

Supplementary Information

Ti₃C₂ supported transition metal oxides and silver as catalysts toward efficient electricity generation in microbial fuel cell

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Experimental section

Preparation of Ag-Ti₃C₂

Ti₃C₂ was synthesized by selectively etching Ti₃AlC₂ using HF. Briefly, 2.0 g commercial Ti₃AlC₂ was added to 50 mL of HF, and stirred at 30 °C for 24 h. After that, the resulting mixture was further washed to neutral by centrifugation with deionized water. Then, the exfoliated Ti₃C₂ clay was collected and dried under vacuum at 60 °C for 24 h. Till now, the multi-layer stacked Ti₃C₂ has been prepared.

Ag-Ti₃C₂ was obtained by a facile silver ions reduction method, in which Ti₃C₂ was employed as both support and reductant. In detail, 0.1 g Ti₃C₂ was immersed in 100 mL of deionized water and then sonicated for 30 min to separate the stacked layers. 0.1 g AgNO₃ was dissolved in 20 mL of deionized water and slowly dropped into the homogeneous Ti₃C₂ suspension. Afterwards, the mixture was kept stirring at 30 °C for 20 min, and then centrifuged and dried under vacuum at 60 °C for 24 h.

Preparation of Ti₃C₂-M_xO_y

Ti₃C₂-Co₃O₄. 0.2 g Ti₃C₂ was added to 20 mL of deionized water dissolved 0.623 g Co(CH₃COO)₂·4H₂O and 3.96 g C₆H₁₂O₆·H₂O, followed by ultrasound to uniformly disperse. Then, 0.5 g NaHCO₃ was dissolved in 25 mL of deionized water and slowly dropped into the former. After reaction with gentle magnetic stirring at 25 °C for 12 h, the precipitate was washed to neutral with deionized water and dried in a vacuum at 80 °C for 12 h. The precursor was further heated to 250 °C in air and maintained for 2 h. Subsequently, the production was washed with deionized water and dried in a vacuum at 80 °C for 12 h.

Ti₃C₂-Fe₃O₄. 2.0 g FeCl₂·4H₂O and 5.2 g FeCl₃·6H₂O were dissolved in 25 mL of deionized water saturated with gaseous N₂, followed by mixing into 1.7 mL 6.0 mol L⁻¹ HCl. Then, the mixture was poured to N₂-saturated 250 mL 1.5 mol L⁻¹ NaOH with 0.2 g dispersive Ti₃C₂. After reaction with gentle magnetic stirring at 80 °C for 1 h, the precipitate was washed to neutral with deionized water and dried in a vacuum at 80 °C for 12 h.

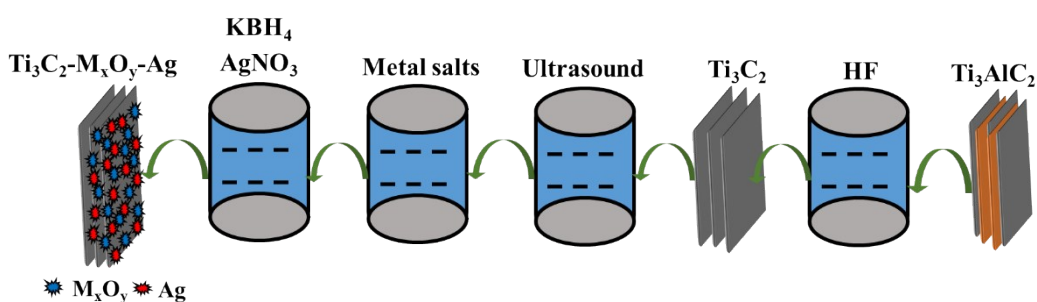
Ti₃C₂-MnO₂. 2.535 g MnSO₄·H₂O was dissolved in 100 mL of deionized water, and then 0.2 g Ti₃C₂ was added and dispersed by ultrasound. Then, 1.58 g KMnO₄ dissolved in 100 mL of deionized water was poured to the former. After reaction with gentle magnetic stirring at 25 °C for 6 h, the precipitate was centrifugally washed with deionized water and dried in air at 100 °C for 2 h.

