Active Sulfur Sites in Semimetallic Titanium Disulfide Enable CO₂ Electroreduction

Abdalaziz Aljabour,[†] Halime Coskun,[†] Xueli Zheng,^{‡,⊥} Md Golam Kibria,^{‡,#}
Moritz Strobel,[¶] Sabine Hild,[¶] Matthias Kehr,[§] David Stifter,[§] Edward H.
Sargent,[‡] and Philipp Stadler^{*,†,||,‡}

[†]*Institute of Physical Chemistry, Johannes Kepler University Linz, Altenbergerstrasse 69,
4040 Linz, Austria*

[‡]*Edward S. Rogers Sr. Department of Electrical and Computer Engineering, University of
Toronto, 10 King's College Road, Toronto, Ontario M5S 3G4, Canada*

[¶]*Institute of Polymer Science, Johannes Kepler University Linz, Altenbergerstrasse 69,
4040 Linz, Austria*

[§]*Center for Surface and Nanoanalytics, Johannes Kepler University Linz,
Altenbergerstrasse 69, 4040 Linz, Austria*

^{||}*Linz Institute of Technology, Johannes Kepler University Linz, Altenbergerstrasse 69,
4040 Linz, Austria*

[⊥]*Current address: Department of Materials Science and Engineering, Stanford University,
Stanford, CA 94305, USA*

[#]*Current address: Department of Chemical and Petroleum Engineering, University of
Calgary, 2500 University Drive, NW Calgary, Alberta T2N 1N4, Canada*

E-mail: *philipp.stadler@jku.at

Abstract

Electrocatalytic CO₂-to-CO conversion represents one pathway to upgrade CO₂ to a feedstock for both fuels and chemicals (CO, deployed in ensuing Fisher-Tropsch or bioupgrading). It necessitates selective and energy-efficient electrocatalysts – a requirement met today only using noble metals gold and silver. Here we show that the 2-dimensional sulfur-planes in semimetallic titanium disulfide (TiS₂) provide an earth-abundant alternative. In-situ FTIR mechanistic studies reveal that CO₂ binds to conductive disulfide planes as intermediate monothiocarbonate. The sulfur-CO₂ intermediate state steers the reduction kinetics towards mainly CO. Using TiS₂ thin films we reach cathodic energy efficiencies up to 64% at 5 mA cm². We conclude with directions for the further synthesis and study of semimetallic disulfides developing CO-selective electrocatalysts.

Keywords

CO₂ reduction reaction, titanium disulfide, electrocatalysis, sulfur activation, monothiocarbonate, transition metal dichalcogenide

Introduction

Electrocatalysis is an attractive pathway to recycle CO₂, upgrading it using renewable energy.¹ Presently, the electrochemical CO₂-to-CO conversion process is the most efficient, but requires catalyst materials with appreciable activity and selectivity to optimize energy efficiency.² Currently, these conditions are met by 4d and 5d transition metals such as Ag and Au.³⁻⁷ Recent works have instead focused on the application of 2-dimensional transition metal dichalcogenides (2D-TMDCs) such as WSe₂ and MoS₂ with the goal of equaling the best CO₂-to-CO electrocatalyst performance,⁸⁻¹⁷ but poor intrinsic conductivity and comparative complex synthesis are still subjects to be improved. Nonetheless, transition metal dichalcogenides are in general attractive electrocatalysts, because more-earth-abundant metals with limited catalytic properties can be activated for electrochemical energy conversion.^{14-16,18-24} We here follow particularly this hypothesis and replace recently used Mo or W by the less electronegative 3d metal titanium. A similar concept has been recently demonstrated relying on nickel, iron and tin oxides or sulfides where electronic properties were adapted for superior electrocatalytic performances.²⁵⁻²⁸ Particularly, we found titanium disulfide (TiS₂) is one promising candidate for CO₂-to-CO conversion, since structurally it possesses cohesive van der Waals type of bonding similar to Mo- and W 2D-TMDCs, but electronically has a narrow overlap of conduction and valence band (zero gap) and thus belongs to the class of semimetals with a conductivity similar to that of graphite.^{29,30} We show here that TiS₂ can enhance CO₂ reduction, since a major limitation in earlier used MoS₂ and related, the poor electrical conductivity, is resolved. We found that the increased conductivity activates a dangling site mechanism in the TiS₂ 2D-sulfur planes and as such exemplifies non-metallic and CO-selective catalytic centres: Here performed in-situ FTIR studies reveal that under cathodic bias intermediate monothiocarbonates and thioles are formed. We show that in organic electrolyte the intensity of the monothiocarbonate-based CO₂ reduction is favored over the competing hydrogen evolution thus leading to a relative high selectivity for CO. Further we found that the mechanism reported here is similar to earlier observations on

conducting MoS₂ systems.³¹ We demonstrate the selective electrosynthesis of CO at overpotentials less than 0.4 V at 5 mA cm⁻² operation current density with a total Faradaic yield up to 83% using thin-films of TiS₂ in the range of 200 nm. We tested the electrocatalyst in initial 16 h continuous operation electrolysis and found no significant degradation effects limiting the process. The electrocatalytic performance of TiS₂, *i.e.* the selectivity for CO and the overpotential, can compete with other 3d-metal based CO₂ catalysts.^{25,28,32} We found these aspects merit further exploration to harness cathodic-activated (conductive) sulfur planes as powerful catalytic centres. In this context TiS₂ represents a new frontier in electrochemical CO₂ conversion.

