Photocatalytic CO₂ Reduction Using $Ti_3C_2X_y$ (X = Oxo, OH, F, or Cl) MXene–ZrO₂: Structure, Electron Transmission, and the Stability

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photocatalyst is a promising option for completing a new carbon– neutral cycle. The short lifetime of charges generated owing to light energy is one of the most critical problems in further improving the performance of semiconductor-based photocatalysts. This study shows the structure, electron transmission, and stability of $Ti_3C_2X_y$ (X = oxo, OH, F, or Cl) MXene combined with a ZrO_2 photocatalyst. Using H₂ as a reductant, the photocatalytic CO formation rate increased by 6.6 times to 4.6 μ mol h⁻¹ g_{cat}⁻¹ using MXene (3.0 wt %)–ZrO₂ compared to that using ZrO₂, and the catalytic route was confirmed using ¹³CO₂ to form ¹³CO. In clear contrast, using H₂O (gas) as a reductant, CH₄ was formed as the major product using Ti₃C₂X_y MXene (5.0 wt %)–ZrO₂ at the rate



of $3.9 \ \mu$ mol h⁻¹ g_{cat}⁻¹. Using ¹³CO₂ and H₂O, ¹²CH₄, ¹²C₂H₆, and ¹²C₃H₈ were formed besides H₂¹²CO, demonstrating that the C source was the partial decomposition and hydrogenation of Ti₃C₂X_y. Using the atomic force and high-resolution electron microscopies, 1.6 nm thick Ti₃C₂X_y MXene sheets were observed, suggesting ~3 stacked layers that are consistent with the Ti–C and Ti…Ti interatomic distances of 0.218 and 0.301 nm, respectively, forming a [Ti₆C] octahedral coordination, and the major component as the X ligand was suggested to be F and OH/oxo, with the temperature increasing by 116 K or higher owing to the absorbed light energy, all based on the extended X-ray absorption fine structure analysis.

INTRODUCTION

Photocatalytic CO_2 reduction is one of the highly expected options to complete a new carbon neutral cycle applicable in a sustainable society. Various types of photocatalysts have been researched for this purpose, and among them, semiconductor-based photocatalysts are expected to be stable in comparison to molecular and/or metal complex photocatalysts.

Semiconductor photocatalysts utilize charge separation owing to the electron excitation at the band gap for the oxidation reaction utilizing hole(s) at the valence band (VB) and the reduction reaction utilizing excited electron(s) at the conduction band (CB). However, the efficiency of the photocatalytic reaction is determined by how long the separated charges remain. In this context, nanomaterials used to transmit such charges quickly have been tested in combination with semiconductors: MXenes,¹ covalent organic frameworks,² and graphene.³

Among them, recently, the applications of MXenes to photocatalysis as nanoscale conductive components have been intensively studied combined with semiconductors. When the Fermi level (E_F) of MXene is in the band gap of the

semiconductor and the $E_{\rm F}$ value of the combined MXene is near the CB minimum of the semiconductor, the electrons effectively transfer from the semiconductor to MXene via the band bending (Schottky junction).^{4,5} Especially, photocatalytic reduction of CO₂ utilizing MXenes is highly expected and has been reported to generate CO, CH₄, and CH₃OH.^{1,6} The general formula of MXene is $M_{n+1}Z_nX_y$, where Z is C and/or N; X is oxo, OH, F, or Cl; and n is 1–4. However, a detailed photocatalytic reaction pathway from CO₂ has been rarely reported except for the evaluation of electron conductivity by MXenes and implication of photoreduction by the transmitted electrons via MXenes. In this paper, the structure of MXene– ZrO₂, electron transmission via MXene, and the photocatalytic reaction pathway starting from CO₂ are investigated. The

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effects and the stability of $Ti_3C_2X_y$ (X = oxo, OH, F, or Cl) MXene on CO₂ photoreduction were critically evaluated using H_2 or H_2O as a reductant. The layered structural unit of Ti_3C_2 and the X ligand that was introduced for the exfoliation was analyzed in relation to the promoting effects on the photocatalytic reduction of CO₂ over the ZrO₂ surface.

MATERIALS AND METHODS

Synthesis of Ti₃C₂X_y MXene. Ti₃C₂X_y MXene nanosheets were prepared using a revised method as reported in the literature.⁷ Ti₃AlC₂ (1.0 g) was slowly added to a solution in a Teflon liner, which consisted of HCl (6.0 mL), HF (1.0 mL), and deionized (DI) water (3.0 mL; <0.055 μ S cm⁻¹), for etching. The suspension was stirred at a rate of 400 rotations per minute (rpm) for 24 h at 314 K. Then, the resultant solid was washed with DI water and centrifuged (4500 rpm, for 5 min each) several times until the pH of the filtrate became neutral.

Next, the residue was dispersed in DI water (25 mL) containing LiCl (1.5 g) and stirred for 2 h at 293 K. Then, the resultant solid was washed with DI water and centrifuged (10,000 rpm, 10 min) for five times. Subsequently, the separated solid was dispersed again in DI water (100 mL), and the dispersion was ultrasonicated (360 W, 40 kHz) for 6 h under an argon atmosphere cooled by an ice–water bath (278 K) to achieve exfoliation of MXene layers. Then, the dispersion in the middle and upper layers were collected and extracted via centrifugation (13,000 rpm, 30 min). Finally, the thus obtained dispersion was divided into two parts: one part for vacuum freezedrying to obtain solid MXene powder and the other part for the preparation of the MXene–ZrO₂ composite photocatalysts. The concentration of the MXene suspension was determined by weighing the residual solid after drying.

Synthesis of Ti₃C₂X_y MXene–ZrO₂. Scheme 1A illustrates the synthesis steps of the $Ti_3C_2X_{\nu}$ MXene– ZrO_2 composite. ZrO_2 (1.0 g; JRC-ZRO-03, Catalysis Society of Japan, monoclinic phase major, tetragonal phase minor, and a specific surface area of 94.4 m² g⁻¹) was suspended in DI water (200 mL) followed by ultrasonification (360 W, 40 kHz) for 10 min and stirring at a rate of 900 rpm for 10 min. Subsequently, the as-prepared homogeneously distributed $Ti_3C_2X_{\nu}$ MXene dispersion (Scheme 1B) was slowly dropped onto the ZrO_2 suspension and continuously stirred at 900 rpm for 2 h. The upper layer of the suspension was transparent after resting, as shown in Scheme 1C, demonstrating that most of the introduced MXene was supported on ZrO₂ (Scheme 1A). The precipitate was filtered, washed several times with DI water (200 mL each), and dried by vacuum freeze-drying. The Ti₃C₂X_v MXene-ZrO₂ composites with Ti₃C₂X_v contents of 1.0, 3.0, 5.0, and 10 wt % were denoted MZ-1, MZ-3, MZ-5, and MZ-10, respectively. As the Ti₃C₂X_v MXene loading increased, the color of the composites changed from gray (1.0 wt %) to black (10 wt %).

