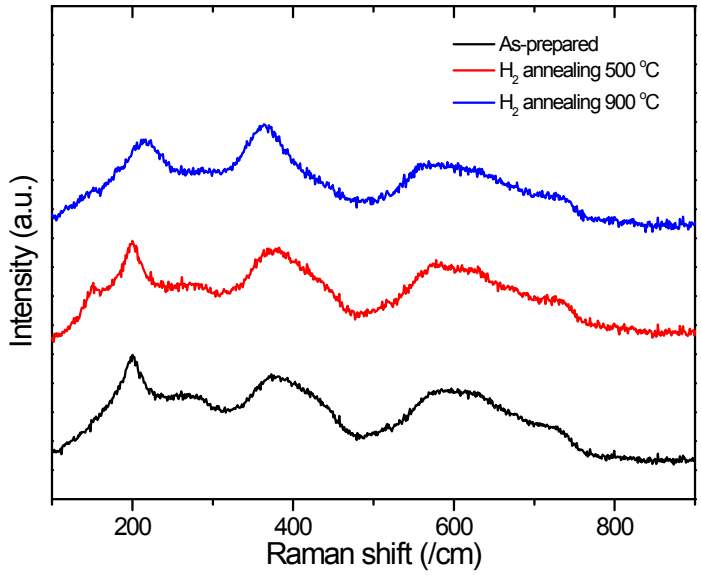

Figure S2. Raman spectra of Ti_3C_2 MXene films subjected to different annealing temperatures.

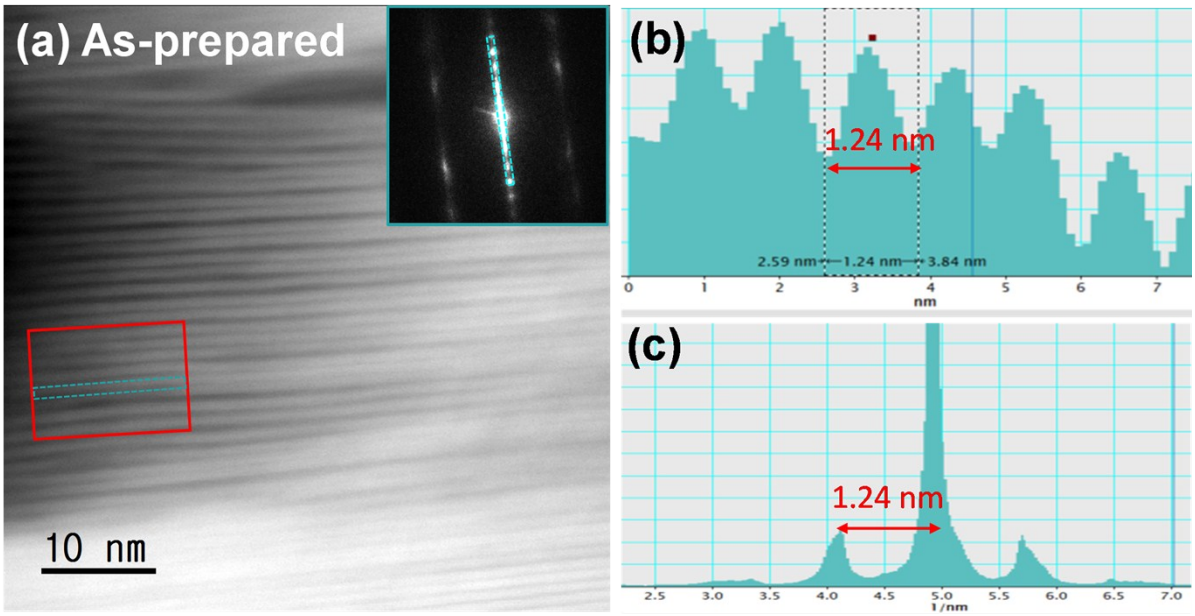

Figure S3. (a) TEM images of as-prepared sample (inset: the corresponding diffraction patterns). (b), (c) the corresponding intensity profile of as-prepared sample.