Results and discussion

We grew TiS₂ by atomic layer deposition (ALD) using sequential reaction of tetrakis (dimethylamido) titanium(IV) (TDMAT) and H₂S at 150°C in vacuo.³³ The resulting thin films (200 nm (*1T*)-TiS₂) were deposited on glass, carbon paper or germanium for the (spectro)electrochemical and electrical-structural studies. The spectral Raman (Figure 1a) revealed the fingerprint vibrational modes at 331 cm⁻¹ (A_{1g})³⁴ related to the layered 2D (*1T*)-phase of TiS₂ (Figure 1c). We conducted resistivity ρ and Hall measurements: the thin films possessed similar values for resistances and the Hall constants R_H compared to earlier reported bulk (*1T*)-TiS₂ crystals (3.7·10⁻³ Ω cm and 5.26·10⁻² cm³ C⁻¹ at room temperature⁴ and Hall mobility on the order of 13.6 cm² V⁻¹ s⁻¹, respectively) (Figure 1b). The temperature coefficient of resistivity (TCR) was negative, and, the carrier concentration was relatively constant as a function of temperature in the range of 10⁺²⁰ cm⁻³. Both observations are signature characteristics of semimetals (Figure 1d and supporting information, SI, Figure S1).

These results confirmed the high electrical conductivity of the TiS₂ thin-films synthesized by ALD. As reported previously, the electrical properties of TiS₂ are found to be affected by

Figure 1: **TiS_2 spectroscopic, structural and electrical characterization.** (a) Raman-shift of $(1T)\text{-TiS}_2$ films show the characteristic band at 331 cm^{-1} (A_{1g} modes).³⁴ (b) Resistivities ρ (ascending order) and carrier concentration of TiS_2 -crystals and TiS_2 films compared to other transition metal dichalcogenides previously used as CO_2 electrocatalyst.^{4,35,36} (c) Schematic of TiS_2 structure (layered $1T$ -phase). (d) Temperature-dependent Hall-effect and resistivity ρ of TiS_2 films show negative temperature coefficient of resistivity (TCR) and constant carrier concentration n_e .

exposure to ambient air.³⁷ Therefore all reported experiments were conducted in oxygen-free atmosphere using organic electrolytes with oxygen levels below 1 ppm. The electrocatalytic experiments showed TiS_2 works as electrocatalytic layer on carbon paper as conductive substrate. The parasitic voltage drops such as reported for MoS_2 and other TMDCs were negligible for the as-synthesized semimetal TiS_2 .

Table 1: Electrical parameters at 300 K of thin-film and bulk TiS_2 .

TiS_2 system	$\rho / \Omega \text{ cm}$	$R_H / \text{cm}^3 \text{ C}^{-1}$	$\mu_H / \text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	thickness
single crystal*	$3.26 \cdot 10^{-3}$	$5.50 \cdot 10^{-2}$	16.87	crystal
ALD thin film	$3.77 \cdot 10^{-3}$	$5.35 \cdot 10^{-2}$	14.17	200 nm

* taken from Friend et al.;⁴

Central intention of this work was to harness the proven catalytic activity of TiS_2 for the CO_2RR . Earlier reports demonstrated that sulfides enhanced the catalyst performance.^{9,16,26}

To reveal the reaction mechanism on TiS_2 we elucidated its surface reactivity by in-situ FTIR spectroscopy (internal reflection mode, Figure 2b). We report the presence of carbonyl vibrations at 1724 cm^{-1} and O-C-S stretch oscillations at 1171 cm^{-1} and at 1153 cm^{-1} as soon as TiS_2 is under cathodic bias (Figure 3a and 3b). These features relate to monothiocarbonate features (MTC , S-COO^-) formed as CO_2 -sulfide reaction intermediate.³⁸ The quantity of these features increased by rising cathodic reduction potentials, in contrast to the (relative intense), but constant solvent related background features. MTC represents an intermediate capture state similar to metal-complexes found on metallic surfaces necessary to accelerate further electroreduction.^{8,38-41} A similar sulfide-based mechanism has been proposed for vacancies in the basal planes of $1T$ -phase TMD-sulfides.^{31,42-44} Particularly, Tsai *et al.*³¹ proposed S-H intermediates at the cathode in analogy to our proposed MCT.