Photocatalytic CO₂ Reduction. The CO₂ photoreduction tests were conducted using 20 mg of the photocatalysts. The photocatalyst fine powder was placed in a quartz reactor (bottom plate area 9.56 cm² and internal volume 38 mL) connected to a Pyrex glass circulation system (100 mL; Perfect 6A, China) and kept under vacuum for 1 h using a rotary pump (10^{-2} Pa). The reaction gas of either CO₂ (2.5 kPa), H₂ (22.5 kPa), and Ar (25 kPa) or CO₂ (2.3 kPa) and H₂O (2.3 kPa) was introduced into the glass circulation system. The photocatalyst was irradiated with Ultraviolet–visible (UV–vis) light from a 300 W xenon lamp (PLS-SXE300UV, Perfect Light, China), and the distance between the UV–vis light exit and the photocatalyst was 50 mm. The light intensity was 500 mW cm⁻² at the center of the photocatalyst.

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The isotope tracing photocatalytic tests were also performed to investigate the photocatalytic reaction path. The isotope labeled ¹³CO₂ (2.3 kPa, chemical purity >99.9%; 99.0% ¹³C, 0.1% ¹⁷O, 0.7% ¹⁸O, Cambridge Isotope Laboratories, Inc., Tewksbury, MA) and D₂O (2.3 kPa; D 99.9%, chemical purity >99.5%, Cambridge Isotope Laboratories) were used. The U-shaped quartz reactor (internal volume 46.0 mL) containing the catalyst (20 mg) was irradiated with UV-vis light using a 500 W Xe arc lamp (SX-UID502XAM, Ushio, Japan) through a Y-shaped quartz light guide (model 1.2S15-1000F-1Q7-SP-RX; 40 cm long fiber and 80 cm-long branches; Optel, Tokyo, Japan). The distance between the fiber light exit and the photocatalyst was 20 mm. The light intensity at the center of the sample was 142 mW cm⁻². A packed column of 13X-S molecular sieves (3 m length, 3 mm internal diameter; GL Sciences, Inc., Japan) was used for online gas chromatography-mass spectrometry (GC-MS) analyses (Model JMS-Q1050GC, JEOL, Tokyo, Japan), and helium (0.40 MPa, purity >99.9999%) was used as the carrier gas.

Characterizations. The X-ray diffraction (XRD) pattern was measured using an Ultima IV (Rigaku, Japan) at 40 kV and 40 mA. The Cu K α (wavelength $\lambda = 0.15419$ nm) and Ni filter was used as a source light at a Bragg angle (θ_{Bragg}) of $2\theta_{\text{Bragg}} = 5-85^{\circ}$ with a scan step of 0.02° and the scan rate of 1 s per step.

The images of samples were observed by field-emission scanning electron microscopy (FE-SEM) using a Model Apreo 2C (Thermo Scientific, Waltham, MA). Atomic force microscopy (AFM) was also utilized to monitor the thickness and surface flatness using a Model Dimension Icon (Bruker, Billerica, MA). The high-resolution transmission electron microscopy (HR-TEM) image was observed using a Model Talos F200S (Thermo Scientific). The elemental mapping was also performed using the energy-dispersive detector Model SUPER X, which is attached to the Model Talos F200S. The high-angle annular dark-field—scanning transmission electron microscopy (HAADF—STEM) image was also observed using the Model Talos F200S.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Model ESCALAB XI+ photoelectron spectrometer (Thermo Scientific) using a 150 W X-ray radiation source of Al K α .



Figure 1. Photocatalytic reduction tests conducted under (A) CO_2 (2.5 kPa) H_2 (22.5 kPa), and Ar (25 kPa) and (B) CO_2 (2.3 kPa) and H_2O (2.3 kPa) for ZrO_2 and $Ti_3C_2X_y$ MXene (1.0–10 wt %)– ZrO_2 using UV–vis light irradiation of wavelength in the range of 300–700 nm. The photocatalyst amount used was 20 mg.

XPS data were analyzed by the software Advantage, and the binding energies were calibrated by the C 1s line for adventitious C to 284.8 eV for samples of ZrO_2 , $Ti_3C_2X_y$ MXene, and $Ti_3C_2X_y$ MXene– ZrO_2 for the C 1s, O 1s, Zr 3d, and Ti 2p electron orbitals.

UV-visible-near-infrared (UV-vis-NIR) spectra were recorded on a Model LAMBDA 1050+ spectrometer (PerkinElmer, Waltham, MA) using deuterium and tungsten-halogen lamps below and above 340 nm, respectively, equipped with a photomultiplier tube and an integrated sphere of 150 mm diameter for diffuse reflectance detection within the range between 200 and 2000 nm. The Kubelka-Munk function was used to transform the diffuse reflectance spectra. The integrated sphere contains two detectors: a photomultiplier tube for UV-vis light monitoring and an InGaAs photodiode detector for NIR light monitoring.

The absorption-fluorescence spectra were recorded on FLS1000 fluorescence spectrometer (Edinburgh Instruments, UK) using a 450 W Xe arc lamp equipped with a photomultiplier tube for the excitation at 200-400 nm within a fluorescence range of 250-600 nm. The incident excitation light from the Xe lamp was monitored by a Si photodiode, and the monitored fluorescence light emitted from the sample was normalized based on the incident light intensity at each wavelength. The excitation spectra were corrected for the incident light intensity, and the emission spectra were corrected for the spectral sensitivity of the recording system.

In situ Fourier transform infrared (FTIR) spectra were collected using a Tensor II NEXUS (Bruker) operating at 1 cm⁻¹ resolution in the range of 4000–400 cm⁻¹, and the data accumulation included 256 scans. The prepared sample was under vacuum for 1 h to remove the gases adsorbed on the surface, and then, a spectrum was recorded under vacuum as the background spectrum. Then, a mixed gas comprising CO₂ (5.0 kPa), H₂ (45 kPa), and Ar (50 kPa, balance gas) or one comprising CO₂ (97 kPa) and H₂O (2.3 kPa) was introduced to the reaction chamber, followed by the light irradiation from a 300 W Xe arc lamp, and the in situ FTIR spectra were collected in time course to monitor the intermediate species and the further conversion toward the products under UV-vis light irradiation.

