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Supplementary Information

Two Dimensional $Ti_3C_2T_x$ MXene Nanosheets for CO_2 Electroreduction in Aqueous DElectrolytes

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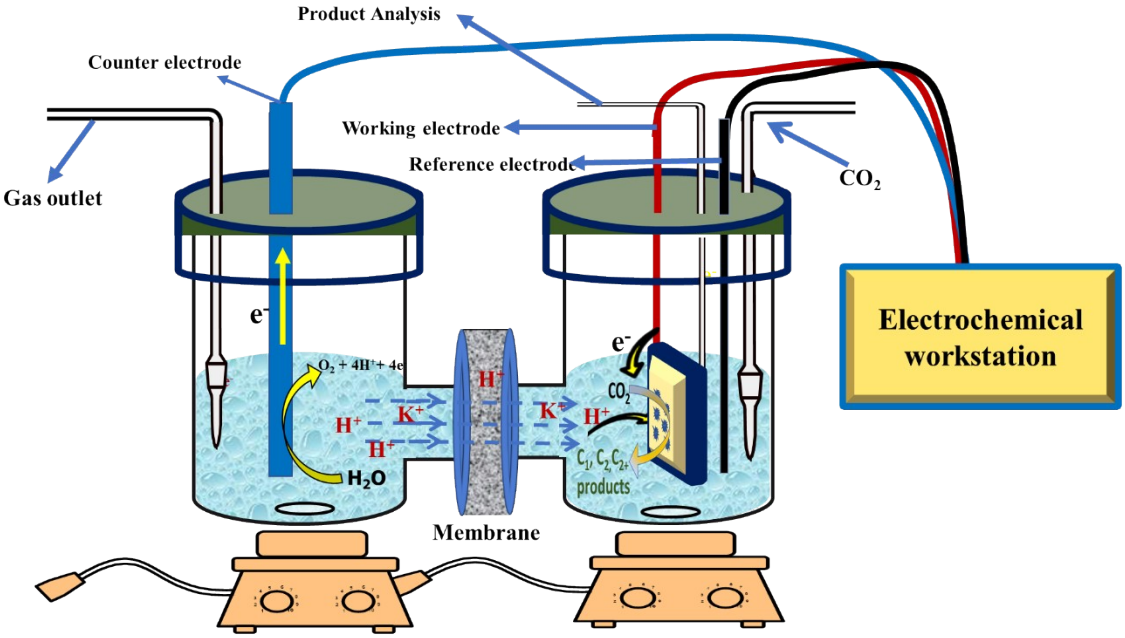