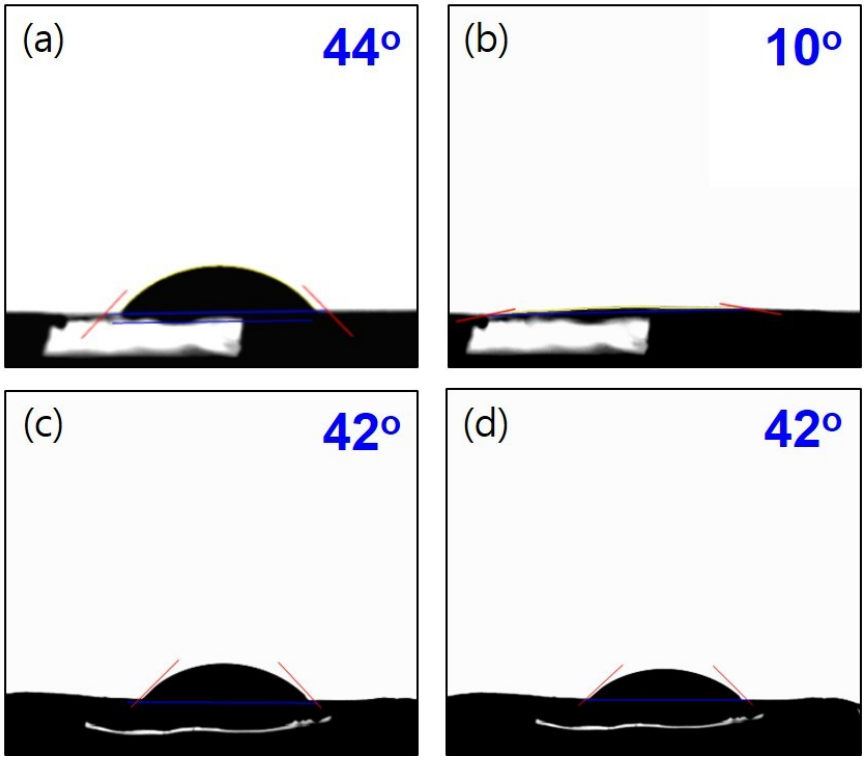

Figure S4. Results of contact angle measurements for as-prepared and hydrogen-annealed (900°C) samples. (a) as-prepared, (b) as-prepared in 10 seconds, (c) H_2-annealed (d) H_2-annealed in 1 minute.

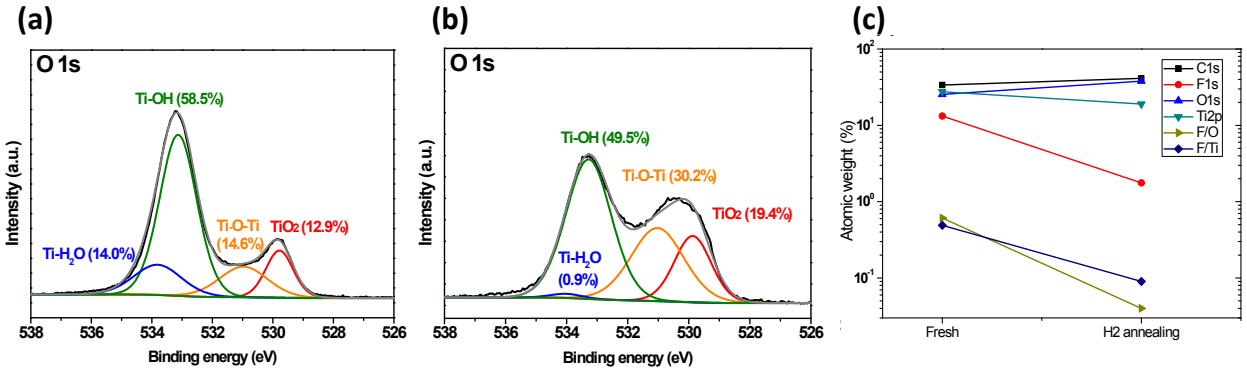

Figure S5. The O 1s regions of the XPS spectra of the (a) as-prepared and (b) hydrogen-annealed samples. (c) Changes in the ratio of fluorine functional groups after hydrogen annealing.

