

Supplementary Materials for

Nanostructured transition metal dichalcogenide electrocatalysts for CO_2

reduction in ionic liquid

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Supplementary Materials

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S1. Chemical Vapor Transport (CVT) growth technique

The TMDCs in this study are synthesized through direct reaction of the pure elements followed by a vapor transport process in an evacuated ampule at elevated temperatures. In this method, the powders of the transition metals and chalcogens (>99.99% trace metal basis purity) were mixed in desired stoichiometric ratio and loaded in a quartz ampule. The total loaded weight was about one gram and quartz ampule had one cm internal diameter and 20 cm length. The ampule was then evacuated with a turbo molecular pump (<10⁻⁶ mbar) and sealed with a hydrogen torch. The ampule was then placed in a two-zone CVD furnace and the temperature of the both zones was raised to 1080°C in a day. The temperature of the empty part of the ampule (cold zone) was then gradually cooled down to 950°C in four days, while the other end was maintained at 1080°C, in order to form single crystalline grains with pristine structure via direct vapor transport. The system was then slowly cooled down to room temperature in one day and the material was taken out for tests and characterizations. The crystalline grains were finally grounded before liquid exfoliation method.

S2. TMDC catalysts synthesis

TMDC nanoflakes (NFs) were synthesized using an exfoliation method(*34*, *35*). The CVT grown TMDC crystalline grains e.g., MoS₂, MoS₂, WS₂ and WSe₂ were ground before liquid exfoliation.

The nanoflakes were synthesized by sonicating a solution containing a mixture of 300 mg of powder (TMDC) dispersed in 60 ml isopropanol solution. The sonication was carried out for 30 hours using a sonication probe (Vibra Cell Sonics 130 W). The obtained dispersions were centrifuged for 60 minutes at 2000 rpm. After centrigugation, the supernatant (top two thirds of the centrifuged solution) was collected by a pipette and stored in a glass vial. Figure S2 shows the synthesized TMDC NFs dispersed in IPA.

S3. Dynamic Light Scattering (DLS) of TMDC catalysts

Dynamic light Scattering (DLS) experiments were carried out to measure flake sizes using the NiComp ZLS 380 system at 25°C. The instrument includes a 35 mW semiconductor laser with 670 nm emissions and a thermoelectric temperature control for samples. Synthesised TMDC NFs dispersed in isopropanol were used for DLS experiments. Typical error in DLS data is in the order of 5-8%. Figure S3 shows normal distributions of synthesized flakes for different TMDC NFs.

S4. Raman characterization of the TMDC NFs

Raman characterization of the TMDC NFs were shown in Fig. S4. The data are obtained with a HORIBA LabRAM HR Evolution confocal Raman microscope. The instrument was configured with a 532 nm laser source, 1200 g/mm grating, a Horiba Andor detector, and a 100x objective. Laser powers at the sample were between 1-15 mW. Integration times and averaging parameters were chosen to maximize the signal-to-noise ratio.

S5. Scanning Electron Microscopy (SEM)

SEM characterization of WSe₂ nanoflakes was carried out to understand the morphology at microscale (Fig. S5). The Carl Zeiss SEM used for characterizing WSe₂ NFs was integrated in a Raith e-LiNE plus ultra- high resolution electron beam lithography system. A distance of 10 mm was kept from the electron source and a voltage of 10 kV was used while imaging.

S6. Three-electrode electrochemical setup

Two-compartment three-electrode electrochemical cell was used to perform CO₂ reduction reaction (Fig. S6). The working electrode (WE), reference electrode (RE) and counter electrode (CE) were immersed into the 50 vol% ionic liquid solution (EMIM–BF₄ and water). The synthesized TMDC NFs (e.g., MoS₂, MoS₂, WS₂, and WSe₂) coated on glassy carbon (GC) substrate, Platinum (Pt) gauze 52 mesh (Alfa Aesar) and Ag/AgCl (BASi) were used as working, counter and reference electrode, respectively. All the potentials were converted to the Reversible Hydrogen Electrode (RHE) using Eq. S1 by considering the pH of the solution (Table S1).