Figure S1. Schematic diagram of H-type cell

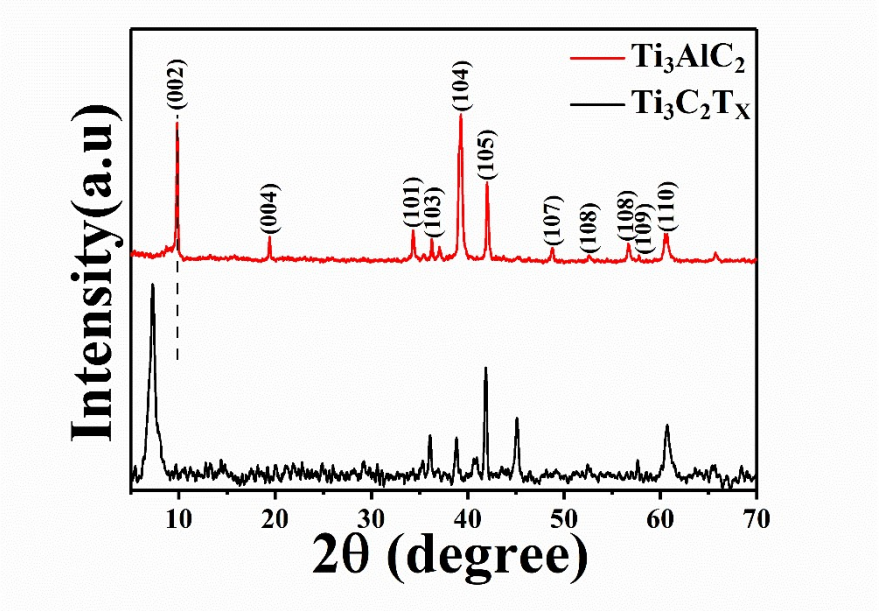

Figure S2. Powder-XRD patterns of Ti_3AlC_2 MAX phase and $Ti_3C_2T_x$

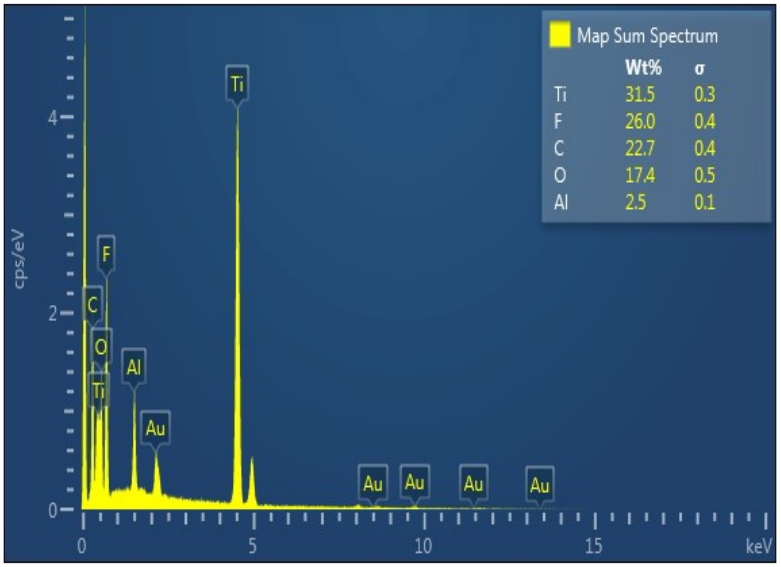

Figure S3. EDX spectra of $Ti_3C_2T_x$

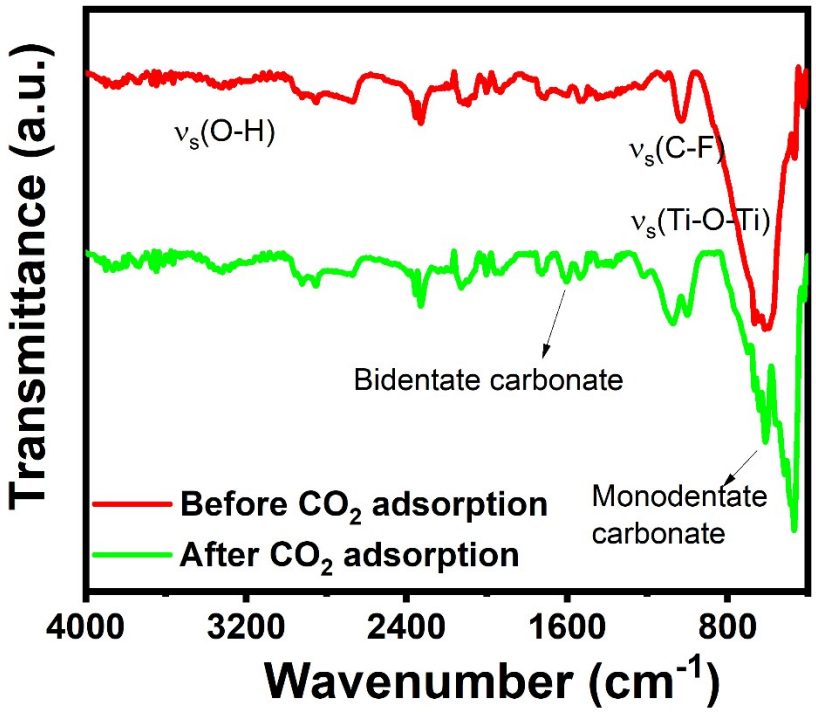

Figure S4. FT-IR spectra of $Ti_3C_2T_x$ before and after CO_2 adsorption

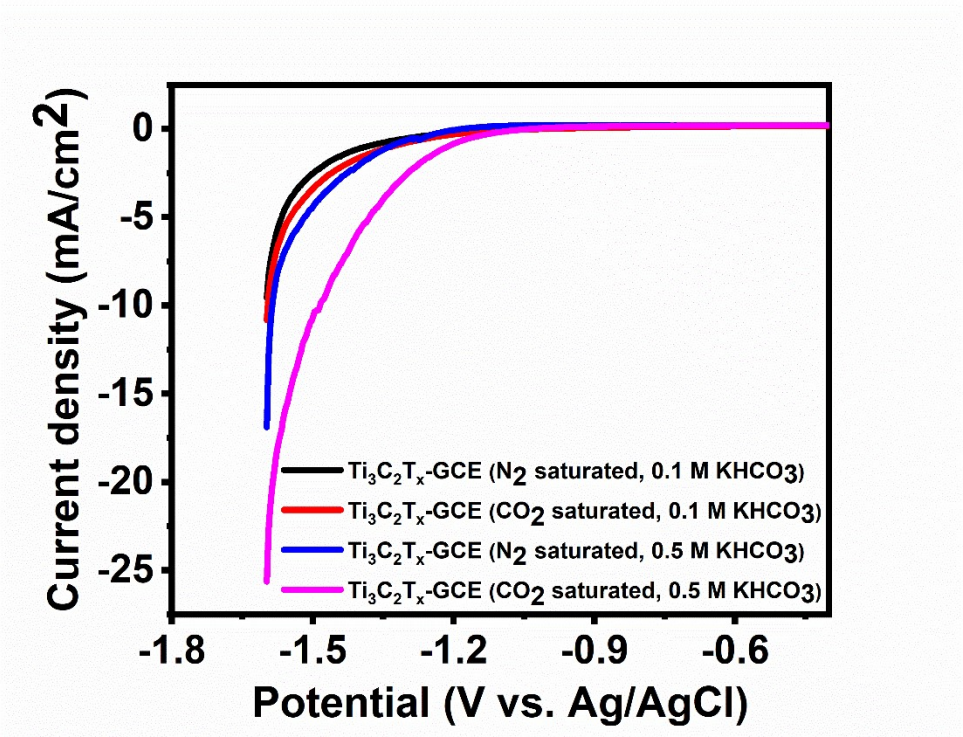

Figure S5. LSV curves comparison at two different electrolyte concentrations, 0.1 M $KHCO_3$ and 0.5 M $KHCO_3$.