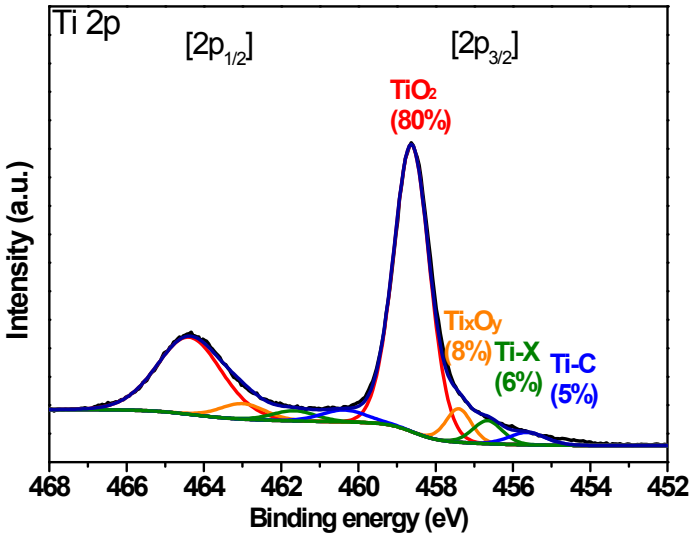

Figure S6. Component peak-fitting of the Ti 2p region of the XPS spectrum of an as-prepared Ti_3C_2 MXene film after the storage at 70°C with 100% RH for 1 day.

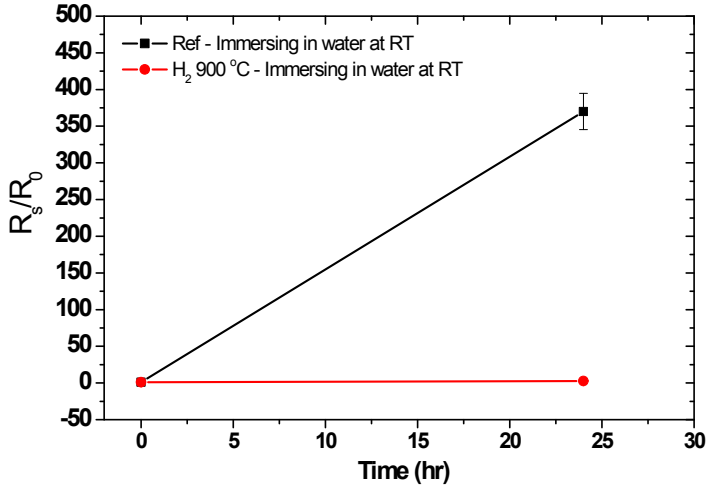

Figure S7. Change in the sheet resistance after immersion of a hydrogen-annealed sample (900 °C) and an as-prepared sample in water at room temperature for 1 day.

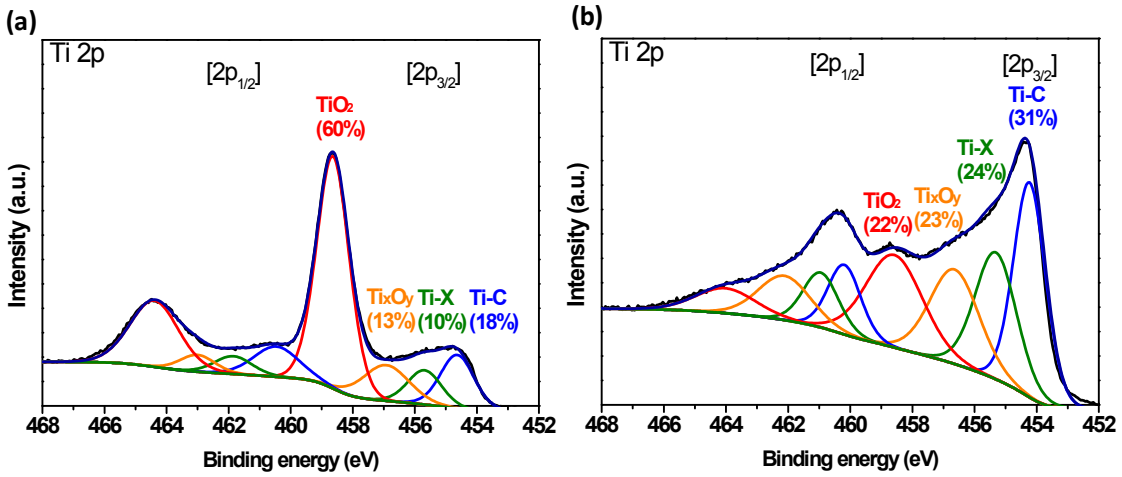

Figure S8. Component peak-fitting of the Ti 2p region of the XPS spectrum of an annealed Ti_3C_2 MXene film (a) before sputtering and (b) after sputtering, after the annealed film was kept at 70°C and 100% RH for 1 day. After sputtering, MXene layers approximately 5 nm thick were etched from the outermost surface.