The control experiment without CO_2 (N_2 control experiment) showed no presence of MTC and only the spectral responses of electrolyte ($\text{NBu}_4\text{-PF}_6$) and solvent (CH_3CN) (Figures 3c and 2a). The mechanism proposed from the in-situ spectral response is the nucleophilic attachment of sulfur to CO_2 enforced by the reducing environment (Figure 3d). Similar activation processed has been reported in MoS_2 for hydrogen evolution reaction (HER) proposing

Figure 2: **In-situ FTIR on TiS_2 under electrochemical bias.** (a) Survey of the differential absorption ($-\Delta T/T \propto \text{Abs.}$) spectra of changes related either to monothiocarbonate (MCT) formation in presence of CO_2 and changes related to solvent/electrolyte intercalation. The control spectra (N_2) show only features related to the electrolyte ($\text{NBU}_4\text{-PF}_6$) and solvent (reference spectrum of CH_3CN is included). (b) Schematic of the in-situ FTIR-setup. Internal reflection mode (attenuated total reflection, ATR-FTIR) measurement using a germanium parallelepiped as reflection element and the electrochemical flow cell mounted on top to elucidate the surface reaction on TiS_2 during CO_2 electroreduction.

intermediate H-S bonds. The corresponding intermediates in CO_2RR , formal MTC, as the competing HER-intermediate S-H (5% hydrogen evolution) are indicated in the difference spectra: Apart from (i) the carbonyl-vibration (1724 cm^{-1} , Figure 3a) and (ii) the O-C-S stretch vibrations (1171 and 1153 cm^{-1} , Figure 3b) we found a spectroal S-H peak at 2565 cm^{-1} (SI, Figure S8) that emerged from the competing HER.

The presence of a proton will lead the further decomposition of MTC to CO gas and hydroxyl (or water in neutral/acidic environment, Figure 3d). We denote that as-formed CO can react further to formate, which we detect as unavoidable byproduct (CO hydrolysis).^{45,46}

We utilized in-situ FTIR to test the stability window of TiS_2 and possible unwanted side-reactions. In all our experiments we used hybrid organic-water electrolytes (water content is $1\%_{\text{vol}}$ in CH_3CN , $0.1\text{ M NBU}_4\text{-PF}_6$) and report reversibility up to -1020 mV vs. RHE (Figure 3c). The presence of water (or protons) is requisite to allow the electroreduction of CO_2 . In addition, water slightly increases the ionic conductivity and it buffers the pH in acetonitrile

Figure 3: **Detailed differential absorptin and mechsanism of CO₂RR on TiS₂.** (a) and (b) represent in-situ differential absorption ($-\Delta T/T$) in the fingerprint regime showing the spectral changes related to monothiocarbonate (MTC, S-COO⁻) carbonyl- and O-C-S stretch-vibrations rising with cathodic bias. (c) Spectral comparison of MTC carbonyl at maximum reductive bias at -1020 mV vs. RHE in CO₂-saturated electrolyte is compared to a control experiment without CO₂ (N₂-flushed). (d) Proposed mechanism of CO₂RR on TiS₂: (i) nucleophilic reaction of cathodic-biased sulfide to CO₂, (ii) formation of intermediate MTC and (iii) further reduction including an proton to CO (and OH⁻).

at CO₂ saturation to 7.9. We did not find evidence of side reactions or decomposition of the TiS₂ itself. In the control experiment without CO₂ the in-situ FTIR spectra show only features relating to CH₃CN (included as reference spectrum) and the electrolyte (NBu₄-PF₆) (Figure 3c, detailed spectra in the supporting information, SI, Figures S5).

Figure 4: **Electrocatalytic performance and stability analysis of CO₂-to-CO.** (a) Cyclic voltammograms of TiS₂ in EMIM-BF₄ and NBu₄-PF₆. The inset show the reference E₀ value for ferrocene/ferrocenium (Fc/Fc⁺) standard. (b) Chronoamperometric (j_{CO}) scan for 16 h hours. (c) Faradaic efficiencies (FE) for CO shown in both electrolytes and (d) the corresponding CO-Tafel slopes based on j_{CO}.

The electrochemical CO₂-to-CO conversion was measured in the same electrolyte system in an electrolysis cell using continuous chronoamperometry (CA) and cyclic voltammetry