Ti₃C₂-NiO. 0.2 g Ti₃C₂ was added to 50 mL 0.15 mol L⁻¹ Ni(NO₃)₂, followed by ultrasound to uniformly disperse. Then, 50 mL 0.4 mol L⁻¹ Na₂O₂ was poured to the former. After reaction at 25 °C for 12 h, the precipitate was centrifugally washed to neutral with deionized water and dried in air at 100 °C for 6 h. The precursor further was calcined in air at 350 °C for 2 h. Subsequently, the production was washed with deionized water and dried in a vacuum at 80 °C for 12 h.

The as-prepared Ti₃C₂-Co₃O₄, Ti₃C₂-Fe₃O₄, Ti₃C₂-MnO₂, Ti₃C₂-NiO were dubbed as Ti₃C₂-M_xO_y (M=Co, Fe, Mn, Ni).

Preparation of Ti₃C₂-M_xO_y-Ag

Ti₃C₂-M_xO_y-Ag catalysts were fabricated by a two-step method. Firstly, the different Ti₃C₂-M_xO_y were prepared by chemical precipitation. Secondly, 0.1 g Ti₃C₂-M_xO_y and 0.1 g AgNO₃ were added to 100 mL of deionized water, sonicated for 5 min and transferred to a 250 mL beaker. 0.1 g KBH₄ dissolved in 20 mL of deionized water was slowly dropped into the former solution. After that, the mixture was kept stirring at 30 °C for 5 min, and then centrifuged and dried in a vacuum at 80 °C for 12 h.



Scheme S1 The diagram of $\text{Ti}_3\text{C}_2\text{-M}_x\text{O}_y\text{-Ag}$ for preparation.

Material characterizations

Field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) was used to observe morphology of the as-prepared catalysts. Then, nitrogen adsorption-desorption measurement was conducted on Micromeritics instruments (ASAP 2460, US), where the specific surface area and pore size distribution were further calculated by Brunauer-Emmet-Teller and Barrett-Joiner-Halenda formulas. The X-ray diffraction (XRD, MiniFlex600, Japan) and Fourier transform infrared spectroscopy (FT-IR, VERTEX 70, Germany) were carried out to investigate the crystal structure and functional groups. Furthermore, the X-ray photoelectron spectroscopy (XPS, PH1-5700, US) was performed to analyze the surface chemical composition and elemental valence state.

Electrochemical tests

The electrochemical measurements were conducted on an electrochemical workstation (CHI700D, Chenhua Co. Ltd., China) equipped with the RRDE-3A apparatus (RRDE-3A, ALS, Japan) at room temperature. A glassy carbon electrode (4mm in diameter) with platinum outer ring was used as working electrode. Typically, the platinum wire and saturated calomel electrode (SCE) were employed as counter and reference electrodes to form current and voltage circuits, respectively. The 20 mg of $\text{Ti}_3\text{C}_2\text{-M}_x\text{O}_y\text{-Ag}$ was uniformly dispersed in 2 mL of absolute ethanol and 8 mL of deionized water by ultrasound. Then, 10 μL suspension was deposited onto polished glassy carbon disk, followed by drying and immobilizing by 5 μL commercial Nafion (5 wt%) binder. All the tests were performed in 50 mmol L^{-1} phosphate buffer solution (PBS, $\text{pH}=7.2$).

MFC construction and operation

In this work, the single chamber air-cathode MFC with an inner volume of 28 mL was assembled using Plexiglas tube, where the anode and cathode at a distance of 4 cm were connected with titanium wires across a fixed external resistor (1000 Ω). The carbon felt pretreated by acetone for 8 h was used as an anode to colonize active bacteria, and a gas diffusion cathode (projected area of 7.0 cm^2) was fabricated by stainless steel mesh substrate, air-diffusion layer consisted of carbon powder (Vulcan XC72) and PTFE (60 wt%) and catalytic layer prepared by a certain proportion of catalysts, deionized water, Nafion and isopropanol. Electrochemically active bacteria were provided with activated sludge obtained from secondary sedimentation tank of local wastewater treatment plant. The MFC was inoculated with a mixture containing 100 mmol L^{-1} PBS, 1 g L^{-1} glucose and active microorganisms in vaccination phase. When voltage output was stable for 2~3 cycles, it indicated that the MFC has been started successfully. After initiation, the nutritive medium with 50 mmol L^{-1} PBS and 1 g L^{-1} glucose was supplied for MFC. The voltage was recorded by a data acquisition (PISO-813S, ICP DAS Co., Ltd, Taiwan). Subsequently, polarization measurements were performed to estimate the power output for MFC.