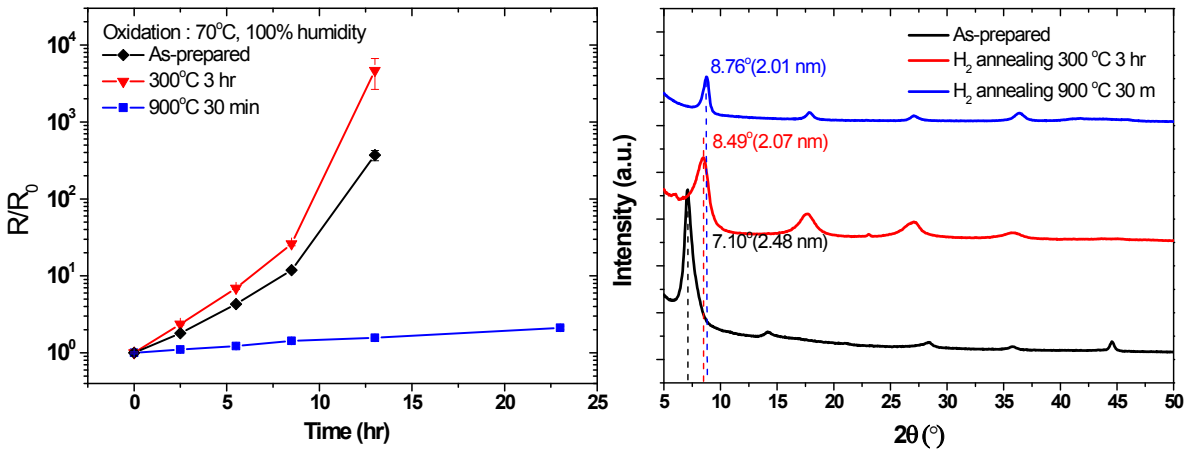

Figure S9. (a) Time evolution of the sheet resistances for as-prepared and hydrogen-annealed (300°C for 3 h and 900°C for 30 min) MXene films. (b) X-ray diffraction patterns and the corresponding d-spacings for as-prepared and hydrogen-annealed (300°C for 3 h, 900°C for 30 min) MXene films.

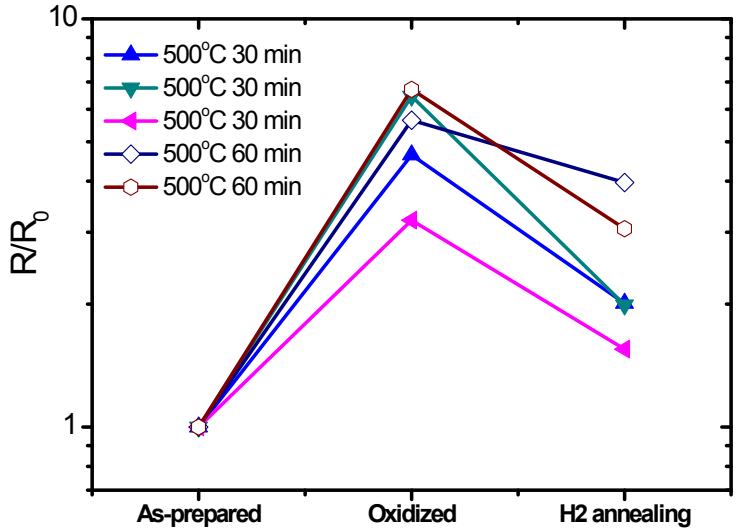

Figure S10. The changes in the sheet resistance of the Ti_3C_2 MXene film (the annealing temperature is fixed as 500 ˚C).