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Potential in RHE= Applied potential vs Ag/AgCl + 0.197 V + 0.0592 \times pH (Eq. S1)
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The potential of the reference electrode (RHE) is mostly effected by the electrolyte composition considering constant potential for Ag/AgCl electrode (0.197 V). Since we used two-compartment cell with the nafion membrane in between to separate the cathode and anode part of the cell, the composition variation of the electrolyte is negligible at the entire experiments. This is also confirmed by the pH measurement during the experiments that remains almost constant (pH =3.2). The cathode and anode part of the cell were separated through ion exchange membrane to eliminate the effect of product oxidation at the anode surface. All experiments were performed using rotating disk electrode (RDE) by submersing working electrode in the three electrode cell. To eliminate the effect of mass transport during the reaction working electrode was rotated at 1000 rpm rotating speed. The cell was connected to the potentiostat (CH Instruments) for electrolysis characterization. The potentiostat was connected to the computer through CH instruments software. A 6mm polyethylene tube was used to bubbling the gas (CO₂, 99.9% UHP from Praxair) into the electrolyte for 30 minutes prior to starting the experiment.

S7. pH variation of different IL/water composition

Table S1 shows the pH of EMIM-BF₄ ionic liquid electrolyte at different water volume fractions. As shown in Table S1, the 1:1 volume ratio of IL and water composition offers the highest proton concentration for CO_2 reduction reaction.

S8. WSe₂ NFs catalytic activity at different IL/water compositions

WSe₂ NFs catalytic activity was also tested at a potential of -0.764 V vs RHE using a chronoamperometry experiment under different acidity conditions (i.e., with different concentrations of the IL). The results shown in Fig. S7 indicate that the acidity associated with the 50 vol% of water gives the maximum activity. These results are consistent with our previous studies for bulk $MoS_2(12)$ and silver nanoparticles(15).

S9. Number of active sites and turn over frequency (TOF) measurement

To further characterize the catalytic activity of WSe₂ NFs, Bulk MoS₂ and Ag NPs in Fig. 1A (main manuscript), we applied a roughness factor (RF) technique to determine the number of active edge sites of the catalysts (*23*, *36-38*). All experiments were performed using the same surface areas. However, the catalysts loading for WSe₂ NFs and Bulk MoS₂ were different. Since the electronic, structural and physical properties of WSe₂ and MoS₂ are pretty similar(*35*, *39*), the RF number of WSe₂ catalyst is estimated by comparing its double layer capacitor (C_{dl}) with a flat standard capacitor of MoS₂ (*23*) (Table S2). The CV experiments at different scan rates e.g., 20, 50, 80, 120, 160 and 200 mV.s⁻¹ were performed in the 0.5M H₂SO₄ to calculate the C_{dl} of each catalyst (*36*) (Fig. S10 A-B). Figure S10 C-D show the extracted C_{dl} values of 2.6, 2.23 and 3.71 mF.cm⁻¹ at the potential of +0.2 V vs RHE for WSe₂ NFs, bulk MoS₂ and Ag NPs, respectively.

Moreover, RF values of 44, 37 and 148 were obtained for WSe₂ NFs, bulk MoS₂ and Ag NPs, respectively (Table S2). The calculated number of active sites for each catalyst was obtained using Eq. S2.

Additionally, the CO formation turn over frequency (TOF) of active sites for CO_2 reduction reaction in the WSe₂ NFs, bulk MoS_2 and Ag NPs inside the ionic liquid (EMIM-BF₄) was calculated at different over-potentials using Eq. S3 (23, 37, 38):

CO formation TOF(s⁻¹) = i_0 (A.cm⁻²) × CO formation F.E. /{[active sites density(sites/cm²)] × [1.602 × 10⁻¹⁹ (C/e⁻)] × [2e⁻/CO₂]} (Eq. S3)

S10. GC calibration

The GC apparatus was calibrated to determine number of the mole of the products (i.e., CO and H_2) using 2, 5, 10 and 20 vol% of CO and H_2 mixed in Helium and Nitrogen (99.99% research grade, Praxair), respectively. The known volume of standard samples (1 mL) were injected to GC at the constant pressure (10 psi) and temperature (25°C) using Helium and Nitrogen as carrier gases for detecting CO and H_2 , respectively. A clear CO peak appeared at 3.83 mins while H_2 was detected at 0.98 mins. The calibration curves (Fig. S11 A-B) were obtained based on the peak surface area with respect to the number of the mole of the injected gases (i.e., CO and H_2). Finally, the molar quantity of products was calculated during the reduction reaction by correlating the product peak area with the obtained calibration curves.