Titanium K-edge X-ray absorption fine structure (XAFS) spectra were measured on beamlines 9C and 12C at the Photon Factory, High Energy Accelerator Research Organization (KEK, Tsukuba, Japan). The spectra for 30 wt % Ti₃C₂X_y MXene–ZrO₂ samples in a Pyrex glass cell ($\Phi = 20 \text{ mm}$, t = 2.0 mm) equipped with polyethene terephthalate film windows (Toyobo Film Solutions, Japan, a model G2; 38 μ m thick) for both UV–vis and X-ray transmission were measured in the transmission mode at 295 K. The storage ring energy was 2.5 GeV, and the ring current was 449.9–450.0 mA. A Si (1 1 1) double-crystal monochromator and a Rh-coated focusing bent cylindrical mirror were inserted into the X-ray beam path. A piezotransducer was used to detune the X-ray to two-thirds of the maximum intensity to suppress the higher harmonics. The Ti K-edge absorption energy was calibrated at 4964.5 eV using the spectrum of the Ti metal (5.0 μ m thick).

The obtained Ti K-edge XAFS data were analyzed using the XDAP software package.⁸ The pre-edge background was approximated with a modified Victoreen function, $C_2/E^2 + C_1/E + C_0$, where *E* is the photon energy and C_0 , C_1 , and C_2 are constants. Multiple-shell curve fit analyses were performed with the data obtained from the Fourier-filtered angular wavenumber k^3 -weighted extended XAFS (EXAFS) using the empirical amplitude extracted from the EXAFS data for the Ti metal. The fit parameters for the EXAFS data were theoretically generated using the ab initio multiple-scattering calculation code, FEFF8.40,⁹ with the interatomic distance (R) and coordination number (N) values for the Ti–C, Ti–Ti, Ti–O, Ti–F, and Ti–Cl interatomic pairs in Ti₃C₂X₂ (X = O, F, or Cl) model structures set to 0.2164 nm and 3 (in the top and bottom Ti layers) and 6 (in the

middle Ti layer),¹⁰ 0.30604 nm and 9 (in the top and bottom Ti layers) and 12 (in the middle Ti layer),^{10,11} 0.2164 nm and 3 (in the top and bottom Ti layers),¹⁰ 0.190 nm and 3 (in the top and bottom Ti layers),¹² and 0.218 nm and 3 (in the top and bottom Ti layers),¹³ respectively. The Debye temperature of $Ti_3C_2X_2$ (X = O, F, or Cl) was approximated to that of TiC (863.3 K)¹⁴ for the calculation using FEFF8.40.

Density Functional Theory Calculations. Periodic density functional theory (DFT) calculations were conducted using the Vienna ab initio simulation package code version 6.4.1¹⁵ computed on a VT64 Server XS2-2TI comprising four units of Intel Xeon Platinum 9242 processors (2.3 GHz, 48 cores; Visual Technology, Tokyo, Japan). The projector augmented wave method was employed at the DFT-D3 level¹⁶ to incorporate the van der Waals interaction. The generalized gradient approximation-revised Perdew-Burke-Ernzerhof (RPBE) exchange–correlation functional^{1/} was used for structural optimization, with the cutoff set at 500 eV and adding Hubbard U (4.0 eV for both Ti and Zr).^{18,19} The calculations of electronic states including the density of states (DOS) and the band structure were performed using the HSE06 hybrid functional for the structures optimized using RPBE + U. A $3 \times 3 \times 1$ k-point mesh was used for the structural optimization, while a $1 \times 1 \times 1$ k-point mesh was used for the calculations of electronic states. The Ti₃C₂X_v hexagonal five layers model²⁰ exposing the X ligand (X = OH, F, or Cl) on both sides of the Ti₃C₂ layer was used combined with the Zr₁₁O₂₂ cluster based on the monoclinic phase ZrO_2^{21} as a slab model with a vacuum spacing of 2.0 nm between the slabs in the direction perpendicular to the $Ti_3C_2X_{\nu}$ layer (Chart S1).

RESULTS AND DISCUSSION

Photocatalytic CO₂ (¹³CO₂) Reduction. Photocatalytic CO₂ reduction was tested using H₂ and Ti₃C₂X_v MXene-ZrO₂ photocatalysts in comparison to using ZrO₂ (Figure 1A). In all the tests using the photocatalysts, CO was the major product and the activity continued for more than 30 h of the reaction [Figure 1A(b)]. Some amounts of CH_4 were also formed as the byproduct [Figure 1A(a)]. The CO formation rate was the maximum using $Ti_3C_2X_{\nu}$ MXene (3.0 wt %)–ZrO₂ at 4.6 μ mol $h^{-1} g_{cat}^{-1}$, which was an increase by 6.6 times compared to the rate using ZrO_2 (0.70 μ mol h⁻¹ g_{cat}⁻¹), indicating the electron-conducting effect of MXene to promote the CO₂ photoreduction over the ZrO_2 surface. Unsupported $Ti_3C_2X_{\nu}$ MXene (20 mg) exhibited only poor activity for CO formation compared to ZrO_2 , and the rate was 0.021 μ mol h⁻¹ g_{cat}⁻¹ (Figure S1A), suggesting that $Ti_3C_2X_{\nu}$ MXene itself did not comprise an independent major photocatalytic active site for CO₂ reduction.

The dependence of the CO formation rate on the ratio of the MXene content in the composite photocatalyst was a volcano-like peak at MXene 3.0 wt % [Figure 1A(b)], suggesting the counterbalance of the electron-conducting effect versus the blocking of exciting light by MXene layers over the ZrO_2 surface.

Next, photocatalytic CO₂ reduction was tested using H₂O and Ti₃C₂X_y MXene–ZrO₂ (Figure 1B). In clear contrast to using H₂ (Figure 1A), methane was the major product and the formation rate was the maximum using Ti₃C₂X_y MXene (5.0 wt %)–ZrO₂ at 3.9 μ mol h⁻¹ g_{cat}⁻¹ [Figure 1B(c)]. The rate was comparable to those using the composites of MXene 1.0 and 3.0 wt %; however, volcano-like dependence on the MXene content was evident. As a byproduct, the CO photoformation rate also followed volcano-like dependence, and the maximum rate was 1.1 μ mol h⁻¹ g_{cat}⁻¹ [Figure 1B(d)]. The photocatalytic CO₂ reduction was also tested using H₂O

and unsupported $Ti_3C_2X_y$ MXene to selectively form CH₄, but the rate was only 0.45 μ mol h⁻¹ g_{cat}⁻¹ (Figure S1B).