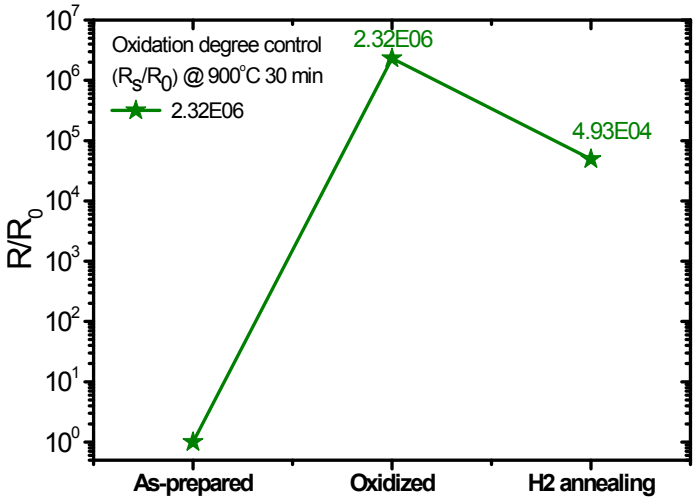

Figure S11. Changes in the sheet resistance of a highly oxidized Ti_3C_2 MXene film after the hydrogen annealing process.

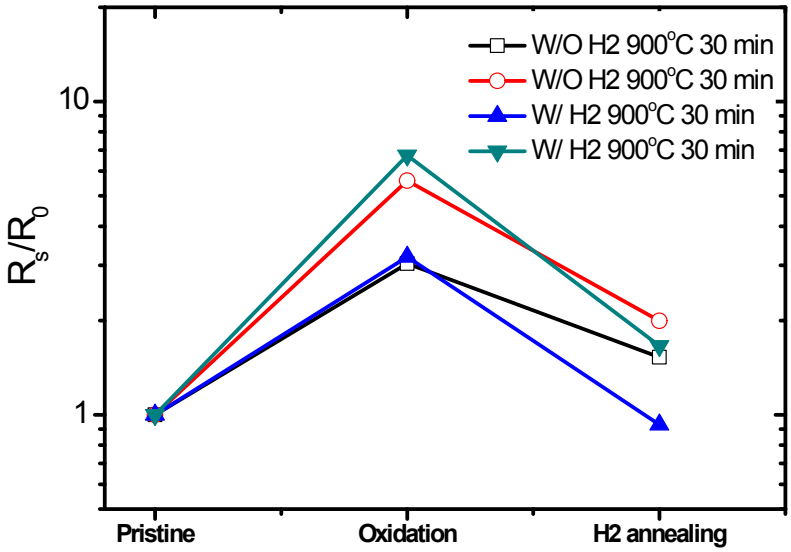

Figure S12. Changes in the sheet resistance of Ti_3C_2 MXene films annealed in the presence and absence of flowing hydrogen gas.

Table S1. Changes in the sheet resistances of the Ti_3C_2 MXene films.

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
As-prepared	Sheet resistance (Ω/sq) (R_0)	549.4	413.1	391.3	328.7	212.9	369.6	168.2	57.27	834.0	500.4	170.3	116.74	167.7	146.4	278.3
Oxidized	Sheet resistance (Ω/sq)	2663.2	1718.6	1815.1	2124.4	683.5	21424.4	491.4	283.7	3868.3	2343.3	542.9	3147.8	1130.5	2112.9	30525.3
	R_{ox}/R_0	4.9	4.2	4.6	6.5	3.2	58.0	2.9	5.0	4.6	4.7	3.2	27.0	6.7	14.4	109.7
	Conditions	100°C 30 min	300°C 30 min	500°C 30 min	500°C 30 min	500°C 30 min	500°C 30 min	500°C 30 min	500°C 30 min	700°C 30 min	900°C 30 min	900°C 30 min	900°C 30 min	900°C 30 min	900°C 30 min	900°C 30 min
H_2 annealing	Sheet resistance (Ω/sq)	2466.8	1313.9	786.0	653.0	329.9	5187.9	229.4	152.1	1180.3	621.5	159.2	350.5	277.9	350.5	1216.0
	R_{re}/R_0	4.5	3.2	2.0	2.0	1.6	14.0	1.4	2.7	1.4	1.2	0.9	3.0	1.7	3.0	4.4
$(R_{ox} - R_{re})/(R_{ox} - R_0)$		0.09	0.31	0.72	0.82	0.75	0.77	0.81	0.58	0.88	0.93	1.03	0.92	0.89	0.85	0.97

Table S2. Elemental XPS analysis of as-prepared and H_2-annealed samples in Ti, O, C, and F regions.