S11. Product analysis of three-electrode electrochemical cell experiments

The product analysis for the electrochemical experiments was carried out using an SRI 8610C GC system equipped with 72 \times 18 inch S.S molecular sieve-packed column. A thermal conductivity

detector was used to analyze and differentiate the injected samples. Ultra-high purity helium and nitrogen (purchased from Praxair), respectively, were used as carrier gases to detect CO and H₂. To characterize the gas product, at first, the chronoamperometry experiments have been performed for the appropriate time intervals (e.g., 10 mins). Then, the volume of 1 mL of produced gas in the dead volume of the cell (~30 mL) was injected into the GC at identical experimental conditions e.g., pressure, temperature, and time using sample lock syringe (Hamilton). Only CO and H₂ peak were detected at 3.83 mins (in He carrier gas) and at 0.98 mins (in N₂ carrier gas), respectively. In order to identify the other possible carbon based products, we also performed isotope 13-CO₂ experiment. The experiment was carried out using differential electrochemical mass spectroscopy (DEMS)(*40*, *41*) with quadrupole detector (HPR-20 purchased from Hiden Analytical Inc). The DEMS was operated at the Ultra-high vacuum pressure (1×10^{-6} torr) during the mass spectroscopy analysis. The product stream was injected to the DEMS with a flow rate of 0.8-1 mL/min using quartz coated very low flow capillary liner. The bar scan mode of the product stream (Fig. S12) shows that CO is the only detectable carbon based product during reduction reaction.

S12.Faradaic efficiency measurement for TMDCs

The F.E. of TMDC catalysts were calculated using Eq. S4 where CO and H_2 mole fractions of injected samples were calculated using calibration curve. The theoretical mole fraction of product was also extracted via dividing number of coulombs (measured by calculating the curve area of current density vs time plot) by number of electrons required for CO₂ reduction reaction (n=2) multiply by Faradic number (Eq. S4).

$$\frac{\text{moles of product (measured by GC)}}{j (\text{mA/cm2}) \times t(\text{s}) / \text{nF}} \times 100 \quad \text{(Eq. S4)}$$

Faradaic efficiency (F.E.) calculations indicate that the CO and H_2 are dominant products in TMDC NFs/ionic liquid co-catalyst system at potential widow of 0 to -0.764 V with the overall

F.E. of 90%±5. Therefore, the formation efficiency of other products such as HCOOH, methanol and other liquid phase products in the system is ~10%. Figure S13 A-D also show the variation in the faradaic efficiency of CO and H₂ formation for MoS₂, MoSe₂, WS₂, and WSe₂. Faradaic efficiency (F.E.) results for TMDCs NFs indicate that at very lower potentials (0 to -0.2 V), H₂ is the major product, while at higher potentials (-0.2 to -0.764 V) CO become the major product. The variation in FE of CO and H₂ with respect to the applied potential is attributed to the differences in the CO₂ reduction and HER mechanisms. In principle, the favorable thermodynamic potential for the H₂ evolution is lower than CO₂ reduction. As the applied potential exceeds the onset potential of the CO₂ reduction (-0.164 V), this reaction is activated and the active catalytic sites becomes occupied by the intermediates of the CO₂ reduction. Essentially, two H⁺ are consumed for one CO formation as a result of one CO₂ molecule reduction. Thus, a fraction of both existing H⁺ (from the electrolyte) and the electrons (on the catalyst surface) are consumed in the CO₂ reduction reactions, instead of HER reactions.

S13. Stability test of WSe₂ NF catalyst

Long term stability of WSe₂ NFs were studied by performing chronoamperometry experiment (CA) in a three-electrode two-compartment cell using the same method and materials as explained in section S6. A 6mm polyethylene tube was used to continuously bubble the gas (CO₂, 99.9% UHP from Praxair) throughout the entire length of the experiment into the electrolyte. A magnetic stirrer was placed into the electrolyte solution to evade any mass transport issues. Stability of the catalyst was recorded for prolonged period (27 hours, limit of our instrument) by running the cell at potential of -0.364 V (0.254 V overpotential) using Voltalab PGZ100 potentiostat (purchased via Radiometer Analytical SAS) calibrated with a RCB200 resistor capacitor box. The potentiostat was connected to a PC using Volta Master (Version 4) software. Figure S14 shows the stability of

the WSe₂ NFs. The spikes observed along the current density vs time curve are mainly due to the fluctuations in the flow rate of the CO_2 being bubbled into the electrolyte solution.