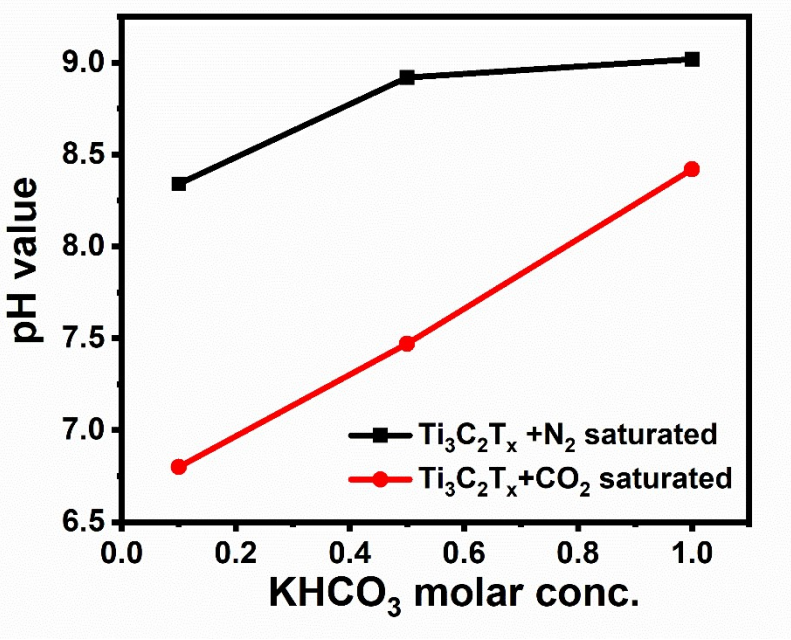

Figure S6. The pH values of the various concentration of $KHCO_3$ electrolytes before and after CO_2 purging

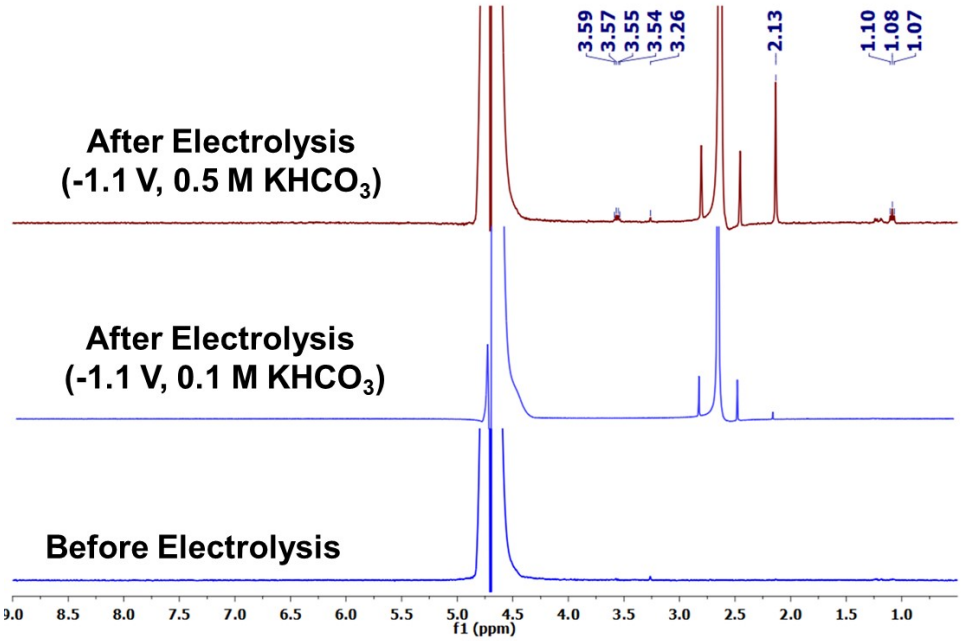

Figure S7. ^{1}H NMR spectra of electrolysis products formed in two different electrolyte concentrations before and after 3 h

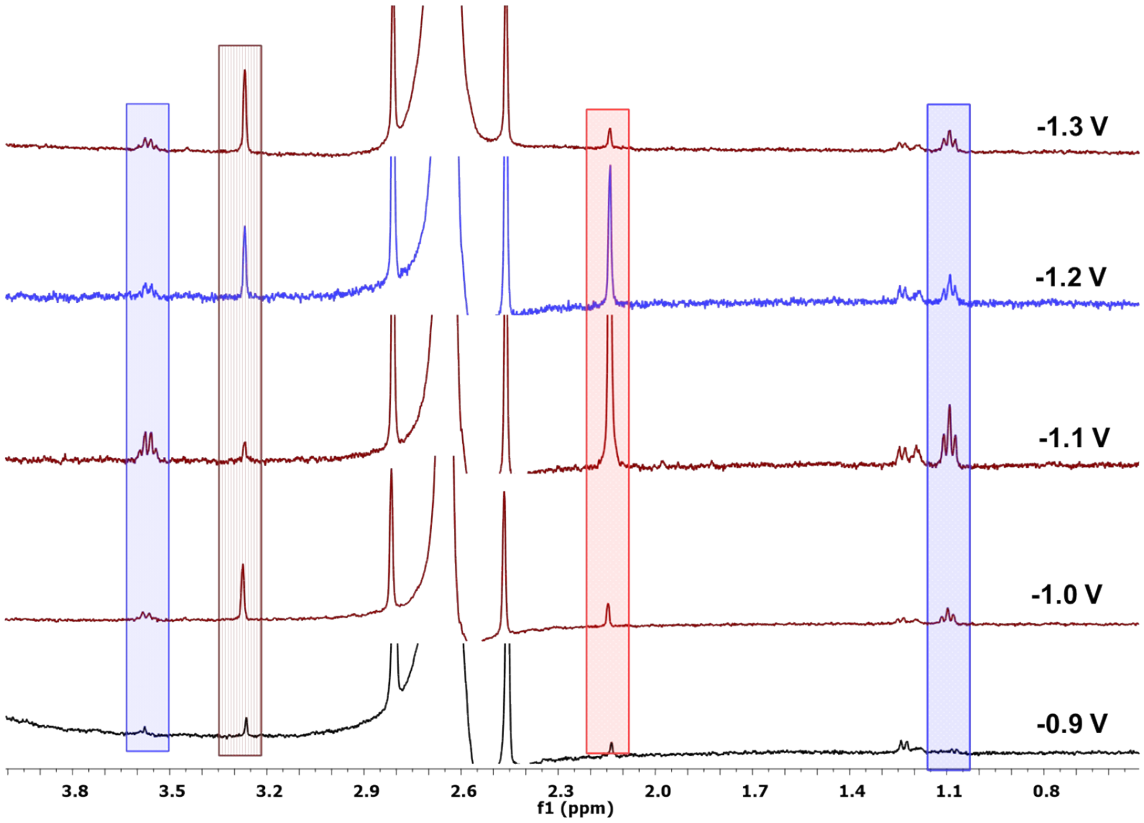

Figure S8. ^{1}H NMR spectra of products obtained from CA analysis with different potential (vs. Ag/AgCl) for 3 h.