(CV). The corresponding cell constants and the electrochemical surface area (ECSA) and the calibration of the reference electrode is presented in the SI (Figure S2 and S3) or shown as inset (Figure 4c). All Faradaic reduction currents are referenced to the ECSA and revealed the activity of TiS_2 as potential CO_2 reduction electrocatalyst (*i.e.* $j_{\text{ECSA}} = 20 \text{ mA cm}^{-2}$ at -800 mV vs. RHE) (Figure 4a). At -0.5 V vs. RHE (corresponding to 0.39 V overpotential) we reached the maximum Faradaic efficiency (FE) of 83% at a Faradaic reduction current density of 5 mA cm^{-2} in $0.1 \text{ M NBu}_4\text{-PF}_6$ for CO (j_{CO} , Figure 4c). As side product also formate (13%) and hydrogen (4%) are produced. We repeated the same experiments using an alternative ionic liquid – CH_3CN electrolyte (EMIM- BF_4 at 4%_{vol}, including 1%_{vol} water). The presence of ionic liquid increased the electrolyte conductivity (SI, Figure S2 and Table 1), but decreased the selectivity for CO by a factor 2 (maximum is 55%, Figure 4c). The main side-product was here hydrogen (and negligible amounts of formate). In both electrolytes there exists a general optimum potential range for CO at around 0.4 V overpotential. We performed the product analysis using gas (CO, H_2) and ion chromatography (formate) ex-situ after continuous electrolysis (example shown in the SI, Figures S6). To demonstrate the electrode stability we included an initial 16 h continuous electrosynthesis of CO (Figure 4b) and, similar to the in-situ FTIR-studies, found reversibility/stability with only negligible changes in the product yield and current. In particular the spectral changes after electrode bias related to the solvent (acetonitrile) and electrolyte intercalation inside TiS_2 as suggested by the in situ FTIR spectra (Figure 2a). In summary we showed that TiS_2 possesses selectivity for CO_2RR producing mainly CO. From the experimental data on TiS_2 on carbon paper in two different electrolyte solutions ($0.1 \text{ M NBu}_4\text{-PF}_6$ and EMIM- BF_4 at 4%_{vol}) we calculated the CO Tafel slopes (Figure 4d): the lowest slope was achieved using $\text{NBu}_4\text{-PF}_6$ at 130 mV dec^{-1} . In EMIM- BF_4 , the j_{CO} and the Tafel slope increased to 185 mV dec^{-1} . In this context, TiS_2 behaves similar as compared to earlier reports on 4d and 5d transition metal dichalcogenides investigated for CO_2RR and/or HER.^{20,47–52} We estimated the cathodic energy efficiency (EE_{cathodic}) is 64% at 0.39 V overpotential (equation 1, Gibb's

free reaction energy ΔG_r for CO_2 splitting to CO and O_2 at $257.23 \text{ kJ mol}^{-1}$), the number of transferred electrons $n = 2 \text{ e}^-$, the Faraday constant F and Faradaic efficiency FE for CO at 83%).

$$EE_{cathodic} = \frac{1}{nF} \cdot \frac{\Delta G_r}{\Delta G_r + nF \cdot \eta_{cathodic}} \cdot FE \quad (1)$$

A common observation from the present results on TiS_2 and related other dichalcogenide electrocatalysts is their compatibility with non-aqueous solvents.^{16,20}

Conclusions

Chalcogenide semiconductors have been frequently proposed as alternative systems in electrocatalysis to replace classic noble and precious metals, in particular for strategic aims in converting substantial amounts of anthropogenic emitted CO_2 . However, compared to metals, the ultimate surface activities of chalcogenide semiconductors can be limited by poor electrical transport properties. We therefore found it compelling to elucidate the potential catalytic performance of the semimetallic dichalcogenide TiS_2 in the CO_2 reduction reaction. TiS_2 possesses an intrinsic electrical conductivity of approximately 260 S cm^{-1} , but also offers cathodic reaction activity in sulfur batteries (to intercalate sodium and lithium ions) and for the hydrogen evolution reaction. We transfer these insights now for CO_2RR and found excellent carbon conversion (CO and formate) efficiencies *i.e.* combined Faradaic yield beyond 95% and overpotential below 0.4 mV at $j_{\text{CO}} = 5 \text{ mA cm}^{-2}$. Interestingly, we reveal a sulfur- CO_2 intermediary monothiocarbonates that drive the reduction and lead to the reported high selectivity for CO. In particular the cathalytic activity of sulfur is a central aspect, which merits further exploration for rational design of electrocatalytic materials without consuming energy-critical elements for large-scale CO_2 reduction.

Experimental

ALD growth of TiS_2

Tetrakis (dimethylamido) titanium(IV) (TDMAT, 99.99% Ti; Strem Chemicals) and H_2S are used as precursors in alternating pulsed ALD at a constant growth rate of 0.1 nm per cycle measured by DekTak. Nitrogen is used as a carrier gas (99.9999% pure, Carbagas) with a flow rate of 10 mL min^{-1} (sccm). TDMAT and H_2S are alternately exposed to the deposition chambers using 20 s exposure time and 150°C in vacuo at 2000 repeating loops. As substrate we use glass, carbon paper and germanium.

Electrical measurements

The final TiS_2 layer has a film thickness of 200 nm as measured by DekTak (Bruker). The films are brownish-opaque and conduct electricity. For the Hall measurements, we employ a van-der-Pauw specimen configuration. We use a shadow mask to deposit thin films of TiS_2 onto a patterned substrate. The electrical conductivity and the Hall constant are measured in Helium atmosphere between 300 K and 100 K using a LakeShore Hall measurement Setup 8400. The Hall parameters were set to 1 mA DC-current and 0.91 T.