S14. Photoelectrochemical methods and materials

All chemicals were used as received without any purification unless required. Cobalt nitrate hexahydrate (($Co(NO_3)_2.6H_2O$), Alfa Aesar), Potassium based buffer solution (0.071 M KPi, pH=7, Sigma-Aldrich), Nafion 117 (10.0 cm × 10.0 cm, FuelCellsEtc) were purchased from the indicated supplier. Triple a-Si solar cells were purchased from Xun-light Corp. (Toledo, OH). The acrylic plastic used for building the phot-reduction chamber was purchased from Total Plastics Inc (CHEMCAST GP).

S14.1.Custom made wireless solar cell setup

The photochemical chamber as shown in Fig. S15 and S16 is an acrylic plastic based transparent chamber that was machined according to the required dimensions and assembled together using acrylic glue. The transparent chamber is separated into two compartments by two tandem amorphous silica based triple junction (a-Si/a-SiGe/a-SiGe) photovoltaic (PV) cells connected through a copper tape and a piece of nafion membrane (Fig. S15). Silicon was chosen for the artificial leaf experiment due to its earth abundance and application across various fields. The illuminated side of PV cells was electrodeposited with another Earth abundant metal cobalt (Co) catalyst to initiate oxygen evolution reaction (OER)(*20*). The self-healing properties of cobalt make it a suitable candidate for oxygen evolution reaction (OER) (*19*, *42*). Cobalt coated ITO (light illuminated side) side of the solar cell forms a photo-anode and is dipped with Potassium based buffer solution (2.6 ×10⁻⁴ M of K⁺ and pH=7), is responsible to initiate water splitting reaction(*43*). The back stainless substrate of the solar cell was coated with synthesized WSe₂ NFs using drop casting coating method. This WSe₂ coated stainless steel substrate forms the

photocathode and is placed in a 50 vol% EMIM-BF₄ in water electrolyte solution(5) which is saturated with CO_2 prior to the experiment. WSe₂/IL co-catalytic system worked towards the conversion of CO_2 to CO. The nafion membrane treatment was done using standard activation treatment in using 5 wt% KOH solution so as to keep the membrane active in the solution. This membrane acts as a barrier in the photo chamber separating the two electrolytes and permeating H⁺ ions generated through OER to transfer to the other compartment to participate in the CO₂ reduction reaction(*15*).

S14.1.1. Co-OEC electrodeposition

Co–OEC was electrodeposited onto the ITO surface of the solar cell from cobalt (II) nitrate hexahydrate (Co(NO₃)₂.6H₂O, Alfa Aesar). The electrodeposition was carried out using a solution prepared by mixing 73 mg of cobalt nitrate hexahydrate (Co(NO₃)₂.6H₂O, Alfa Aesar) in 500 ml of potassium phosphate (2.6×10^{-4} M of K⁺ and pH 7) using a three–electrode cell configuration comprising of ITO working, platinum mesh as counter and Ag/AgCl reference electrode. The solar cell was placed in the Co – Pi solution and the deposition process took place for 5 minutes. The electrodeposition was done by running the three electrode and solar cell configuration in a chronoamperometry experimental setting at 1.5 V vs Ag/AgCl without stirring and without any i-R compensation. New solutions were prepared for each experiment. The stainless steel substrate of the solar cell was not supposed to be coated with Co and hence was wrapped up in scotch tape.

S14.1.2. WSe₂ drop casting

After the solar cell was electrodeposited with cobalt, the back stainless steel substrate of the solar cell was coated with synthesized WSe₂ NFs through drop casting. The synthesis process is described in the material synthesis section (section S1-S5) of the SI file. The stainless steel surfaced was initially roughed up by using sand paper to enable appropriate adhesion of the catalyst to the surface. The catalyst ink was continuously drop casted on the stainless steel substrate and was allowed to dry until the isopropanol evaporates from the surface and a fine uniform coating of MoS₂ developed.

S14.1.3. Preparation of Ionic Liquid

Prior to starting any of the photo-reduction experiments, pure ionic liquid was diluted with water in appropriate amounts to achieve 50 vol% EMIM–BF₄ in water. CO₂ (99.9% UHP, Praxair) was flown at 1 ml/min using a mass flow controller and was directed into the EMIM–BF₄/water electrolyte for 30 minutes so as to saturate the ionic liquid with CO₂.

S14.2. Operation mechanism of the artificial leaf:

In the artificial leaf system, the CO_2 reduction and oxygen evolution (OER) reactions are electrically coupled together through the triple junction solar cell (PV-a-si-3jn). Considering that electrons cannot be stored in the solar cell due to its very small capacitance, the electron production and consumption rates on the two sides of the cell must be equal. As a result, the CO_2 reduction and oxygen evolution reaction rates are always equal.