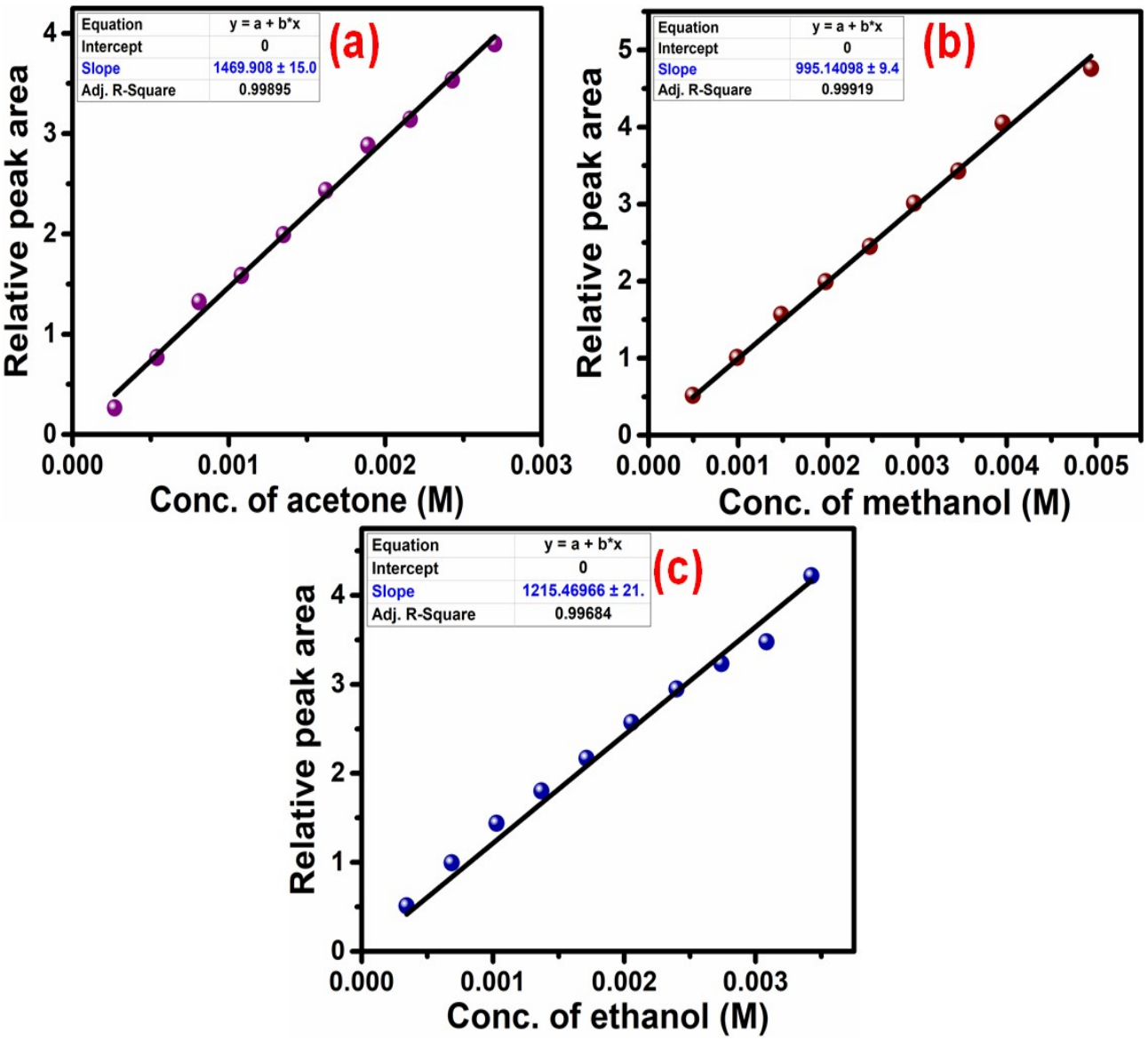

Figure S9. Linearly fitted **s**tandard calibration plots for (a) acetone, (b) methanol and (c) ethanol. The relative peak areas refer to ratios of ^{1}H-NMR peak areas (for methyl (-CH_3) protons) of the organic products (keeping a varying known concentration) with that of an internal standard DMSO (keeping a fixed known concentration) recorded in the identical solvent system as in the electrolysis.