Electrochemical measurements

For the evaluation of the TiS_2 electrocatalyst, electrochemical studies were conducted in a standard three-electrode arrangement in an H-cell configuration. TiS_2 was set as the working electrode (WE), Ni as a counter electrode (CE) and Ag/AgCl as quasi reference electrode (QRE), all dipped into a 0.1 M $\text{NBu}_4\text{-PF}_6$ or 4% EMIM- BF_4 in acetonitrile water with 1%_{vol} (0.555 mol L^{-1}). The electrolyte solutions are purged with CO_2 for 1 h before characterization. The complete electrochemical system releases CO at the cathode compartment and evolves oxygen at the anode space (schematic in SI, Figure S5). The WE and QRE were placed in the same compartment of the H-cell, whereas the CE is in the second zone to avoid

any back oxidation at the counter electrode. The anode and cathode compartments were separated by a glass frit as the membrane between the cells. The Ag/AgCl quasi reference electrode are calibrated against the ferrocene/ferrocenium couple (Fc/Fc^+) as internal reference. The actual applied potentials are consistently plotted versus the reversible hydrogen electrode (RHE). For this, we measured the pH using indicators and pH-meters in both electrolytes and determined at 7.9 ($\text{NBu}_4\text{-PF}_6$) and 5.9 (4% EMIM-BF_4).⁵³ We calculated the RHE potential based on the calibrated QRE and the pH-value (equation 2). Density functional theory (DFT) calculations of the same electrolyte yielded similar values for the RHE (or, the standard hydrogen electrode, SHE, respectively).⁵⁴

$$E_{\text{RHE}} = E_{\text{QRE vs. Fc/Fc}^+} + 0.641 \text{ V} + \text{pH} \cdot 0.0591 \text{ V} \quad (2)$$

All electrochemical experiments were performed using a JAISSE Potentiostat Galvanostat IMP 88 PC and the amount of CO gas was analyzed with TRACETM Ultra Gas Chromatograph equipped with a thermal conductivity detector (TCD) (example chromatogram for CO detection shown in SI, Figure S7). The electrochemical experiments were performed in the glovebox atmosphere. The compartments of the H-cell were purged with N_2 and CO_2 before starting each experiment, For the analysis of the CO gas, 2 mL samples were taken from the headspace with a gas-tight syringe and injected to the gas chromatograph. Helium was used as the carrier gas with a flow rate of 20 mL min^{-1} . The thermal conductivity detector (TCD) was kept at 200°C . Capillary ion chromatography (CAP-IC) (Dionex ICS 5000, conductivity detector, AG19, CAP, $0.4 \times 50 \text{ mm}$ pre-column, AS19, CAP, $0.4 \times 250 \text{ mm}$ main column) with potassium hydroxide (KOH) as eluent for isocratic chromatography was adjusted for the analysis of liquid samples before and after CPE. Before injecting, the samples were diluted 1:20 with $18 \text{ M}\Omega\text{cm}$ water. The CAP-IC injection was followed by injecting 1 mL of diluted sample with a syringe. The electrochemical cell parameters and the electrochemical surface area (ECSA) are measured using electrochemical impedance spectroscopy (EIS) carried out using a CompactStat (IVIUM). The impedance spectra were recorded

between 100 mHz and 0.1 MHz with an AC-amplitude of 50 mV. From this, we derive an equivalent circuit and the electrolyte resistance R_{el} , the membrane resistance R_m and the capacitance of the working electrode C_{WE} (summarized in the SI, Table S1, Figure S2). From the electrochemical capacitance we derived the ECSA. To verify this decisive parameter we crosschecked the ECSA using cyclic voltammogram sweeps of the working electrode at different scan rates (5 to 200 mV s⁻¹) (SI, Figure S3). The current densities reported in this manuscript are all normalized according to the ECSA.

In-situ FTIR

A flow cell is tightened inside a Bruker IFS/66 FTIR spectrometer, where the incident IR-beam is aligned using confocal mirrors through the germanium attenuated total reflection (ATR) element (parallelepiped, multiple reflections at 45°, schematic in Figure 2). During the measurement of the voltammograms and FTIR spectra, the cell is continuously flushed with electrolyte solution (0.1 M NBu₄-PF₆). Reference spectra and control cyclic voltammograms are recorded in N₂ and CO₂ purged electrolyte (SI, Figure S6). The resulting in-situ spectra at different electrochemical potentials are plotted as differential transmission ($-\Delta T$) and differential absorption ($-\Delta T/T \propto \text{absorbance}$). The spectra show the spectroscopic changes induced by the electrochemical reaction on the surface. Negative spectroscopic signals correspond to a fading process and positive signals relate to an emerging, new features. The monothiocarbonate features represent the latter class (emerging).

Supporting Information Available

The supporting information includes details of electrical transport measurements, material characterization, the electrochemical and chromatographic characterization during CO₂ electrolysis and further information on the in-situ spectroelectrochemical probing. This information is available free of charge on the ACS Publication.

Acknowledgement

The authors thank the Government of Upper Austria within the Sabbatical program “Internationalization of the University of Linz” at the University of Toronto. The authors acknowledge the financial support of the Austrian Science Foundation (FWF I3822-N37, Sustainable Catalysis), the Linz Institute of Technology (LIT, LIT-2017-4-YOU-005, Biopolymer-based carbonate reduction) at the Johannes Kepler University Linz and European Regional Development Fund (EFRE, IWB2014-2020, 2018-98299, Artificial Food).