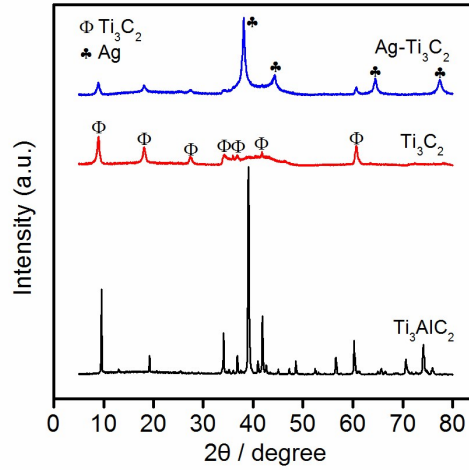


Fig. S1 XRD patterns of commercial Ti_3AlC_2 , Ti_3C_2 and $\text{Ag-Ti}_3\text{C}_2$.

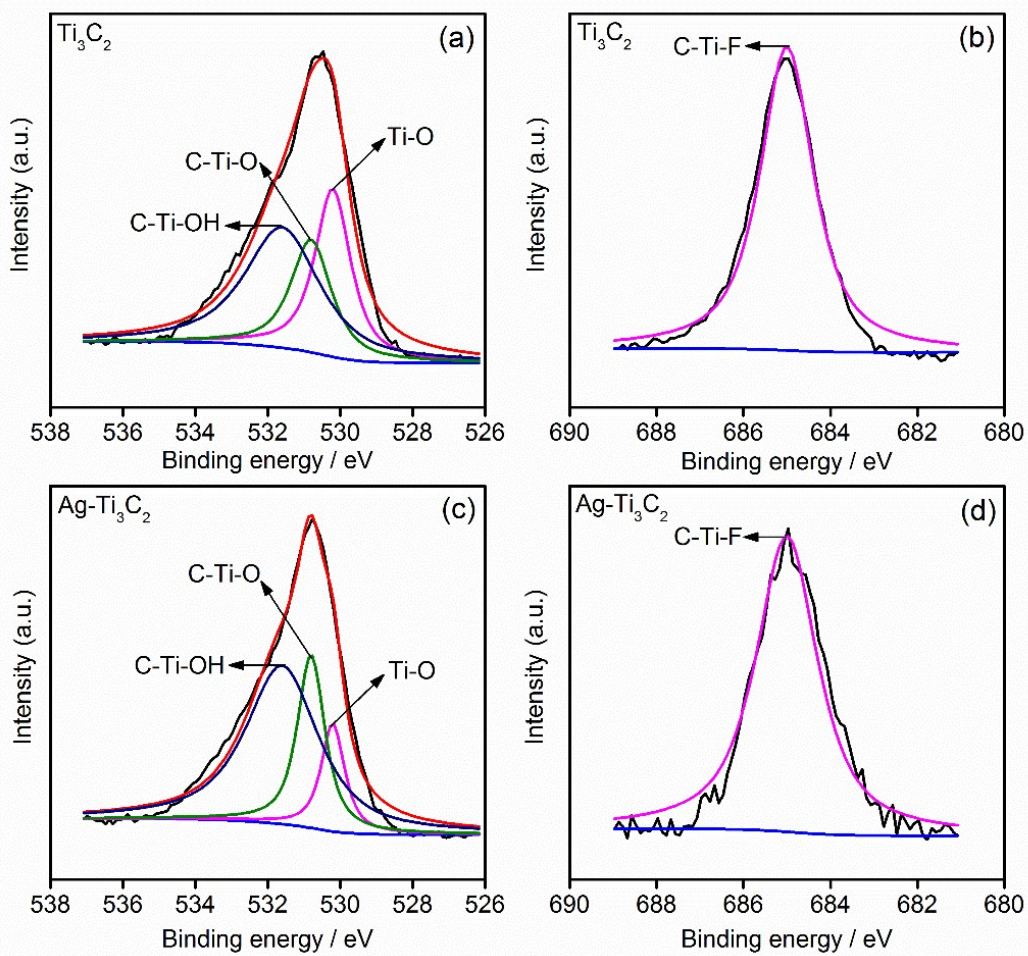


Fig. S2 High-resolution spectra in O_{1s} and F_{1s} regions of (a, b) Ti_3C_2 and (c, d) $\text{Ag-Ti}_3\text{C}_2$.