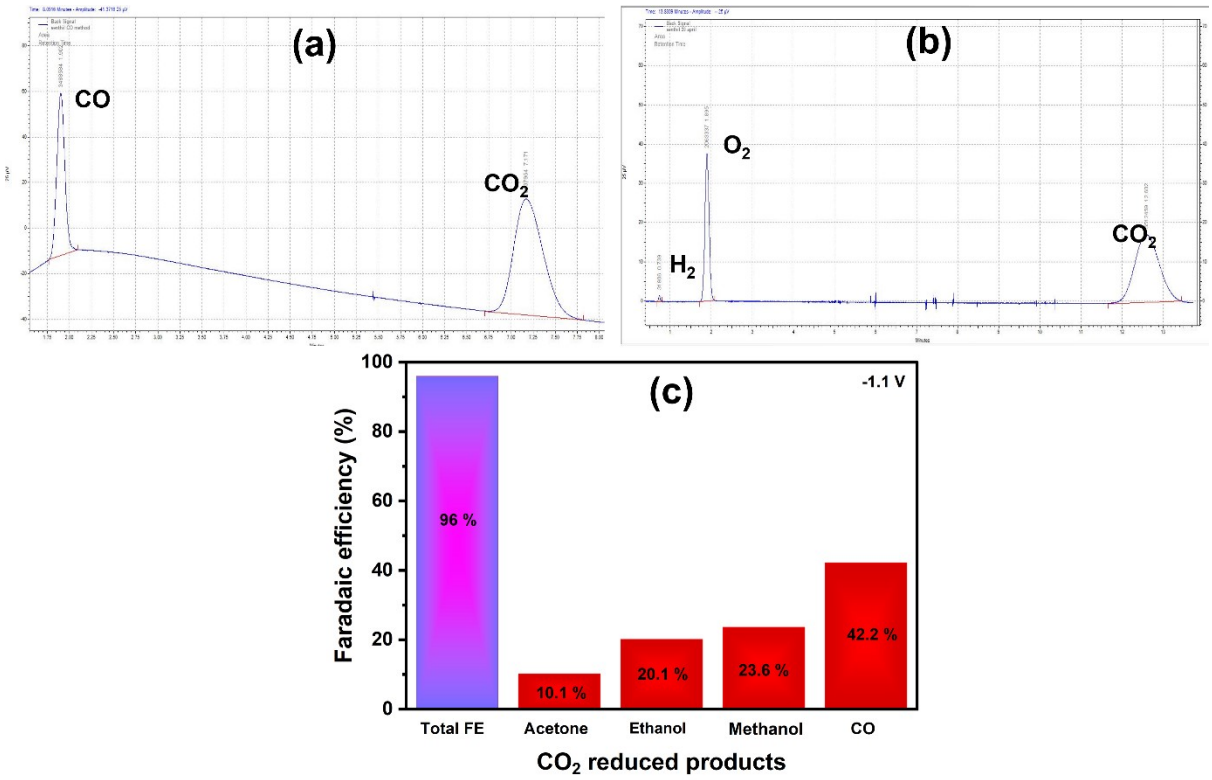

Figure S10. Gas chromatography profiles showing the formation of (a) CO, (b) H_2 and (c) overall CO_2-reduced products carried out at the constant potential of -1.1 V (vs. Ag/AgCl) for 3 h.

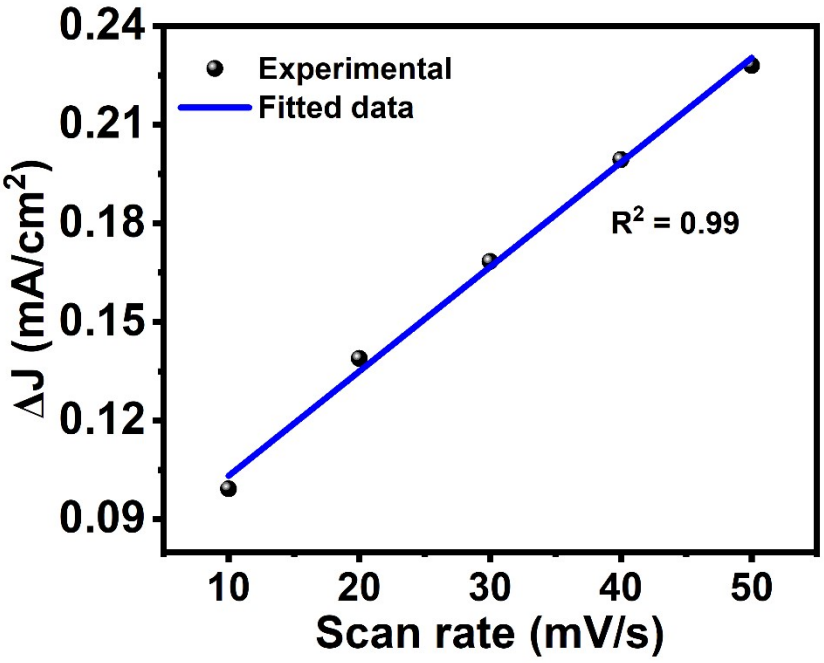

Figure S11. Electrochemical double layer plot (Scan rate vs. ΔJ) of modified $\mathbf{Ti_3C_2T_x}$ -GCE

Table S1. Electrocatalytic properties $\mathbf{Ti_3C_2T_x}$ -GCE with recently reported 2D materials towards C_1 and C_{2+} products.

Electrocatalyst	**Electrolyte**	**Operating potential**	**Products**	**Faradaic efficiency**	**References**
$\mathbf{Ti_3C_2T_x}$ **-GCE**	0.5 M $KHCO_3$	-0.45 V (vs RHE)	Ethanol, Methanol & Acetone	96 %	**This work**
Ti_2CT_x	Acetonitrile+ DI water+ $BMIMBF_4$	-1.8 V (vs SHE)	HCOOH	56.1 %	[1]
N-doped Ti_3C_2	Seawater	-0.7 V (vs RHE)	CO	92 %	[2]
Mo_2C & Ti_3C_2	(1-ethyl-2 methylimidazolium tetrafluroborate)	-2.5 V (vs SHE)	CO	90 % & 65 %	[3]
$Cu/Ti_3C_2T_x$	1M KOH	-0.7 V (vs RHE)	C_2H_4, EtOH & acetate	71 %, 25 % & 2.2 %	[4]
$Ti_3(Al_{1-x}Cu_x)Cu$	0.1M $KHCO_3$	-1.4 V (vs SHE)	CH_3OH	59.1 %	[5]
BiOBr templated catalyst	0.1M $KHCO_3$	-1.0 V (vs RHE)	Formate	90 %	[6]