The above-described MXene-promoted photocatalytic formation was confirmed by a ¹³C-labeled CO₂ photoreduction study. Using ¹³CO₂ (2.3 kPa), H₂ (21.7 kPa), Ti₃C₂X_x MXene (1.0 wt %)–ZrO₂, and UV–vis light irradiation, CO was formed at a rate of 0.78 μ mol h⁻¹ g_{cat}⁻¹ (Figure 2A). The



Figure 2. Photocatalytic reduction tests using $Ti_3C_2X_y$ MXene (1.0 wt %)–ZrO₂ (20 mg) and the irradiation of UV–vis light under (A) $^{13}CO_2$ (2.3 kPa) and H₂ (21.7 kPa) and (B) $^{13}CO_2$ (2.3 kPa) and H₂O (2.1 kPa).

formation rate was higher using CO_2 and H_2 in the previous paragraph because of the greater light intensity (500 mW cm⁻²) versus that using ¹³CO₂ and H₂ (142 mW cm⁻²). The ¹²CO ratio in the total CO (¹³CO and ¹²CO) was 30%, significantly higher than the ¹²C ratio in the reactant ¹³CO₂ (1.0%), suggesting that the reaction intermediate comprising ¹²C was concentrated during the photocatalytic test starting from ¹²CO₂ adsorbed on surface O vacancy (V₀^{••}) sites from air.²¹⁻²³

Using ¹³CO₂ (2.3 kPa), H₂O (2.2 kPa), Ti₃C₂X_y MXene (1.0 wt %)–ZrO₂, and UV–vis light irradiation, photocatalytic ¹³CO generation was only at the rate of 0.004 μ mol h⁻¹ g_{cat}⁻¹ compared to the reported rate of 0.12 μ mol h⁻¹ g_{cat}⁻¹ using ZrO₂.²² Instead, H₂¹²CO, ¹²CO, ¹²CH₄, ¹²C₂H₆, and ¹²C₃H₈ were formed at lower rates of 0.19, 0.032, 0.25, 0.037, and 0.019 μ mol h⁻¹ g_{cat}⁻¹, respectively (Figure 2B). The corresponding ¹³C-containing hydrocarbons and formaldehyde were negligibly formed, strongly suggesting that these were formed by the decomposition of Ti₃C₂X_y MXene under H₂O and the irradiation of UV–vis light. This result was consistent with the quite poor photoactivity using CO₂, H₂O, and Ti₃C₂X_y decomposition was effectively accelerated by the separated charges originating from ZrO₂ under light [Figure 1B(c)].

A blank photocatalytic test using H₂O (2.1 kPa), Ti₃C₂X_y MXene (1.0 wt %)–ZrO₂, and UV–vis light irradiation was also performed (not shown). H₂¹²CO, ¹²CO, ¹²CH₄, ¹²C₂H₆, and ¹²C₃H₈ were formed at the rates of 0.001, 0.033, 0.039, 0.013, and 0.012 μ mol h⁻¹ g_{cat}⁻¹, respectively, also supporting the partial decomposition of MXene under H₂O and the light irradiation. The product distribution was compared between the conditions of under ¹³CO₂ and H₂O and under H₂O. In the absence of CO₂, the decomposition of Ti₃C₂X_y MXene possibly at the edge section became slower because the intermediate CO was stably adsorbed at the MXene site and was not further hydrogenated, while CO₂ was adsorbed at the site in the presence of CO₂.



Figure 3. (A) XRD patterns of (a) Ti_3AlC_2 , (b) $Ti_3C_2X_y$ MXene, (c) ZrO_2 , and (d-g) $Ti_3C_2X_y$ MXene- ZrO_2 composite. The MXene content in each sample was 1.0, 3.0, 5.0, or 10 wt %. (B) FE-SEM (a,b) and AFM (c,d) images of $Ti_3C_2X_y$ (a,c) and the 3.0 wt % Ti_3C_2X MXene- ZrO_2 composite (b,d). The yellow inset and the scale show the cutaway height for the $Ti_3C_2X_y$ sample observed in (c).



Figure 4. (a,b) TEM, (c–e) HR-TEM, (f) HAADF–STEM, and (g) corresponding STEM energy-dispersive elemental mapping for Ti K α , Zr K α , O K α , C K α , Cl K α , and F K α for (a) Ti₃C₂X_y MXene and (b–g) Ti₃C₂X_y MXene (3.0 wt %)–ZrO₂ samples.

XRD Analysis. The crystal structure during the sample synthesis was studied by XRD. The Ti_3AlC_2 phase exhibits intense peaks [Figure 3A(a)] in accord with the previous report.²⁴ In the first step of synthesis, after etching treatments with HCl and HF (see the Materials and Methods section), the Al content in Ti_3AlC_2 was eliminated, and intense diffraction peaks [(0 0 2) and (1 0 4) diffractions] for Ti_3AlC_2

disappeared. A broad (0 0 2) diffraction peak and weaker (0 0 4) and (1 0 4) diffraction peaks appeared [Figure 3A(b)], demonstrating that Ti_3AlC_2 was successfully transformed into the thinner layered $Ti_3C_2X_y$ compound (Scheme 1A, right). Furthermore, the diffraction peak of $Ti_3C_2X_y$ (0 0 2) shifted from $2\theta_{Bragg} = 10.1-8.1^{\circ}$ after the treatment with LiCl [Figure 3A(b)], indicating an expansion of the interlayer distance of

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Ti₃C₂X_y from 0.874 to 1.09 nm. At the final step of the synthesis of Ti₃C₂X_y MXene, by the centrifugation at 13,000 rpm, even thinner layers of Ti₃C₂X_y nanosheets were successfully achieved, and the layer interval further increased to 1.26 nm based on the XRD peak at $2\theta_{\text{Bragg}} = 7.0^{\circ}$ (not shown).