The operation of the artificial leaf system in time domain can be divided into a transient regime followed by a steady-state operation (Fig. S17). Initially, the H⁺ concentration in the KPi (potassium buffer solution, 2.6×10^{-4} M of K⁺) side (pH=7) is much lower than that of IL (ionic liquid), pH=3.23. When the reaction starts, H⁺ starts to produce in the KPi side through the OER (decreasing the pH) and on the IL side the CO₂ reduction reaction consumes H⁺ available in the IL electrolyte (increasing the pH). During this transient time, diffusion of the K⁺ ions through the PEM (proton exchange membrane) from the anode to the cathode side compensates the charge imbalance to achieve the charge neutrality. However, after this initialization time (approximately five minutes), the pH in the KPi solution decreases down to a certain level (here 3.35) and the pH

in the IL increases by a small amount to about the same value. At this point, the operation of the artificial leaf system becomes steady-state and diffusion of the H⁺ ions takes over from the K⁺ diffusion. Overall, the K⁺ diffusion to the IL is not large enough to affect the performance. This is confirmed by the pH of the artificial system after equilibration (3.35) where the negligible pH variation (3.23 to 3.35) was observed at the cathode side. This implies that the net quantity of K⁺ crossover is relatively small and do not affect properties of the ionic liquid medium.

To quantify the K⁺ crossover in the artificial cell we performed elemental analysis using a PerkinElmer Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES, Optima 5300DV) instrument. The collected samples at different time intervals were diluted 5 and/or 20 times using 2% HNO₃ based on the sample volume. Samples were analyzed using ESI Fast auto-sampler coupled with ICP-OES. Data were calculated by the instrument software. Our measurement shows that the K⁺ concentration at the ionic liquid electrolyte reaches to 1.43×10^{-4} M after five minutes of the artificial leaf operation and stay almost constant for the rest of experiment. This is also consistent with the change in the concentration of H⁺ (1.52×10^{-4} M) in the ionic liquid.

S14.3. Product analysis of the artificial leaf

The product stream of artificial leaf was also analyzed using GC with TCD detector. The product stream was injected to the GC every five minutes to analysis the type and molar quantity of products in the gas stream. The GC results indicate that H_2 and CO are the main products produced by the chemical reaction. No other detectable carbon based products was observed during reduction reaction in the gas product stream. The bar mode scan of DEMS also confirmed that CO is the only carbon based product in the product stream (section S11). Figure S18 shows the number of the mole of the CO and H_2 formation during five hour of the cell operation.

S14.4. Stability analysis of the artificial leaf

It should be noted that the performance of artificial leaf was suddenly dropped after five hours of continuous operation. Our characterization results (Fig. S19) show that the failure occurs mainly due to the corrosion of indium tin oxide (ITO) layer which acts as a protective layer for the PV-a-si-3jn at the anode side of the cell. However, the pH drop of anodic side (pH=3.4) during the cell operation seriously damages this layer (after 5 hours) resulting in the degradation of PV-a-si-3jn cell and correspondingly the failure of the artificial leaf. The performance of artificial leaf returns to its normal level by replacing the PV-a-si-3jn cell.

In order to test the stability of ionic liquid (50 vol% EMIM-BF₄ in water) and KPi electrolytes, the PV-a-si-3jn cell was replaced every four hours for a cumulative time of 100 hours. This time interval has conservatively been chosen since the PV cell can only stand up to five hours of continuous operation. It is noted that the same electrolytes have been used during the experiments. Results shown in Table S3 indicate that the same molar quantities of CO and H₂ are produced during 100 hours operation of the artificial leaf confirming the durability of both anode (KPi) and cathode (50 vol% IL/water) electrolytes. We also did not observe significant changes in the pH of the solution (section S14.2).

S14.5. Water production at the cathode side

We also calculated the volume of the produced water during CO_2 reduction reaction in the artificial leaf. Eq. S5 shows the stoichiometric cathodic reaction where the molar rate of produced water and CO are equal during the reduction of one mole of CO_2 molecules.