Sn sheets confined graphene	0.1M $NaHCO_3$	-1.8 V (vs SHE)	Formate	89 %	[7]
2D SnO_2	0.1M $NaHCO_3$	-1.13 V (vs RHE)	Formate	90 %	[8]
SnO_2 @ N-doped nanocarbon	0.1M $KHCO_3$	-1.2 V (vs RHE)	Formate	93.2 %	[9]
Bi_2O_3	0.5M $KHCO_3$	-0.9 V (vs RHE)	Formate	91 %	[10]
Cu nanosheets	2 M KOH	-	Acetate	48 %	[11]
SnO_2 on CuO	0.5M $KHCO_3$	-1.0 V (vs RHE)	C_2H_4	22 %	[12]
Cu-Cu_2O	0.1M $KHCO_3$	-1.1 V (vs RHE)	C_2H_4	36 %	[13]
Pd/SnO_2	0.1M $NaHCO_3$	-0.26 V (vs RHE)	CH_3OH	34 %	[14]
CuO/TiO_2	0.1M $KHCO_3$	-0.85 V (vs RHE)	EtOH, acetone &acetate	47.4 %	[15]

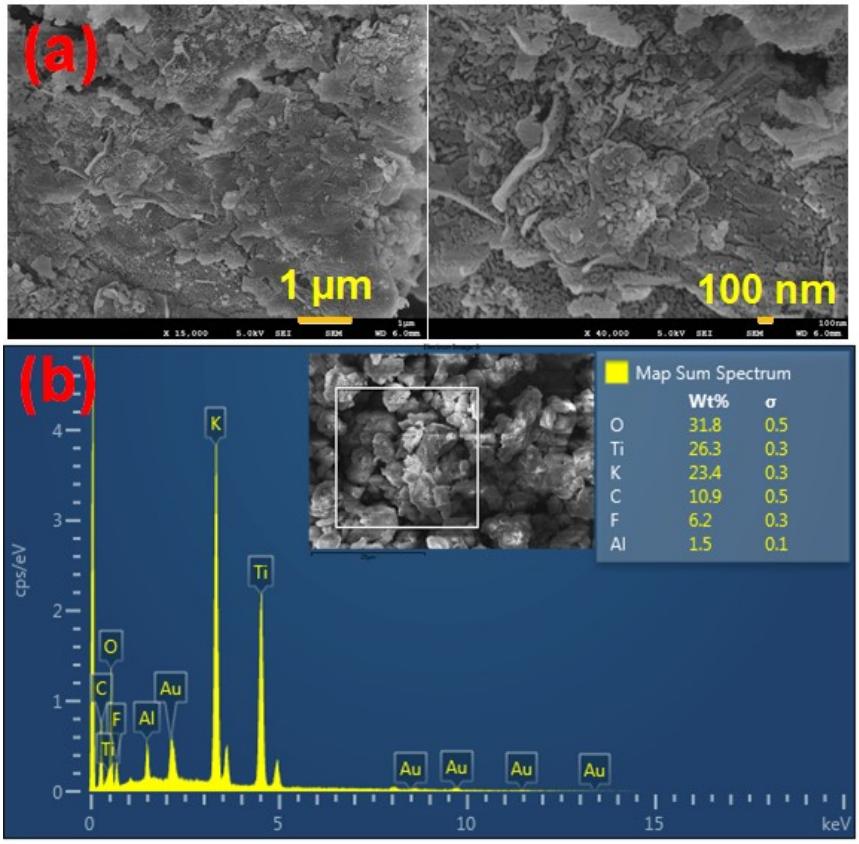

Figure S12. (a) FE-SEM and (b) EDX spectrum of $Ti_3C_2T_x$ -GCE after 72 h of electrocatalysis