For all the MXene– ZrO_2 composites (MXene 1.0–10 wt %), the XRD peaks were exclusively ascribed to the monoclinic phase ZrO_2 , while no obvious diffraction peaks attributable to the $Ti_3C_2X_y$ moiety were found [Figure 3A(c-g)]. It was due to the low content and/or higher dispersion of $Ti_3C_2X_y$ in the composites, as supported by TEM micrographs (see the following Microscopy Observation section for HR-TEM analysis).

Microscopy Observation. The microstructure and morphology of the samples were investigated by FE-SEM and AFM. The $Ti_3C_2X_y$ prepared via centrifugation at the rate of 13000 rpm at the final step of synthesis (see the Materials and Methods section) exhibits a sheet-like morphology [Figure 3B(a)], and the cutaway height overdrawn on the image in [Figure 3B(c)] demonstrated a mean 1.6 nm thickness of the nanosheets, which corresponds to three layers of $Ti_3C_2X_y$ units, in accordance with the previous report.²⁵ In contrast, when the centrifugation rate was reduced from 13,000 to 4000 rpm, incompletely exfoliated thick layers of $Ti_3C_2X_y$ are observed, for which the AFM images showed multiple stacked layers 50–100 nm thick (not shown), demonstrating that sufficiently high centrifugation rates, e.g., 13,000 rpm, are required for obtaining ultrathin $Ti_3C_2X_y$ nanosheets.

In the FE-SEM image for the 3.0 wt % MXene– ZrO_2 composite, the $Ti_3C_2X_y$ portion tightly adhered to the ZrO_2 surface [Figure 3B(b)]. Furthermore, the height analysis showed that most of the ZrO_2 nanoparticles (length ~20 nm) adhered on the MXene nanosheets, while no obvious stacking of ZrO_2 nanoparticles was observed [Figure 3B(d)], demonstrating that the two-dimensional MXene contributes to the higher dispersion of ZrO_2 nanoparticles.

Furthermore, the morphology of $Ti_3C_2X_y$ and $Ti_3C_2X_y$ (3.0 wt %) complexed with ZrO_2 was analyzed by TEM and HR-TEM. As shown in Figure 4a, $Ti_3C_2X_y$ MXene exhibits a distinct two-dimensional nanosheet structure with a flattened surface in the range of a few hundred nanometers without stacking, and the edge length of the $Ti_3C_2X_y$ nanosheets was about 100–300 nm.

For the 3.0 wt % MXene– ZrO_2 composite, as shown in Figure 4b,c, ZrO_2 nanoparticles of size 10–20 nm were welldispersed and densely anchored on $Ti_3C_2X_y$ nanosheets, which was further confirmed by the elemental mapping analysis (Figure 4g). By HR-TEM observation (Figure 4d,e), lattice fringes attributed to monoclinic ZrO_2 (1 1 1), (1 1 1), (0 1 1), and (1 1 2) facets were clearly observed at 0.284, 0.317, 0.36, and 0.213 nm, respectively, and the $Ti_3C_2X_y$ interplanar spacing for the edge cross-section view of nanosheets was 1.22 nm corresponding to $Ti_3C_2X_y$ (0 0 2) crystal planes and 0.243 nm for the major exposed (1 0 4) crystal planes (Figure 4e, inset), with a layer thickness of about 1.6 nm due to the three layers (Figure 4d), which was consistent with the AFM observation.

The dispersion of ZrO_2 nanoparticles was more clearly observed as the contrast of Zr (Z = 40) compared to that of Ti (Z = 22) due to the Z^2 dependence of HAADF–STEM (Figure 4f). Furthermore, the elemental mapping revealed the presence of the constituent elements derived from reagents used for the synthesis (Ti, Zr, O, and C) as well as surface terminal groups (Cl and F) derived from solvents used during the synthesis (Figure 4g). Consequently, the termination groups of the $Ti_3C_2X_y$ MXene were identified as X = oxo, OH, Cl, and/or F and especially F and oxo/OH as the major components, consistent with the EXAFS analysis discussed below.

XPS Analysis. The surface chemical states of the prepared $Ti_3C_2X_y$ were analyzed by XPS. As shown in Figure 5A(a), the wide scan XPS spectrum identified that the major elements at the MXene surface included Ti, C, F, and O as well as a not-



Figure 5. (A) (a) Wide scan and (b-d) high-resolution XPS spectra for Ti₃C₂X_y MXene at the binding energy of (b) C 1s, (c) O 1s, and (d) Ti 2p and (B) (a) wide scan and (b-d) high-resolution XPS spectra for ZrO₂ at the binding energy of (b) C 1s, (c) O 1s, and (d) Zr 3d.



Figure 6. (a) Wide scan and (b-e) high-resolution XPS spectra of $Ti_3C_2X_{\nu}$ (3.0 wt %)-ZrO₂ for (b) O 1s, (c) C 1s, (d) Zr 3d, and (e) Ti 2p.



Figure 7. Diffuse reflectance UV-vis-NIr absorption spectra of (a) Ti_3AlC_2 , (b) $Ti_3C_2X_y$, (c) ZrO_2 , and (d-g) $Ti_3C_2X_y$ -ZrO₂. The $Ti_3C_2X_y$ content in the sample was 1.0, 3.0, 5.0, and 10 wt %.

negligible Cl peak, consistent with the STEM energy-dispersive elemental mapping (Figure 4g). Only a very weak Al peak remained, demonstrating that essentially all the Al in the raw Ti_3AlC_2 material was effectively removed during the MXene synthesis, resulting in a well-structured $Ti_3C_2X_{\gamma}$ MXene.

Furthermore, high-resolution XPS spectra of $Ti_3C_2X_y$ MXene are shown in Figure 5A(b-d). The fit to the data in the C 1s region revealed four peaks at 282.3, 284.8, 286.0, and 289.5 eV owing to C atoms forming C-Ti, C-C, C-O, and C-F/C=O bonds, respectively [Figure 5A(b)]. Three typical peaks at 530.1, 531.6, and 534.7 eV were fit to the data in the O 1s region owing to O atoms forming O-Ti, O(surface)-Ti, and HO-Ti bonds [Figure 5A(c)]. In the Ti 2p region, four types of Ti atoms were observed owing to the formed Ti-C (two types), Ti-Cl, and Ti-O bonds [Figure 5A(d)].^{26,27} In contrast, XPS data for the $Ti_3C_2X_y$ (3.0 wt %)– ZrO_2 composite demonstrated the presence of lattice oxygen (O_L) and oxygen vacancy (O_v) (Figure 6b) owing to ZrO_2 [Figure 5B(b)].²⁸ In fact, The O 1s and Zr 3d peak positions owing to ZrO₂ negligibly changed upon composite formation with 3.0 wt % of $Ti_3C_2X_y$ [Figures 5B(c,d) and 6(b,d)]. Furthermore, two Ti $2p_{1/2}$ peaks owing to the Ti–C bond at 461.1 and 462.2 eV for $Ti_3C_2X_y$ MXene [Figure 5A(d)] effectively shifted downward to 460.2 and 461.9 eV, respectively, for the $Ti_3C_2X_y$ –ZrO₂ composite (Figure 6d), strongly suggesting the electron transfer from ZrO₂ to $Ti_3C_2X_y$.