As-prepared						
Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Atomic %
C1s	291.96	281.93	279.08	18069.8	0.78	23.23
F1s	691	685.14	681	27694.82	1.54	12.55
O1s	540	533.2	526	61245.42	1.52	40.79
Ti2p	469	455.48	450	46557.65	2.59	23.43

H_2 annealed						
Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Atomic %
C1s	291.96	281.83	279.16	18977.04	0.77	37.75
F1s	691	685.06	681	6264.19	1.07	2.36
O1s	540	533.02	526	29455.06	2.39	36.85
Ti2p	469	455.19	450	46838.46	1.58	23.05

Table S3. The temperature profiles of the as-prepared and the hydrogen-annealed MXene films with various sheet resistances (measured at 150 s).

Sample	Sheet resistance (Ω /sq)	Temperature measured at 150 s						
		3V	6V	9V	10V	15V	20V	25V
As-prepared	6.5	33.0	61.0	119.7				
	62.5				60.7	110.8	166.3	218.7
	65.3				53.4	96.9	148.5	197.4
	75.4				48.9	80.9	123.2	166.6
H_2-annealed	13.3	40.6	83.4	142.3				
	80.2				72.2	120.5	176.2	231.2
	105.8				53.5	82.6	119.6	158.9

Table S4. Comparison of nanomaterials-based heaters.

Nanomaterials	Sheet resistance (ohm/sq)	Driving voltage (V)	T_{max} or steady state temperature (^{o}C)	Ref
Ti_3C_2 MXene (H_2 annealed)	13.3	6	83.4	This work
		9	142.3	
Ti_3C_2 MXene (H_2 annealed)	80.2	10	110.8	This work
		25	231.2	
Graphene	43	12	100	[1]
Graphene	5	30	115	[2]
AgNW	20	5	73	[3]
AgNW	30	10	200	[4]

Additional Information

In order to gain further insight on how TiO_2 is reduced and remain in the MXene structure, we performed hydrogen annealing on three types of MXene samples with different degrees of oxidation:

1) lightly oxidized sample (MXene solution aged for a week in the fridge),
2) heavily oxidized sample (MXene solution aged for 6 months in the fridge),
3) intermediately oxidized sample (MXene solution aged for 1 month in the fridge).

Also, to see the influence of hydrogen gas on TiO_2 reduction, we conducted similar experiments using different sweep gases.

1) Lightly oxidized sample

For the lightly oxidized MXene samples, TiO_2 nanoparticles were formed along the edges of the MXene flakes (Figure A2-1a). After hydrogen annealing, it was clearly visible in the SEM image (Figure A2-1b) that most of the TiO_2 nanoparticles were eliminated, which is similar to the results shown in Figure 3e, and 3f.

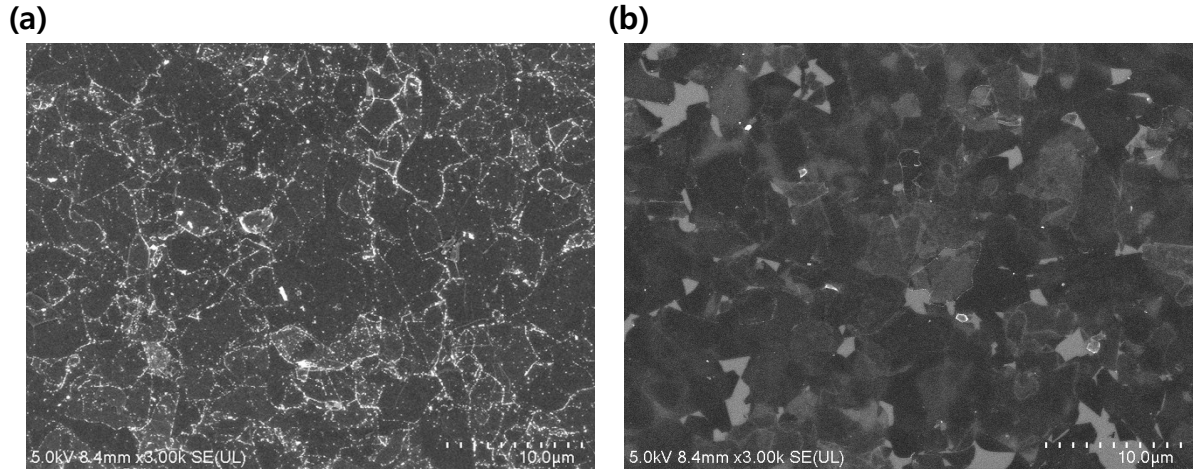

Figure A2-1. SEM images of (a) the lightly oxidized and (b) the hydrogen post-annealed Ti_3C_2 MXene films.