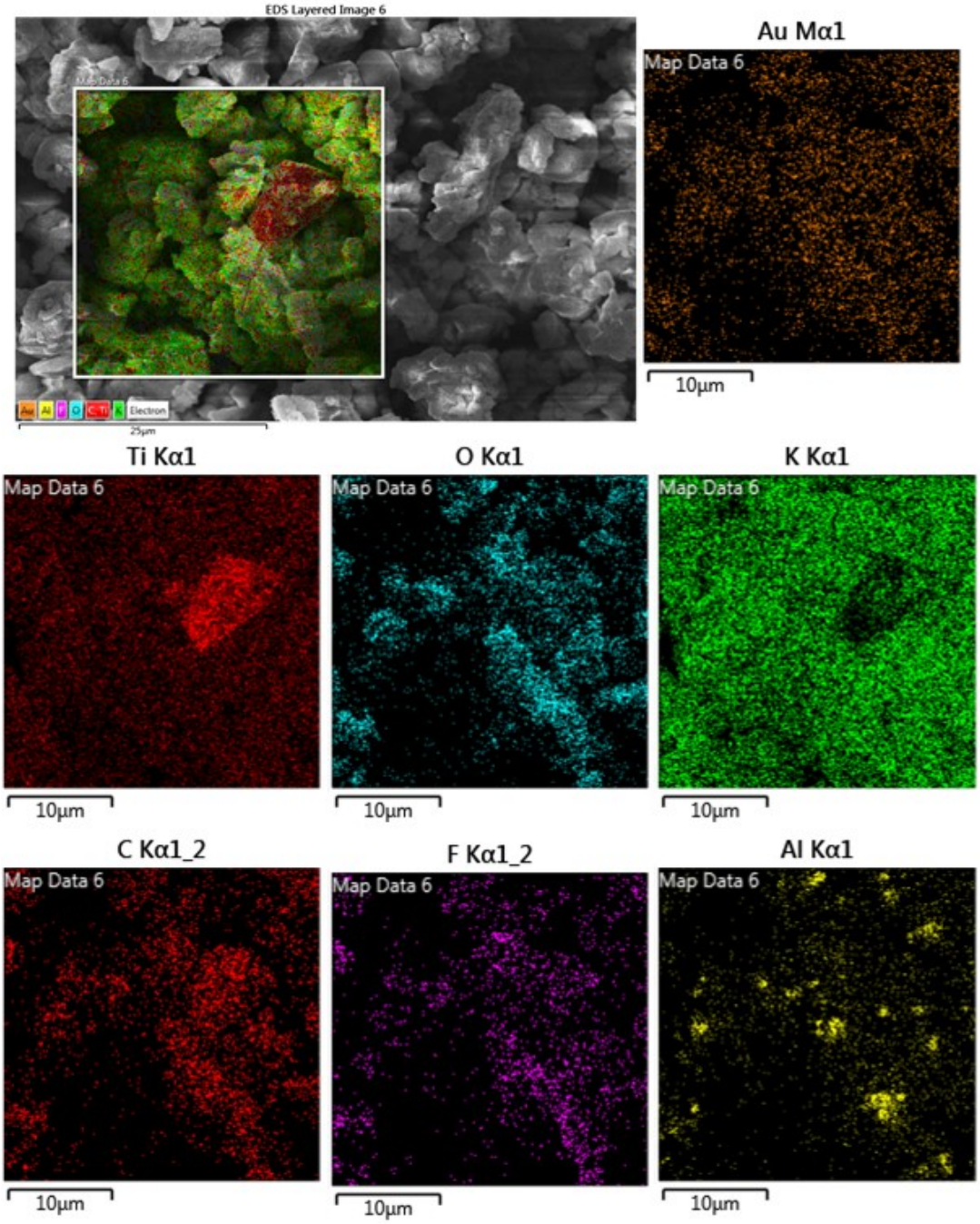

Figure S13. Elemental mapping of $Ti_3C_2T_x$ -GCE after 72 hr stability studies

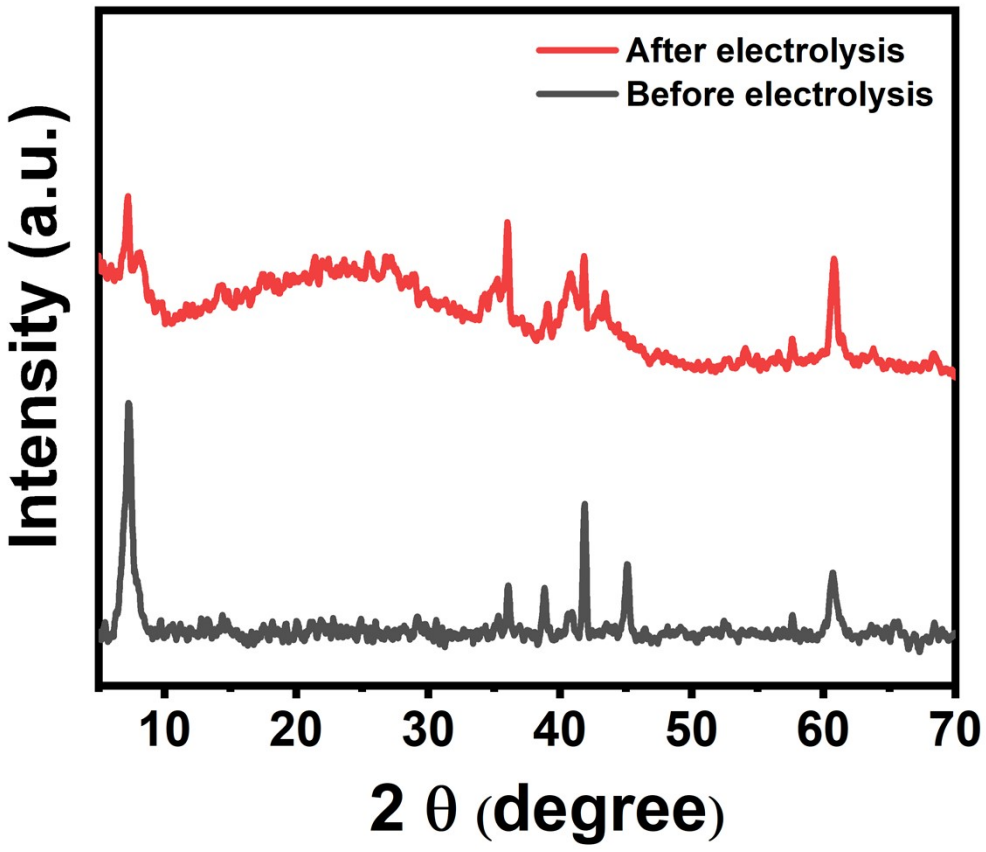

Figure S14. P-XRD pattern of $Ti_3C_2T_x$ before and after 72 hr electrolysis

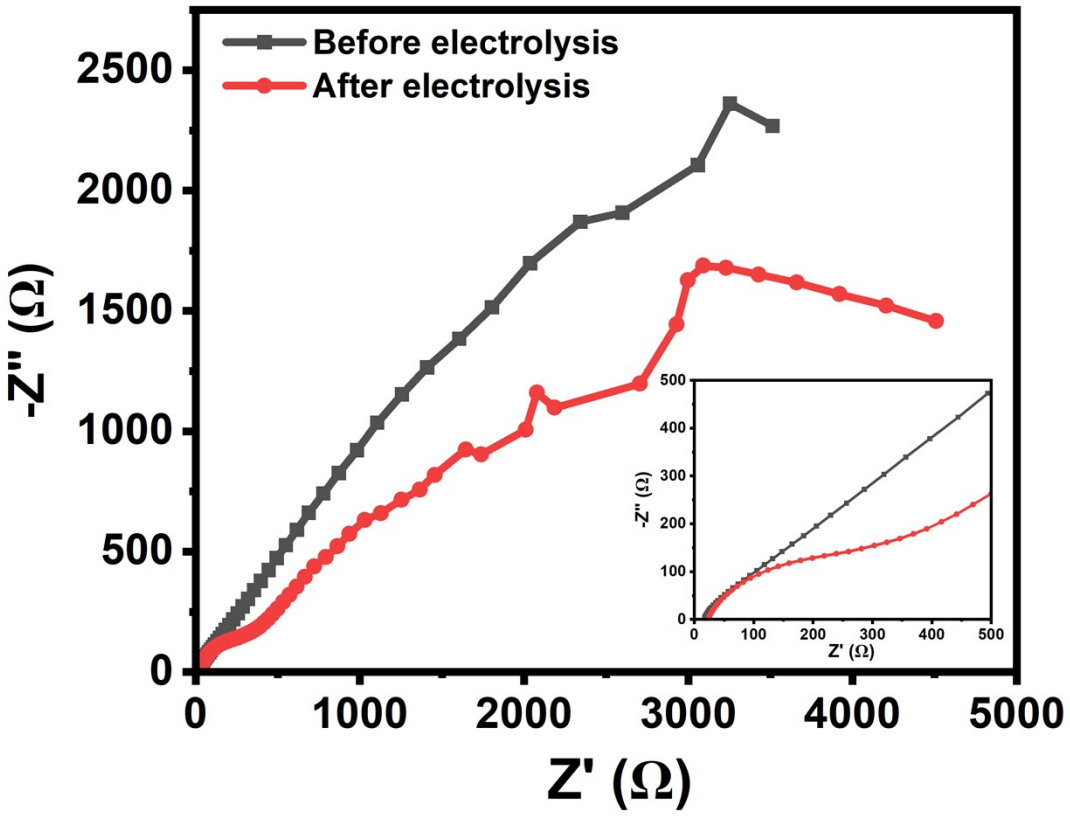

Figure S15. Electrochemical impedance spectroscopy (EIS) of $\mathbf{Ti_3C_2T_x}$ -GCE before and after 72 hr electrolysis

References

1 A. D. Handoko, H. Chen, Y. Lum, Q. Zhang, B. Anasori and Z. W. Seh, *iScience*, 2020, **23**, 101181.

2 D. Qu, X. Peng, Y. Mi, H. Bao, S. Zhao, X. Liu and J. Luo, *Nanoscale*, 2020, **12**, 17191–17195.

3 N. H. Attanayake, H. R. Banjade, A. C. Thenuwara, B. Anasori, Q. Yan and D. R. Strongin, *Chemical Communications*, 2021, **57**, 1675–1678.

4 H. Bao, Y. Qiu, X. Peng, J. ao Wang, Y. Mi, S. Zhao, X. Liu, Y. Liu, R. Cao, L. Zhuo, J. Ren, J. Sun, J. Luo and X. Sun, *Nat Commun*, 2021, **12**, 1–9.

5 Q. Zhao, C. Zhang, R. Hu, Z. Du, J. Gu, Y. Cui, X. Chen, W. Xu, Z. Cheng, S. Li, B. Li, Y. Liu, W. Chen, C. Liu, J. Shang, L. Song and S. Yang, *ACS Nano*, 2021, **15**, 4927–4936.

6 F. P. García de Arquer, O. S. Bushuyev, P. De Luna, C. T. Dinh, A. Seifitokaldani, M. I. Saidaminov, C. S. Tan, L. N. Quan, A. Proppe, M. G. Kibria, S. O. Kelley, D. Sinton and E. H. Sargent, *Advanced Materials*, 2018, **30**, 6–11.