UV–Vis–NIR and Fluorescence Excitation Spectroscopy. The UV–vis–NIR light absorption of Ti_3AlC_2 , $Ti_3C_2X_y$, ZrO₂, and $Ti_3C_2X_y$ –ZrO₂ composites were measured in the wavelength range of 200–850 nm (UV–vis) and 900–2000 nm (NIR). As shown in Figure 7A(a) and B(a), extensive



Figure 8. FTIR spectra of $Ti_3C_2X_y$ (3.0 wt %)-ZrO₂ (20 mg) introducing (a) CO₂ (5.0 kPa), H₂ (45 kPa), and Ar (50 kPa) and (b) CO₂ (97 kPa) and H₂O (2.3 kPa), under UV-vis light irradiation from the Xe lamp for 60 min, and the light was turned off for 20 min.

Table 1. Curve Fit Analysis Results for EXAFS Measured for $Ti_3C_2X_{\nu}$ MXene (30 wt %)-ZrO₂ Photocatalysts

			distance (nm) Coordination number ΔE_0 (eV) Debye–Waller factor (nm)			
entry	ambient gas	conditions	Ti-F	Ti-C	Ti…Ti	goodness of fit
a	air	fresh	0.151 (±0.00035)	0.214 (±0.00055)	$0.302 (\pm 0.00015)$	8.3×10^{5}
			0.6 (±0.025)	2.4 (±0.055)	7.1 (±0.24)	
			3.3 (±0.965)	5.6 (±2.81)	12.3 (±0.235)	
			0.0039 (±0.0004)	0.0043 (±0.0002)	0.0092 (±0.0001)	
b	CO_2 (2.3 kPa) and H_2O (2.3 kPa)	before light irradiation	0.154 (±0.00015)	0.222 (±0.00265)	0.301 (±0.0055)	2.1×10^{4}
			0.7 (±0.015)	1.3 (±0.235)	6.9 (±0.51)	
			$-3.6 (\pm 0.515)$	1.2 (±2.815)	12.5 (±0.095)	
			0.0096 (<± 0.0001)	0.0032 (±0.0017)	0.0091 (±0.0003)	
с		under light irradiation	0.159 (±0.0005)	0.209 (±0.0035)	0.298 (±0.00035)	5.2×10^{5}
			0.3 (±0.01)	1.1 (±0.52)	7.0 (±0.44)	
			$-12.9(\pm 0.6)$	$1.2(\pm 1.87)$	11.2 (±0.02)	
			$0.0070 (\pm 0.0002)$	0.0056 (<± 0.0001)	$0.0102 (\pm 0.0003)$	
d		light off	0.154 (±0.00005)	0.211 (±0.0003)	0.301 (±0.0001)	4.8×10^{5}
			$0.4 (\pm 0.02)$	$0.8 (\pm 0.5)$	7.2 (±0.375)	
			0.03 (±0.29)	11.3 (±1.805)	$13.6(\pm 0.07)$	
			0.0073 (±0.0004)	0.0093 (±0.0025)	0.0099 (±0.0002)	
e	models generated using FEFF8.40		0.190 ¹²	0.2164 ¹⁰	0.30604 ^{10,11}	
			2	4	10	
			0.0055	0.0072	0.0049	

absorption was observed for Ti_3AlC_2 up to 2000 nm. In contrast, the UV–vis absorption on etched and exfoliated $Ti_3C_2X_y$ was significantly suppressed [Figure 7A(b)] but extending to the NIR wavelength region [Figure 7B(b)].

The absorption edge of ZrO_2 was located at 248 nm, correlated to a band gap of 5.0 eV, indicating that the ZrO_2 primarily absorbed UV light to undergo charge separation^{22,23} while no visible and infrared light absorption exists [Figure 7A(c) and B(c)].

Then, for the MXene–ZrO₂ samples, extensive light absorption was observed across the entire UV, vis, and NIR regions, and the absorbance gradually increased as the Ti₃C₂X_y loading increased [Figure 7A(d–g) and B(d–g)]. It should be noted that the same amount of the sample (100 mg) was used for the spectral measurements, but the absorbance of Ti₃C₂X_y (3.0 wt %)–ZrO₂, Ti₃C₂X_y (5.0 wt %)–ZrO₂, and Ti₃C₂X_y (10 wt %)–ZrO₂ (e–g) was significantly greater than the weighted convolution of the absorbance of ZrO₂ (a) and Ti₃C₂X_y (b), demonstrating that the Ti₃C₂X_y moiety was well dispersed in the ZrO_2 matrix and the light absorption efficiency significantly increased. This may also be attributed to light scattering by ZrO_2 and subsequent absorption by $Ti_3C_2X_y$, leading to increased light absorbance.

The fluorescence excitation spectra are depicted in Figure S2. When the excitation wavelength was 200 nm, the fluorescence intensity in the range of 250–450 nm was effectively suppressed for the $Ti_3C_2X_y$ (3.0 wt %)–ZrO₂ sample compared to that for the ZrO₂ sample, demonstrating the charge separation effects of combined $Ti_3C_2X_y$ MXene.

FTIR Spectroscopy. FTIR spectra were monitored for $Ti_3C_2X_y$ (3.0 wt %)–ZrO₂ under photocatalytic CO₂ reduction conditions (Figure 8). When the reactant mixture of CO₂ and H₂ was introduced to the photocatalyst, antisymmetric and symmetric O–C–O stretching vibration [ν_{as} (OCO)] and C–H bending vibration (δ (CH)) owing to bidentate bicarbonate species were observed at 1607, 1424, and 1269 cm⁻¹, respectively. These peaks became intense and more resolved under the light irradiation; however, the

intensity negligibly changed during the light irradiation. The bicarbonate species should be in dynamic equilibrium present under CO_2 , H_2 , and the UV–vis light irradiation, and these peaks became weaker when the light was turned off (Figure 8a).