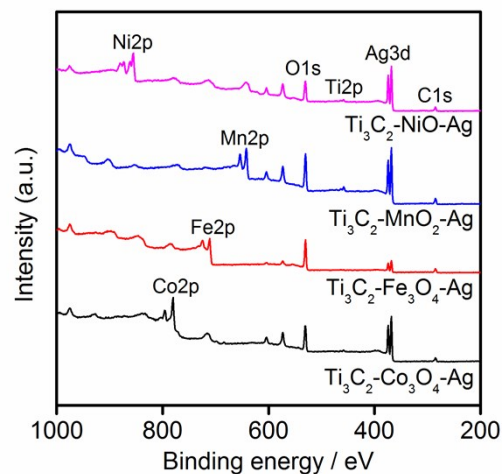


Fig. S3 XPS survey spectra of $\text{Ti}_3\text{C}_2\text{-M}_x\text{O}_y\text{-Ag}$.

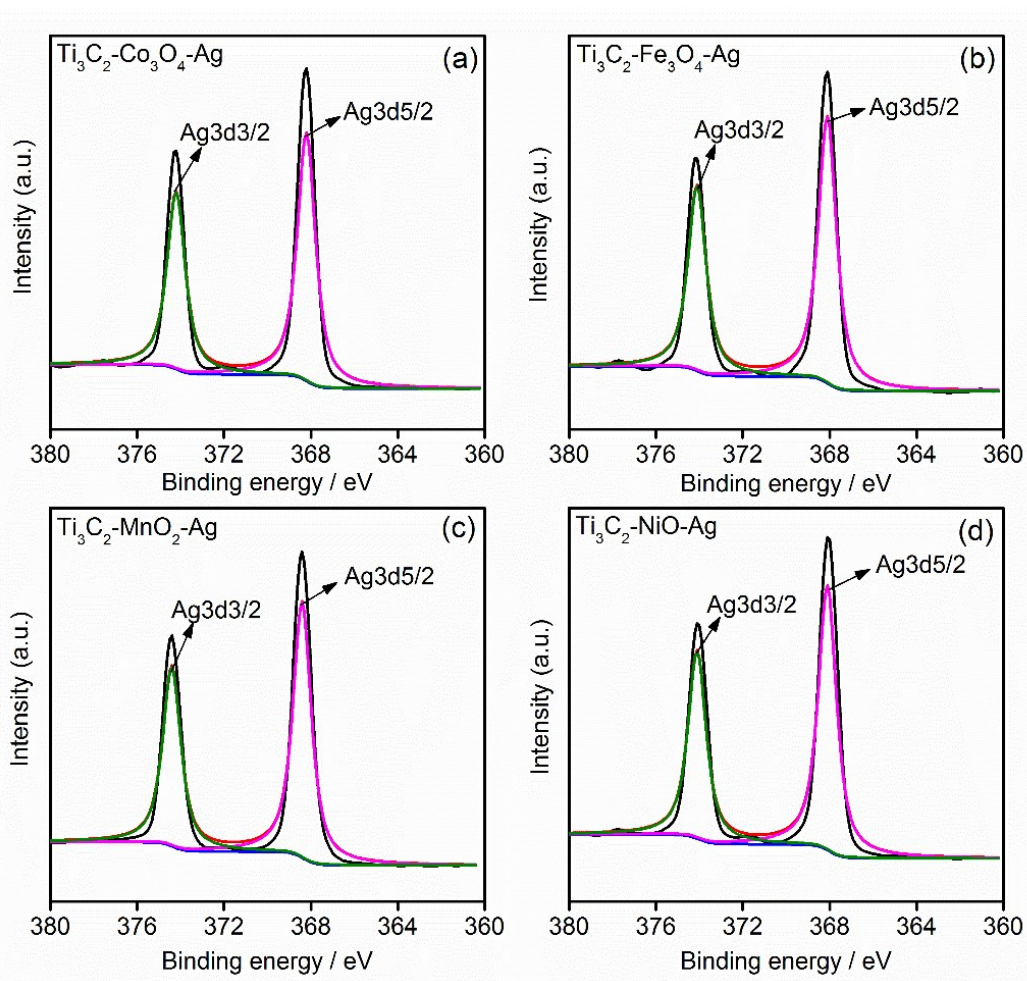


Fig. S4 High-resolution spectrum in Ag_{3d} region of (a) $\text{Ti}_3\text{C}_2\text{-Co}_3\text{O}_4\text{-Ag}$, (b) $\text{Ti}_3\text{C}_2\text{-Fe}_3\text{O}_4\text{-Ag}$, (c) $\text{Ti}_3\text{C}_2\text{-MnO}_2\text{-Ag}$ and (d) $\text{Ti}_3\text{C}_2\text{-NiO-Ag}$.