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$
 (Eq. S5)

The amount of the produced CO was measured by a gas chromatography experiment (section S14.3). The measurement in Fig. 2B (main text) shows that 2.75×10^{-7} mol/s of CO is produced

using one sun illumination energy. Therefore, the rate of water production is also 2.75×10^{-7} mol/s (Eq. S5) resulting in 9.9 x 10^{-4} mole of water generated after an hour experiment. Considering the molecular weight (18 gr/mole) and density (1 gr/cm³) of water, this results in approximately 0.018 mL/h water generation during CO₂ reduction reaction in the artificial leaf cell using one sun illumination energy (Table S4). Hence, a negligible amount of water (1.8 mL) will be produced compared to total volume (100 mL) of IL/H₂O after 100 hours reduction reaction, which will practically not change the pH and composition of IL electrolyte (Table S1). This is also further confirmed by pH measurement of IL where a small pH variation was observed during the experiment. Table S4 also shows the amount of produced water at different sun illumination of artificial leaf cell using stoichiometric Eq. S5. CO production rates at different sun illuminations were calculated using GC (section S14.3 and Fig. 2B).

S14.6. Governing equation

The solar to fuel conversion efficiency (SFE) of our system was determined in terms of gas product using the analyzed data from the GC. In addition to being dependent on the intensity of the incident solar irradiance, the gas generation rate is also proportional to the catalytic surface area (i.e., WSe_2 doped surface area) and most importantly the SFE of the solar cell. The GC results indicate that H₂ and CO are the main products produced by the chemical reaction. Hence, SFE% could be calculated by using the Eq. S6(*19*),

$$\eta = \frac{N_1. E_1 + N_2. E_2}{U_g. A_{cat}}$$
(Eq. S6)

where, N_1 and N_2 are molar quantities of produced gas per unit of time (mol/s) measured using GC, E_1 and E_2 are energy densities of the corresponding gas (kJ/mol), which are 283.24 and 140 kJ/mol for CO and H₂ respectively, A_{cat} is the overall catalytic surface available for the reaction

(cm²), which is equal to 18 cm², and U_g is total solar irradiance (mW/cm²), which is 100 mW/cm² for one sun illumination solar energy.

To estimate the uncertainty of the calculations (error bars), the partial derivative method is used to calculate the sensitivity of the SFE values to different input parameters. For this purpose, we perturbed each parameter in Eq. S6 by a small amount (∂x_i) around its typical value (x_i) and found the corresponding change in the extracted SFE values $(\partial \eta)$. The dimensionless sensitivities are then calculated using Eq. S7:

$$s_i = \frac{x_i}{\eta} \frac{\partial \eta}{\partial x_i}$$
 (Eq. S7)

The overall uncertainty (u_{η}) is also calculated by Eq. S8:

$$\frac{u_{\eta}}{\eta} = \sqrt{\sum_{i} \left(s_{i} \times \frac{u_{x_{i}}}{x_{i}} \right)^{2}}$$
(Eq. S8)

where u_{x_l} is the overall uncertainty of the ith parameter around its typical value (x_i) , s_i is the sensitivity to that particular input and η is the value of SFE. In our measurement $\frac{u_{x_l}}{x_l}$ for N₁ and N₂ is calculated based on standard deviation of three experiments that are 0.07 and 0.09, respectively. Since E₁ and E₂ values are extracted from literature, $\frac{u_{x_l}}{x_l}$ of these two values are considered to be zero. The value of $\frac{u_{x_l}}{x_l}$ for U_g are based on the fluctuation in the response of the photodiode during the measurement. The uncertainty in A_{cat} is 0.05 (based on the vernier caliper). The summary of the uncertainty analysis i.e., the typical values, errors, sensitivities, and the relative and absolute contributions of each parameter to the overall uncertainty for one sun illumination is presented in Table S5. The error bars in Fig. 2C and Fig. S20 represent the calculated overall uncertainty values (u_{η}) using Eq. S8. The uncertainty values for 0.5, 1, 1.5 and 2 sun illumination are 0.39058, 0.40904, 0.40154 and 0.38885, respectively.

The SFE of the artificial leaf was also measured during five hours of the cell continuous operation (Fig. S20) using Eq. S6. The SFEs of the artificial leaf during 100 hours operation via replacing PV-a-si-3jn with a time interval of four hours are also shown in Table S6.