References

- (1) Chu, S.; Cui, Y.; Liu, N. The path towards sustainable energy. *Nature Materials* **2017**, *16*, 16–22.
- (2) Windle, C. D.; Perutz, R. N. Advances in molecular photocatalytic and electrocatalytic CO₂ reduction. *Coordination Chemistry Reviews* **2012**, *256*, 2562–2570.
- (3) Chaturvedi, A.; Edison, E.; Arun, N.; Hu, P.; Kloc, C.; Aravindan, V.; Madhavi, S. Two Dimensional TiS₂ as a Promising Insertion Anode for Na-Ion Battery. *ChemistrySelect* **2018**, *3*, 524–528.
- (4) Friend, R. H.; Jerome, D.; Liang, W. Y.; Mikkelsen, C.; Yoffe, A. D. Semimetallic character of TiSe₂ and semiconductor character of TiS₂ under pressure. *Journal of Physics C: Solid State Physics* **1977**, *10*, L705.
- (5) Saberi Safaei, T.; Mepham, A.; Zheng, X.; Pang, Y.; Dinh, C.-T.; Liu, M.; Sinton, D.; Kelley, S. O.; Sargent, E. H. High-Density Nanosharp Microstructures Enable Efficient CO₂ Electroreduction. *Nano Letters* **2016**, *16*, 7224–7228.
- (6) Liu, M. et al. Enhanced electrocatalytic CO₂ reduction via field-induced reagent concentration. *Nature* **2016**, *537*, 382–386.

- (7) Feaster, J. T.; Shi, C.; Cave, E. R.; Hatsukade, T.; Abram, D. N.; Kuhl, K. P.; Hahn, C.; Nørskov, J. K.; Jaramillo, T. F. Understanding Selectivity for the Electrochemical Reduction of Carbon Dioxide to Formic Acid and Carbon Monoxide on Metal Electrodes. *ACS Catalysis* **2017**, *7*, 4822–4827.
- (8) Gabardo, C. M.; Seifitokaldani, A.; Edwards, J. P.; Dinh, C.-T.; Burdyny, T.; Kibria, M. G.; O’Brien, C. P.; Sargent, E. H.; Sinton, D. Combined high alkalinity and pressurization enable efficient CO₂ electroreduction to CO. *Energy & Environmental Science* **2018**,
- (9) Zhuang, T.-T. et al. Steering post-C–C coupling selectivity enables high efficiency electroreduction of carbon dioxide to multi-carbon alcohols. *Nature Catalysis* **2018**, *1*, 421–428.
- (10) De Luna, P.; Quintero-Bermudez, R.; Dinh, C.-T.; Ross, M. B.; Bushuyev, O. S.; Todorović, P.; Regier, T.; Kelley, S. O.; Yang, P.; Sargent, E. H. Catalyst electro-redeposition controls morphology and oxidation state for selective carbon dioxide reduction. *Nature Catalysis* **2018**, *1*, 103–110.
- (11) Dinh, C.-T.; Burdyny, T.; Kibria, M. G.; Seifitokaldani, A.; Gabardo, C. M.; García de Arquer, F. P.; Kiani, A.; Edwards, J. P.; De Luna, P.; Bushuyev, O. S.; Zou, C.; Quintero-Bermudez, R.; Pang, Y.; Sinton, D.; Sargent, E. H. CO₂ electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. *Science* **2018**, *360*, 783–787.
- (12) Shinagawa, T.; Larrazábal, G. O.; Martín, A. J.; Krumeich, F.; Pérez-Ramírez, J. Sulfur-Modified Copper Catalysts for the Electrochemical Reduction of Carbon Dioxide to Formate. *ACS Catalysis* **2018**, *8*, 837–844.
- (13) Zhou, Y. et al. Dopant-induced electron localization drives CO₂ reduction to C₂ hydrocarbons. *Nature Chemistry* **2018**,

- (14) Mariano, R. G.; McKelvey, K.; White, H. S.; Kanan, M. W. Selective increase in CO₂ electroreduction activity at grain-boundary surface terminations. *Science* **2017**, *358*, 1187–1192.
- (15) Zhang, L.; Zhao, Z.-J.; Gong, J. Nanostructured Materials for Heterogeneous Electrocatalytic CO₂ Reduction and their Related Reaction Mechanisms. *Angewandte Chemie International Edition* **2017**, *56*, 11326–11353.
- (16) Asadi, M.; Kumar, B.; Behranginia, A.; Rosen, B. A.; Baskin, A.; Repnin, N.; Pisasale, D.; Phillips, P.; Zhu, W.; Haasch, R.; Klie, R. F.; Král, P.; Abiade, J.; Salehi-Khojin, A. Robust carbon dioxide reduction on molybdenum disulphide edges. *Nature Communications* **2014**, *5*.
- (17) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nature Chemistry* **2013**, *5*, 263–275.
- (18) Liu, Y.; Liang, C.; Wu, J.; Sharifi, T.; Xu, H.; Nakanishi, Y.; Yang, Y.; Woellne, C. F.; Aliyan, A.; Martí, A. A.; Xie, B.; Vajtai, R.; Yang, W.; Ajayan, P. M. Atomic Layered Titanium Sulfide Quantum Dots as Electrocatalysts for Enhanced Hydrogen Evolution Reaction. *Advanced Materials Interfaces* **2018**, *5*, 1700895.
- (19) Abbasi, P.; Asadi, M.; Liu, C.; Sharifi-Asl, S.; Sayahpour, B.; Behranginia, A.; Zapol, P.; Shahbazian-Yassar, R.; Curtiss, L. A.; Salehi-Khojin, A. Tailoring the Edge Structure of Molybdenum Disulfide toward Electrocatalytic Reduction of Carbon Dioxide. *ACS Nano* **2017**, *11*, 453–460.
- (20) Asadi, M. et al. Nanostructured transition metal dichalcogenide electrocatalysts for CO₂ reduction in ionic liquid. *Science* **2016**, *353*, 467–470.
- (21) Wang, Z.; Yang, G.; Zhang, Z.; Jin, M.; Yin, Y. Selectivity on Etching: Creation of