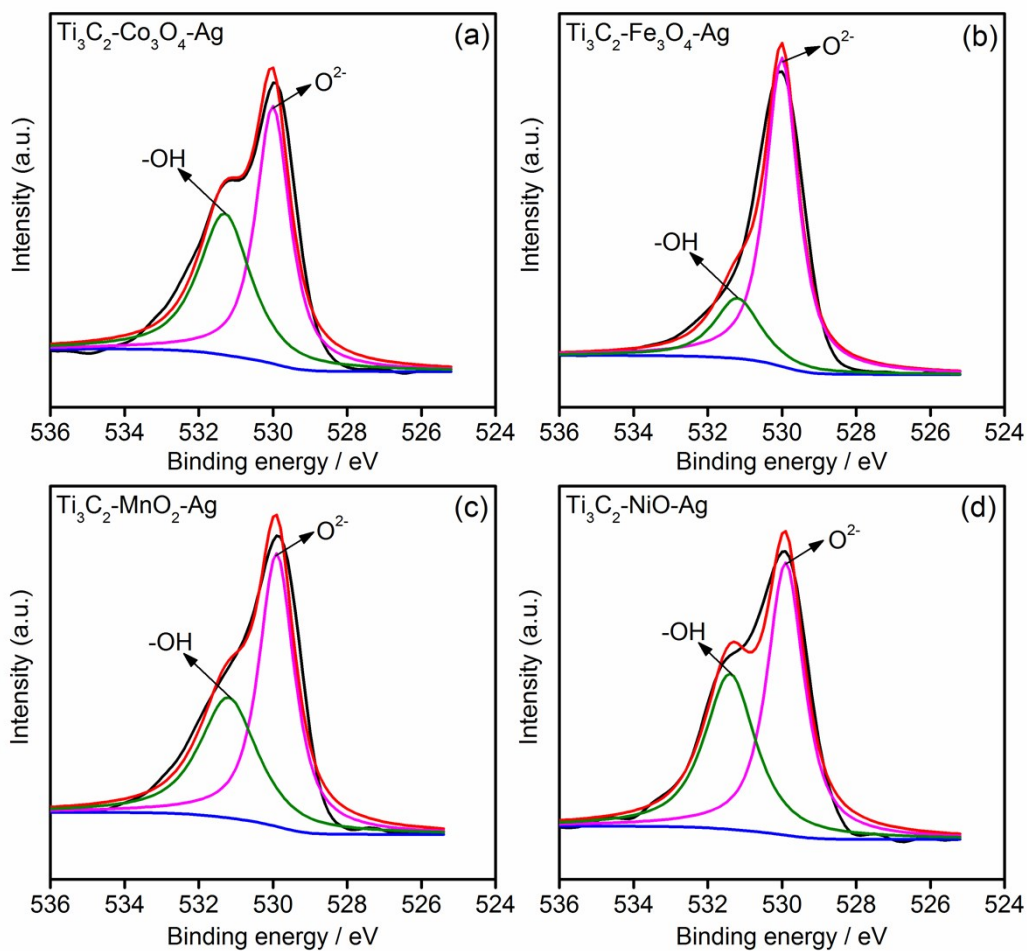


Fig. S5 High-resolution spectrum in O_{1s} region of (a) $Ti_3C_2-Co_3O_4-Ag$, (b) $Ti_3C_2-Fe_3O_4-Ag$, (c) $Ti_3C_2-MnO_2-Ag$ and (d) $Ti_3C_2-NiO-Ag$.