S14.7. PV efficiency measurement

The solar to electricity conversion efficiency of PV-a-si-3jn cell coated with Co catalyst was measured under one sun simulated sunlight illumination. The voltage produced by a PV cell was directly measured with a multi-meter while the resistance of the circuit was changed using variable resistors. An open circuit voltage (V_{oc}), a short circuit current and the average fill factor of PV cell were 2.12 V, 6.1 mA/cm² and 0.55 respectively. Therefore, the dry cell efficiency of 7.1% can be calculated by dividing the product of the above three parameters by the one sun illumination (100 mW/cm²). V_{oc} of two PV cell in series configuration was 3.6 V, which was observed to drop to 3V while the short circuit current remained unchanged when the cell was brought to inside of electrolyte solution. The fill factor was assumed to change rarely within the experimental range. Based on the measurement, the change in V_{oc} affected the PV efficiency that could be reasonably predicted as high as 6% in the electrolyte.

S15. Electrochemical Impedance Spectroscopy (EIS)

EIS experiments were performed inside the two-compartment three-electrode electrochemical cell comprised of synthesized catalysts deposited on a glass carbon (GC) substrate as a cathode, platinum (Pt) gauze 52 mesh (purchased via Alfa Aesar) as the anode and Ag/AgCl (3 M KCl, purchased from BASi) as the working electrode. The Nyquist plot for different CO_2 reduction over-potentials e.g., 150, 200, 300, 400 and 500 mV were recorded at a small (10 mV) AC voltage amplitude (to avoid the nonlinearity) and over a frequency range of 10 to 10^5 Hz using a Voltalab PGZ100 potentiostat. An equivalent Randles circuit model was fit to the data to

calculate R_{ct} for each catalyst system. Figure S21 show the recorded Nyquist plots and fitted curve at overpotentials of 150-500 mV for WSe₂ NFs deposited on GC during CO₂ reduction reaction.

S16. Ultraviolet Photoelectron Spectroscopy (UPS)

The work function for four TMDCs and Ag nanoparticles (Ag NPs) was measured through the use of ultraviolet photoelectron spectroscopy (Fig. S22). UPS data were acquired with a physical Electronics PHI 5400 photoelectron spectrometer using He I (21.2 eV) ultraviolet radiation and pass energy of 8.95 eV.

S17. Scannig Transmission Electron Microscopy (STEM) images of WSe2

Scanning transmission electron microscopy (STEM) measurements were performed on a JEOL JEM-ARM200CF, operated at 200 kV. Images were acquired in either high/low angle annular dark field (H/LAADF) or annular bright field (ABF) mode. Figure S23 shows STEM image of WSe₂ (scale bar, 2 nm) before and after 27 hours chronoamperometry experiment.

S18. X-ray photoelectron spectroscopy (XPS)

XPS experiments were carried out using Thermo Scientific ESCALAB 250Xi instrument. The instrument was equipped with an electron flood and scanning ion gun. All spectra were calibrated to the C1s binding energy at 284.8 eV. As shown in the XPS spectra (Fig. S24) after 27 hours CA experiment a negligible (0.2 eV) change in the W 4f and Se 3d spectra was obtained for WSe₂ NFs compared to the fresh sample. These results confirm the stability of the WSe₂ catalyst after long-term experiment.

S19. Density Functional Theory (DFT) calculatoin

S19. 1. Computational details

Density functional theory (DFT) calculations were carried out to study the catalytic properties of TMDC NFs. Periodic DFT calculations were performed with plane wave basis sets

in VASP package(44, 45). Single-layer nanoribbons of the TMDCs with zigzage edges were used to truncate the NFs for the reaction free energies and density of states (DOS) calculations. Figure S26 shows the calculated partial density of states (PDOS) of the d band (spin up) of the surface bare metal edge atom (Mo and W) of MoSe₂, MoS₂ and WSe₂ NFs, respectively, as well as the surface Ag atom of bulk Ag(111).

Both monolayer slabs and nanoribbons of the TMDCs were used to calculate the work functions. For the nanoribbons, each unit cell includes 4×4 (total 16) metal atoms and 32 S or Se atoms (for low CO coverage calculations the unit cell inclues 6×4 metal atoms and 48 S or Se atoms), containing both the metal and the S/Se edges. A 10 Å vacuum space is set both on top of the metal edge and between two nanoribbon periodic images. For the single-layer slabs for work function calculations, only the minimum atoms to construct a unit cell were used. Ag (111) surface was constructed by a $4 \times 4 \times 4$ slab in a unit cell, with 10 Å vacuum space. A kinetic energy cutoff of 400 eV was used for all the calculations. All the atoms in the system were allowed to relax, while the cell shape and volume were kept fixed. K-points grids of $3 \times 1 \times 1$ and $3 \times 3 \times 1$ were used for the energy calculations of the nanoribbons and Ag (111), respectively. Γ -point was used for gas phase molecules. For calculating the work functions of the monolayer TMDC slabs, a $10 \times 1 \times 1$ K-points grid was used. All the calculations of the nanoribbons are spin-polarized calculations.