FTIR spectra under CO_2 and H_2O gas were also monitored. The peaks owing to bidentate bicarbonate species also appeared (Figure 8b). These peaks became intense and more resolved under the light irradiation; however, the intensity negligibly changed during the light irradiation. The intensity was relatively stronger than those under CO_2 and H_2 , and additional peaks of unidentate and/or bridging bidentate species also appeared, primarily owing to the higher reactivity of H_2O than that of H_2 over the ZrO_2 surface.²⁹

In the photocatalytic point of view, the adsorbed bicarbonate species both under CO_2 and H_2 and under CO_2 and H_2O gas were not in accord with the critical difference of the photocatalytic product: CO, especially ¹³CO from ¹³CO₂ and H_2 (Figures 1A and 2A), and CH₄, especially ¹²CH₄ from ¹³CO₂ and H_2O (Figures 1B and 2B). Thus, bicarbonate species seems to be not the intermediate to CO but just accumulated species over the ZrO₂ surface during the photocatalytic test. ¹²CH₄ was likely derived from MXene decomposition and not the photocatalytic product. True intermediate species, e.g., O-C-OH,^{21,30} was not detected in the FTIR spectrum (Figure 8a) due to the relatively short lifetime on the photocatalyst surface.

The negative peak at 1652 cm⁻¹ appeared when the UV-vis light was turned on, and the negative intensity remained essentially constant under the irradiation of light. As no obvious peaks appeared by the introduction of CO₂ and moisture (Figure 8b) before the light irradiation, the negative peak seems to be not the desorption of the adsorbent but suggested the partial decomposition of the CO part of Ti₃C₂X_y (X = oxo and/or OH) MXene by the effects of moisture, probably at the edge section of the three layers of MXene, e.g., terminal C atom oxidized to CO.³¹

EXAFS Analyses. EXAFS curve fit analyses for the fresh $Ti_3C_2X_{\nu}$ MXene-ZrO₂ composite sample demonstrated a compact [Ti₆C] octahedral coordination of the octahedron side length of 0.302 nm and the C-Ti length of 0.214 nm (Table 1a and Figure 9A) connected at the point forming Ti_3C_2 three layers (Scheme 1). The complete $Ti_3C_2X_2$ model structure should comprise the mean coordination numbers of $\frac{2}{3} \times 3 + \frac{1}{3} \times 6 = 4$ and T i – C : $T\ i\ \cdot\ \cdot\ T\ i:$ $\frac{2}{3} \times 9 + \frac{1}{3} \times 12 = 10$ (see the Materials and Methods section). Compared to the mean values, the values for the fresh $Ti_3C_2X_{\nu}$ MXene-ZrO₂ sample and one under CO₂ and H_2O before light irradiation were 2.4–1.3 and 7.1–6.9 (Table 1a,b), respectively, suggesting the distorted Ti_3C_2 and/or defective layers.

The ligands on both sides of the MXene layer were in relatively close position at the interatomic distance between Ti and X of 0.151 nm (Table 1a), suggesting that F and/or oxo were the major component for MXene in this study, consistent with the STEM energy-dispersive elemental mapping (Figure 4g) and XPS results (Figure 5). Apparently, the Ti₃C₂ layer was responsive for electron transfer via the Schottky barrier from the semiconductor ZrO₂ during photocatalysis, as supported by the metallic nature based on DFT calculations (see the following DFT Calculations section). The complete Ti₃C₂X₂ model structure should comprise the mean coordina-



Angular wave number (10 nm⁻¹) Interatomic distance (10⁻¹ nm)

Figure 9. Ti K-edge EXAFS best fit results for the $\text{Ti}_3\text{C}_2X_\gamma$ (30 wt %)–ZrO₂ photocatalyst. (A) Fresh, (B–D) under CO₂ (2.3 kPa) and H₂O (2.3 kPa) before (B), during (C), and after UV–vis light irradiation (D). Transformed data (black lines) and fits (red lines) to (1) (angular wavenumber k)³ × χ function and (2) its associated Fourier transform.

tion number of Ti–X: $\frac{2}{3} \times 3 + \frac{1}{3} \times 0 = 2$ (see the Materials and Methods section). Compared to the mean value, the values for the fresh Ti₃C₂X_y MXene–ZrO₂ sample and the one under CO₂ and H₂O were 0.6–0.7 (Table 1a,b), suggesting η_1 –X coordination rather than η_3 –X coordination.

Under UV-vis light irradiation, the Debye-Waller factors (σ) for the interatomic pairs of Ti-C and Ti…Ti significantly increased by 0.0013-0.0024 nm and 0.0010-0.0011 nm, respectively, compared to those for samples fresh and before the light irradiation, whereas the σ value for the interatomic pair of Ti-F did not increase under the light irradiation (Table 1a-c).

Based on the correlated Debye model,^{22,23} these trends strongly suggested the warming of Ti₃C₂ MXene layers under UV-vis light, and the temperature change of the photocatalyst was evaluated assuming that the Debye temperature for Ti₃C₂X_y was identical to that for TiC (863.3 K)¹⁴ and using a code FEFF8.40.⁹ The σ values for Ti-C and Ti···Ti interatomic pairs increased from 0.0043 and 0.0092 nm for Chart 1. (A) Band Structure for $Ti_3C_2F_2$ MXene and (B) DOS Distribution for $Ti_3C_2F_2$ MXene Combined with the $Zr_{11}O_{22}$ Cluster



Chart 2. Plane-Averaged Electrostatic Potential Plotted along the Direction Perpendicular to the Vacuum Layer, Where the Zero in the Coordinate Corresponds to the Fermi Energy for (A) $Ti_3C_2F_2$ MXene and (B) $Ti_3C_2F_2$ MXene Combined with the $Zr_{11}O_{22}$ Cluster.



the fresh sample to 0.0056 and 0.0102 nm, respectively, under the UV-vis light irradiation (Table 1a,c and Figure 9A,C), corresponding to the temperature increase of 116 K or even higher.