7 F. Lei, W. Liu, Y. Sun, J. Xu, K. Liu, L. Liang, T. Yao, B. Pan, S. Wei and Y. Xie, *Nat Commun*, 2016, **7**, 1–8.

8 J. Li, J. Jiao, H. Zhang, P. Zhu, H. Ma, C. Chen, H. Xiao and Q. Lu, *ACS Sustain Chem Eng*, 2020, **8**, 4975–4982.

9 Y. Fu, T. Wang, W. Zheng, C. Lei, B. Yang, J. Chen, Z. Li, L. Lei, C. Yuan and Y. Hou, *ACS Appl Mater Interfaces*, 2020, **12**, 16178–16185.

10 P. Deng, H. Wang, R. Qi, J. Zhu, S. Chen, F. Yang, L. Zhou, K. Qi, H. Liu and B. Y. Xia, *ACS Catal*, 2020, **10**, 743–750.

11 W. Luc, X. Fu, J. Shi, J. J. Lv, M. Jouny, B. H. Ko, Y. Xu, Q. Tu, X. Hu, J. Wu, Q. Yue, Y. Liu, F. Jiao and Y. Kang, *Nat Catal*, 2019, **2**, 423–430.

12 Y. Lan, G. Niu, F. Wang, D. Cui and Z. Hu, *ACS Appl Mater Interfaces*, 2020, **12**, 36128–36136.

13 N. Altaf, S. Liang, L. Huang and Q. Wang, *Journal of Energy Chemistry*, 2020, **48**, 169–180.

14 W. Zhang, Q. Qin, L. Dai, R. Qin, X. Zhao, X. Chen, D. Ou, J. Chen, T. T. Chuong, B. Wu and N. Zheng, *Angewandte Chemie - International Edition*, 2018, **57**, 9475–9479.

15 J. Yuan, J. J. Zhang, M. P. Yang, W. J. Meng, H. Wang and J. X. Lu, *Catalysts*, , DOI:10.3390/catal8040171.