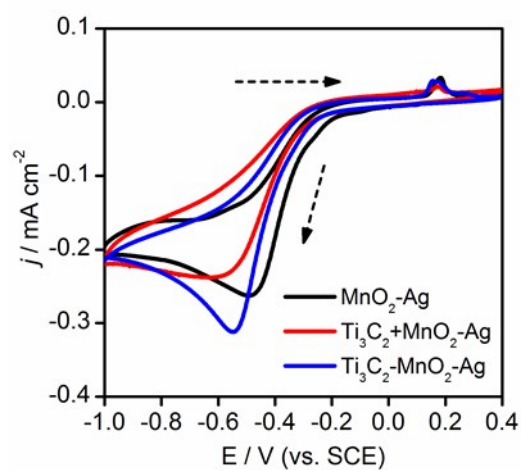


Fig. S6 Cyclic voltammograms of MnO_2-Ag , $Ti_3C_2+MnO_2-Ag$ and $Ti_3C_2-MnO_2-Ag$.

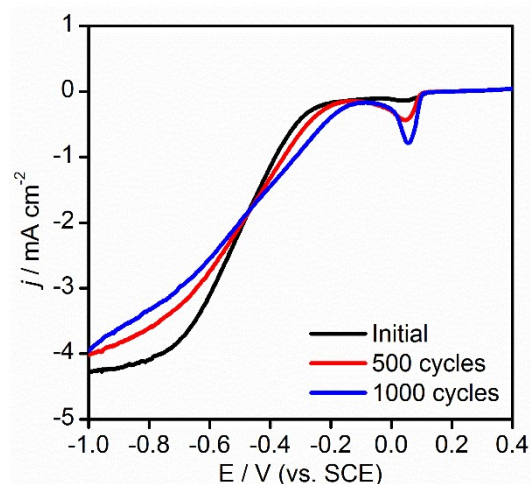


Fig. S7 Linear sweep voltammetry curves of $\text{Ti}_3\text{C}_2\text{-MnO}_2\text{-Ag}$ at 1600 rpm in O_2 -saturated 50 mmol L^{-1} PBS.

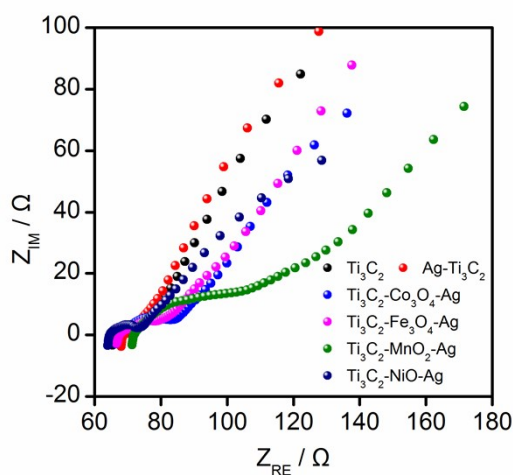


Fig. S8 Nyquist plots based electrochemical impedance spectroscopy of air-cathode with Ti_3C_2 , $\text{Ag-Ti}_3\text{C}_2$ and $\text{Ti}_3\text{C}_2\text{-M}_x\text{O}_y\text{-Ag}$ in MFC.

Table S1 Atomic content of elements in Ti_3C_2 and $\text{Ag-Ti}_3\text{C}_2$.

Sample	Ag _(at%)	Ti _(at%)	C _(at%)	O _(at%)	F _(at%)
Ti_3C_2	---	17.47	52.37	21.24	8.92
$\text{Ag-Ti}_3\text{C}_2$	11.22	9.83	41.99	31.61	5.35

Table S2 Atomic content of elements in $\text{Ti}_3\text{C}_2\text{-M}_x\text{O}_y\text{-Ag}$.

Sample	Co _(at%)	Fe _(at%)	Mn _(at%)	Ni _(at%)	Ag _(at%)	Ti _(at%)	C _(at%)	O _(at%)	F _(at%)
$\text{Ti}_3\text{C}_2\text{-Co}_3\text{O}_4\text{-Ag}$	19.6	---	---	---	11.67	2.98	18.05	44.02	3.68
$\text{Ti}_3\text{C}_2\text{-Fe}_3\text{O}_4\text{-Ag}$	---	27.46	---	---	3.08	1.64	17.95	47.77	2.09
$\text{Ti}_3\text{C}_2\text{-MnO}_2\text{-Ag}$	---	---	16.26	---	10.64	4.57	20.21	45.30	3.03
$\text{Ti}_3\text{C}_2\text{-NiO-Ag}$	---	---	---	24.08	11.44	3.78	19.52	37.90	3.28