Compared to the evaluation, the light intensity used for this study (${}^{13}CO_2$ photoreduction) was 0.17 W cm^{-2,22} the standard reaction enthalpy change for CO formation was 41.16 kJ mol⁻¹, and the heat capacity of the photocatalyst was assumed to the weighted average of values for TiC (0.569 J $K^{-1} g^{-1}$)³² and ZrO₂ (0.456 J $K^{-1} g^{-1}$).³³ The endothermic reaction reduced the temperature of the system at the rate of 0.39 K h⁻¹ at the maximum, while light energy should sufficiently warm the photocatalyst at the rate as high as 1.1 K s⁻¹ at the maximum. In contrast, the σ value was essentially constant throughout the light irradiation, demonstrating the equilibrium of transformed heat from light and the heat dissipation to the sample cell.^{22,23} Judging from the DFT calculations for $Ti_3C_2X_{\nu}$ MXene (Chart 1), $Ti_3C_2X_{\nu}$ is semimetal-like, and the electron conductivity is expected to increase by the thermal excitation of VB electrons to the CB rather than the thermal inhibiting effects of free electrons of the metal.

After the UV–vis light was turned off, the σ values did not decrease to the ones before the light irradiation (Table 1), as expected to by the monitoring of warming and cooling of Ag, Au, and Ni nanoparticles,^{22,23} probably because the increase of disorder and/or defective sites under the irradiation of light and water canceled the effect of cooling on the σ values.

DFT Calculations. Chart 1A shows the band structure calculated for $Ti_3C_2F_2$ MXene based on DFT. At the K point in the Brillouin zone, the electronic configuration of the semiconductor was obtained, while the conduction levels shifted to a lower energy, resulting in the conduction level at -0.2 eV below the $E_{\rm F}$ at the Γ point, suggesting a more semimetal state. The conduction level became even lower at -2.4 eV at the M point. These configurations suggested a semimetal nature rather than a semiconductor nature for $Ti_3C_2X_{\nu}$ MXene and an indirect transition from the -0.2 eV level at the Γ point to the conduction level at the *K* point and/ or from the conduction level between K and Γ points at -0.7eV to -0.2 eV level at the Γ point (Chart 1A). This result was in accord with the discussion for enhanced electron transmission in Ti₃C₂F₂ MXene layers when the light energy was transformed into heat, as monitored by the Debye-Waller factor increase in Ti K-edge EXAFS measurements.

Chart 1B shows the DOS distribution for $Ti_3C_2F_2$ MXene combined with the $Zr_{11}O_{22}$ cluster. The ZrO_2 band gap is shown as the difference between the VB maximum comprising O 2p orbitals and the CB minimum comprising Zr 4d orbitals. Below and near the E_F , the DOS of major Ti and minor C components was clearly present, suggesting the photoexcited electrons from O 2p at the VB for ZrO_2 were band gap excited by the UV light, and then, the electrons excited to the CB could be injected into the Ti_3C_2 MXene layer for electron transmission to assist the charge separation for ZrO_2 . The DOS distribution negligibly changed when the ligand of MXene was replaced to OH or Cl instead of F except for the difference of F 2p, O 2p, and Cl 3p population (Charts 2 and S2). Such comparisons were already reported³⁴ for MXene not combined with the $Zr_{11}O_{22}$ cluster.

Chart 2 shows the plane-averaged electrostatic potential plotted along the direction perpendicular to the vacuum layer. The work function of Ti₃C₂F₂ MXene was calculated to be 4.83 eV, which was comparable to values in the previous report.³⁵ The work function value of Ti₃C₂F₂ MXene combined with the $Zr_{11}O_{22}$ cluster was calculated to be 4.70 eV, similar to the change in the Ti₃C₂OH MXene-TiO₂ system.³⁵ The reason for the shift by -0.13 eV was due to the formation of dipoles at the interface and the $E_{\rm F}$ shifted relative to the band edge of ZrO2, similar to the reported situation.³⁵ Combined with the calculated positions of the VB maximum (-2.0 eV) and CB minimum (2.8 eV) relative to the $E_{\rm F}$ (Chart 1B) as well as the electrostatic potential for the $Zr_{11}O_{22}$ cluster mostly populated above the E_F for $Ti_3C_2F_2$ (Chart 2B), the work function value was located between the band gap of the $Zr_{11}O_{22}$ cluster with reference to the vacuum level, and thus, the light-excited electrons at ZrO2 were injected into Ti₃C₂F₂ MXene.

CONCLUSIONS

The photocatalytic effects for CO₂ reduction, nanoscale and site coordination structures, and electron transmission of $Ti_3C_2X_{\nu}$ (X = oxo, OH, F, or Cl) MXene were investigated. As the active site for CO_2 reduction, ZrO_2 was used in combination with Ti₃C₂X_y MXene. The CO photogeneration rate using $Ti_3C_2X_{\nu}$ (3.0 wt %)-ZrO₂ and H₂ (4.6 μ mol h⁻¹ g_{cat}^{-1}) was increased by 6.6 times compared to the rate using ZrO₂ and H₂, and the reaction route was confirmed by monitoring ¹³CO₂ photoconversion into ¹³CO. In contrast, using $Ti_3C_2X_{\nu}$ (3.0 wt %)-ZrO₂ and moisture, CO photogeneration became negligible and CH₄ formation was found to be due to the partial decomposition of Ti3C2X, under the irradiation of UV-vis light and moisture based on the predominant ¹²CH₄ generation under the reactant comprising ¹³CO₂. FTIR spectroscopy, XRD, FE-SEM, AFM, HR-TEM, and HAADF-STEM analyses confirmed that around three layers of Ti₃C₂X_v MXene and 10-20 nm size ZrO₂ particles were attached to the flat MXene layers. The major X ligands seemed to be F, oxo, and/or OH based on STEM energydispersive elemental mapping, XPS, and Ti K-edge EXAFS analysis. Ti K-edge EXAFS demonstrated compact Ti-C and Ti…Ti coordination, and the Debye-Waller factor increased under the irradiation of UV-vis light, indicating the warming of MXene by ~100 K to enable accelerated electron transmission in photocatalytic CO₂ reduction over ZrO₂, in accord with the semimetal-like electronic configuration of Ti₃C₂X_v MXenes based on DFT calculations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.3c03883.

The following files are available free of charge at ACS Web site. The illustration of the optimized structure and DOS based on DFT calculations for $Ti_3C_2X_2$ (X = O, Cl, or F) MXene combined with $Zr_{11}O_{22}$; photocatalytic reduction tests using $Ti_3C_2X_y$ MXene; and fluorescence emission spectra for ZrO_2 and the $Ti_3C_2X_y$ MXene– ZrO_2 composite (PDF)

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Notes

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