2) Heavily oxidized sample

For the heavily oxidized MXene samples, most particles were transformed to TiO_2 in the solution (Figure A2-2a). Also, the effect of hydrogen annealing on TiO_2 reduction does not seem to be significant. X-ray diffraction patterns for the heavily oxidized sample in Figure A2-3 shows that all the not all anatase TiO_2 particles were removed, rather, a phase transform from anatase to rutile occurs (usually considered to be the high-temperature phase relative to anatase) after hydrogen annealing.

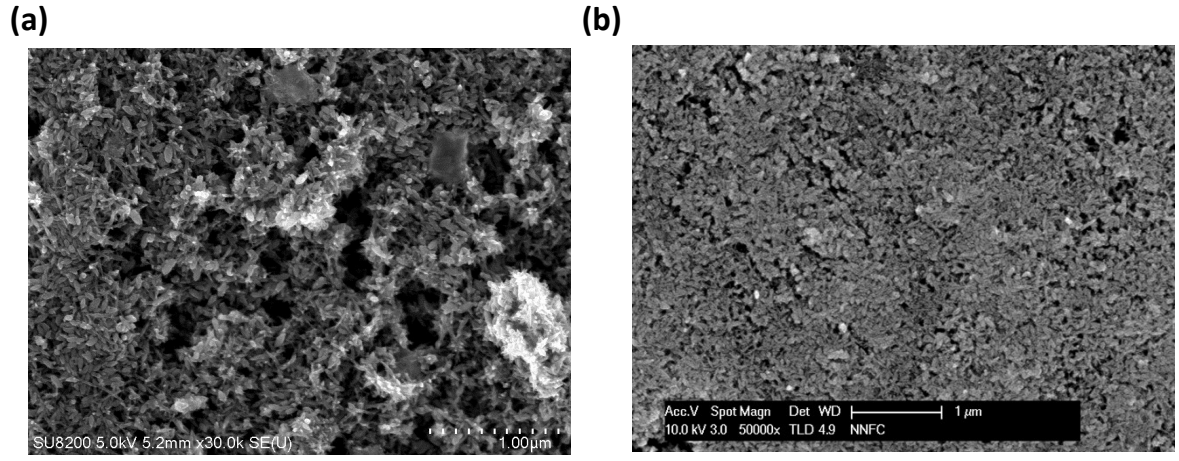

Figure A2-2. SEM images of heavily oxidized MXene film (a) before and (b) after annealing.

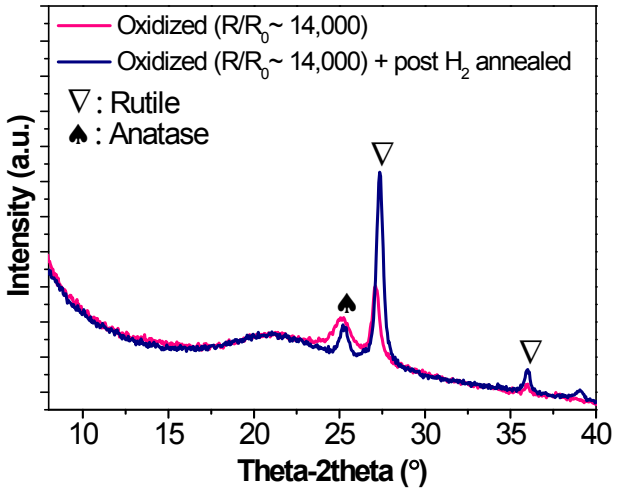

Figure A2-3. XRD patterns of a heavily oxidized sample and the hydrogen post-annealed sample (900°C).