- High-Energy Facets on Copper Nanocrystals for CO₂ Electrochemical Reduction. *ACS Nano* **2016**, *10*, 4559–4564.
- (22) Lu, Q.; Rosen, J.; Zhou, Y.; Hutchings, G. S.; Kimmel, Y. C.; Chen, J. G.; Jiao, F. A selective and efficient electrocatalyst for carbon dioxide reduction. *Nature Communications* **2014**, *5*, 3242.
- (23) Oh, Y.; Vrubel, H.; Guidoux, S.; Hu, X. Electrochemical reduction of CO₂ in organic solvents catalyzed by MoO₂. *Chemical Communications* **2014**, *50*, 3878.
- (24) Oh, Y.; Hu, X. Ionic liquids enhance the electrochemical CO₂ reduction catalyzed by MoO₂. *Chemical Communications* **2015**, *51*, 13698–13701.
- (25) Piontek, S.; Junge, P.; Siegmund, D.; Smialkowski, M.; Sinev, I.; Tetzlaff, D.; Roldan Cuenya, B.; Apfel, U.-P. Bio-inspired design: bulk iron–nickel sulfide allows for efficient solvent-dependent CO₂ reduction. *Chemical Science* **2019**, *10*, 1075–1081.
- (26) Zheng, X. et al. Sulfur-Modulated Tin Sites Enable Highly Selective Electrochemical Reduction of CO₂ to Formate. *Joule* **2017**, *1*, 794–805.
- (27) Gu, J.; Héroguel, F.; Luterbacher, J.; Hu, X. Densely Packed, Ultra Small SnO Nanoparticles for Enhanced Activity and Selectivity in Electrochemical CO₂ Reduction. *Angewandte Chemie International Edition* **2018**, *57*, 2943–2947.
- (28) Gu, J.; Hsu, C. S.; Bai, L.; Chen, H. M.; Hu, X. Atomically dispersed Fe³⁺ sites catalyze efficient CO₂ electroreduction to CO. *Science* **2019**, *364*, 1091–1094.
- (29) Ivanovskaya, V.; Seifert, G. Tubular structures of titanium disulfide TiS₂. *Solid State Communications* **2004**, *130*, 175–180.
- (30) Inoue, M.; Negishi, H. Interlayer spacing of 3d transition-metal intercalates of 1T-cadmium iodide-type titanium disulfide (TiS₂). *The Journal of Physical Chemistry* **1986**, *90*, 235–238.

- (31) Tsai, C.; Li, H.; Park, S.; Park, J.; Han, H. S.; Nørskov, J. K.; Zheng, X.; Abild-Pedersen, F. Electrochemical generation of sulfur vacancies in the basal plane of MoS₂ for hydrogen evolution. *Nature Communications* **2017**, *8*, 1–8.
- (32) Quan, F.; Zhong, D.; Song, H.; Jia, F.; Zhang, L. A highly efficient zinc catalyst for selective electroreduction of carbon dioxide in aqueous NaCl solution. *Journal of Materials Chemistry A* **2015**, *3*, 16409–16413.
- (33) Pore, V.; Ritala, M.; Leskelä, M. Atomic Layer Deposition of Titanium Disulfide Thin Films. *Chemical Vapor Deposition* **2007**, *13*, 163–168.
- (34) Yuwen, L.; Yu, H.; Yang, X.; Zhou, J.; Zhang, Q.; Zhang, Y.; Luo, Z.; Su, S.; Wang, L. Rapid preparation of single-layer transition metal dichalcogenide nanosheets via ultrasonication enhanced lithium intercalation $\dagger\dagger$. *Chemical Communications* **2015**, *52*, 529–532.
- (35) Conroy, L. E.; Park, K. C. Electrical properties of the Group IV disulfides, titanium disulfide, zirconium disulfide, hafnium disulfide and tin disulfide. Ph.D. thesis, 1968.
- (36) Kam, K.-K. Electrical properties of WSe₂, WS₂, MoSe₂, MoS₂, and their use as photoanodes in a semiconductor liquid junction solar cell. Ph.D. thesis, 1982.
- (37) Whittingham, M.; Panella, J. A. Formation of stoichiometric titanium disulfide. *Materials Research Bulletin* **1981**, *16*, 37–45.
- (38) Erben, M. F.; Boese, R.; Della Védova, C. O.; Oberhammer, H.; Willner, H. Toward an Intimate Understanding of the Structural Properties and Conformational Preference of Oxoesters and Thioesters: Gas and Crystal Structure and Conformational Analysis of Dimethyl Monothiocarbonate, CH₃OC(O)SCH₃. *The Journal of Organic Chemistry* **2006**, *71*, 616–622.