3) Intermediately oxidized sample

For the intermediately oxidized sample, two types of particles, 1) small TiO_2 particles formed along the edges of MXene flakes, and 2) relatively large TiO_2 particles formed from the full oxidation of the MXene flake already present in the solution were observed (Figure A2-4). After hydrogen annealing, most of the small TiO_2 nanoparticles formed along the edges were eliminated, while the bigger TiO_2 particles seemed to be still present. For an annealed sample with argon sweep gas, however, no significant change of the surface state was found, even though there might be some changes in the phase of the TiO_2 particles. Ar annealing with flow rate of around 100 sccm did not bring any significant change.

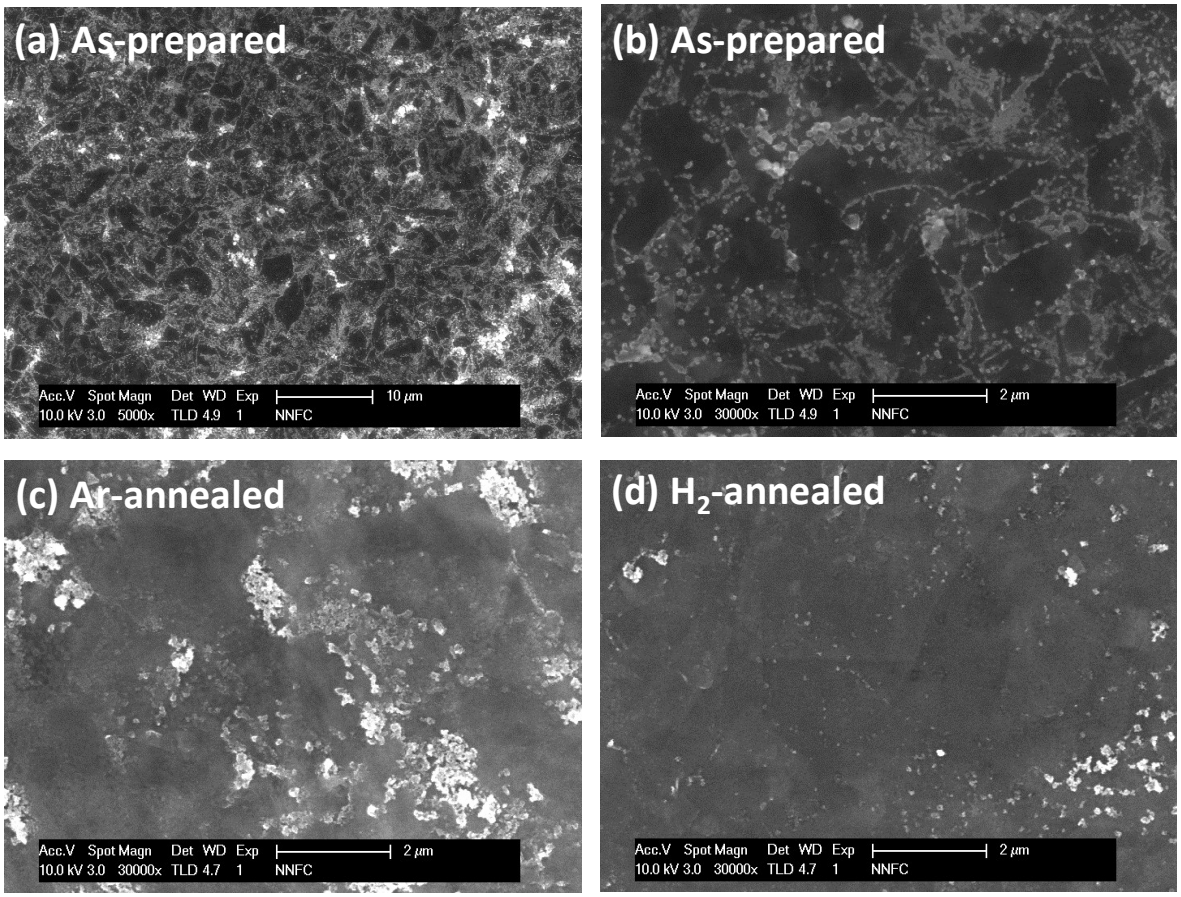

Figure A2-4. SEM images of (a) as-prepared intermediately oxidized sample, (b) is the magnified views, the corresponding samples (c) after annealing with Ar gas, and (d) after annealing with Ar/H_2 gas.

References

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