- (39) Al-Hosney, H. A.; Carlos-Cuellar, S.; Baltrusaitis, J.; Grassian, V. H. Heterogeneous uptake and reactivity of formic acid on calcium carbonate particles: a Knudsen cell reactor, FTIR and SEM study. *Physical Chemistry Chemical Physics* **2005**, *7*, 3587.
- (40) Andrei, H.-S.; Nizkorodov, S. A.; Dopfer, O. IR Spectra of Protonated Carbonic Acid and Its Isomeric H₃O+CO₂ Complex. *Angewandte Chemie International Edition* **2007**, *46*, 4754–4756.
- (41) Phillips, K. R.; Katayama, Y.; Hwang, J.; Shao-Horn, Y. Sulfide-Derived Copper for Electrochemical Conversion of CO₂ to Formic Acid. *The Journal of Physical Chemistry Letters* **2018**, 4407–4412.
- (42) Huang, Y.; Nielsen, R. J.; Goddard, W. A. Reaction Mechanism for the Hydrogen Evolution Reaction on the Basal Plane Sulfur Vacancy Site of MoS₂ Using Grand Canonical Potential Kinetics. *Journal of the American Chemical Society* **2018**, *140*, 16773–16782.
- (43) Voiry, D. et al. The role of electronic coupling between substrate and 2D MoS₂ nanosheets in electrocatalytic production of hydrogen. *Nature Materials* **2016**, *15*, 1003–1009.
- (44) Ji, Y.; Nørskov, J. K.; Chan, K. Scaling Relations on Basal Plane Vacancies of Transition Metal Dichalcogenides for CO₂ Reduction. *The Journal of Physical Chemistry C* **2019**, *123*, 4256–4261.
- (45) Yasaka, Y.; Yoshida, K.; Wakai, C.; Matubayasi, N.; Nakahara, M. Kinetic and Equilibrium Study on Formic Acid Decomposition in Relation to the Water-Gas-Shift Reaction. *The Journal of Physical Chemistry A* **2006**, *110*, 11082–11090.
- (46) Hietala, J.; Vuori, A.; Johnsson, P.; Pollari, I.; Reutemann, W.; Kieczka, H. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2016; pp 1–22.

- (47) Xu, C.; Peng, S.; Tan, C.; Ang, H.; Tan, H.; Zhang, H.; Yan, Q. Ultrathin S-doped MoSe₂ nanosheets for efficient hydrogen evolution. *J. Mater. Chem. A* **2014**, *2*, 5597–5601.
- (48) Tan, C. et al. Preparation of High-Percentage 1T-Phase Transition Metal Dichalcogenide Nanodots for Electrochemical Hydrogen Evolution. *Advanced Materials* **2018**, *30*, 1705509.
- (49) Zhang, X.; Lai, Z.; Zhang, H. Doping-induced phase transition enables better electrocatalysts. *Science China Materials* **2018**, *61*, 1623–1624.
- (50) Lu, Q.; Yu, Y.; Ma, Q.; Chen, B.; Zhang, H. 2D Transition-Metal-Dichalcogenide-Nanosheet-Based Composites for Photocatalytic and Electrocatalytic Hydrogen Evolution Reactions. *Advanced Materials* **2016**, *28*, 1917–1933.
- (51) Li, Z.; Zhang, X.; Cheng, H.; Liu, J.; Shao, M.; Wei, M.; Evans, D. G.; Zhang, H.; Duan, X. Confined Synthesis of 2D Nanostructured Materials toward Electrocatalysis. *Advanced Energy Materials* **2019**, 1900486.
- (52) Shi, J. et al. Two-dimensional metallic tantalum disulfide as a hydrogen evolution catalyst. *Nature Communications* **2017**, *8*, 958.
- (53) Coskun, H.; Aljabour, A.; De Luna, P.; Farka, D.; Greunz, T.; Stifter, D.; Kus, M.; Zheng, X.; Liu, M.; Hassel, A. W.; Schöffberger, W.; Sargent, E. H.; Sariciftci, N. S.; Stadler, P. Biofunctionalized conductive polymers enable efficient CO₂ electroreduction. *Science Advances* **2017**, *3*, e1700686.
- (54) Costentin, C.; Drouet, S.; Robert, M.; Saveant, J.-M. A Local Proton Source Enhances CO₂ Electroreduction to CO by a Molecular Fe Catalyst. *Science* **2012**, *338*, 90–94.