S19. 2. CO Coverage vs. Binding Energies

The effect of the CO coverage on the CO binding energies on the metal edges of the TMDCs was investigated. The DFT results show that each metal atom on the TMDC NF edge can bind up to two CO molecules ($\theta_{CO} = 2ML$). As shown in the Table S7, the binding energies of CO on the

metal edge decrease as the coverage increases. At the highest coverage ($\theta_{CO} = 2ML$), the average binding energy per second CO on the metal atom becomes smaller than 0.5 eV. This suggests that during the catalytic reaction, CO is likely to have a high coverage ($\theta_{CO} > 1ML$) on the metal edges of the TMDCs, and a second CO molecule on the metal atom is easy to desorb. In other words, this indicates that the catalyst site may have at least one CO molecule binding on the metal atom during most time of the catalytic cycle.

S19. 3. Work Functions

Figure S27 shows the calculated work function for the TMDC monolayers. The calculated values are in good agreement with previous studies(46-48). A clear trend was obtained among the four TMDCs, in the order: MoS₂ > WS₂ > MoSe₂ > WSe₂. The calculated work functions of the TMDC nanoribbons are around 0.3 eV lower than those of the monolayers, systematically, keeping the same trend with that of the monolayers. Our experiments showed the TMDC NFs used in this work present bare metal edges both before and after the electrochemical experiments. Thus, the present DFT calculations did not consider the S/Se coverage on the metal edge.

Figures: S1 to S27







Figure S2. Synthesized TMDC NFs after 30 hours of sonication and one hour of centrifugation at 2000 rpm.



Figure S3: size distribution of synthesise TMDC flakes. The average size of ~ 100 nm were obtained for all TMDC NFs.



Figure S4 : Raman characterization of the TMDC NFs. The peak positions are consistent with the observed spectra in the literature(49, 50), revealing that the flakes remain highly crystaline after the sample preparation.



Figure S5 : Scanning Electron Microscopy (SEM) of WSe_2 (scale bar, 2 μ m in the main image and 200 nm in the inset).



Figure S6: Schematic diagram of two-compartment three-electrode electrochemical cell.



Figure S7: The current density of CO₂ reduction of the WSe₂ catalyst (chronoamperometry experiment) and pH of the electrolyte with respect to water volume fraction in EMIM-BF₄.



Figure S8: Catalytic performance of TMDCs in 50 vol% EMIM – BF4 and 50 vol% water electrolyte. Carbon dioxide was bubbled into the ionic liquid solution for 30 minutes prior to the experiment. The polarization curves (i-V) for the synthesized TMDC catalysts were obtained by sweeping the potential between +0.8 and -0.764 V vs RHE (Reversible hydrogen electrode) at 50 mVs⁻¹.



Figure S9: Chronoamperometry (CA) experiments for an hour continuous process at different applied potentials (**A**) -0.164 and -0.264 V (**B**) -0.364, -0.564 and -0.764 V vs RHE for WSe₂ NFs.



Figure S10: Active site measurements of Ag NPs, bulk MoS_2 and WSe_2 NFs (A-C) cyclic voltammetry (CV) curves of Ag NPs, bulk MoS_2 and WSe_2 NFs at different scan rates. The experiments were performed at 0.5 M H₂SO₄ electrolyte by sweeping potential between 0 to +0.3 V vs RHE (non-faradic region). (D-F) Current density of CV experiments at potential +0.2 V vs RHE as a function of scan rates. The slope of this line shows double layer capacitor for each catalyst.



Figure S11. Calibration curve for CO and H_2 using an SRI 8610C GC system equipped with 72 ×18 inch S.S molecular sieve-packed column and a thermal conductivity detector (TCD). The error bars represent the standard deviation of three measurements.



Figure S12: isotope 13-CO₂ experiment using differential electrochemical mass spectroscopy (DEMS) of the product stream. The three-electrode electrochemical product stream was injected to the DEMS using Helium (UHP=99.999%) as a carrier gas. Data is obtained by subtracting injected sample signal from background signal.



Figure S13. Overall Faradaic Efficiency (F.E.) of different TMDC NFs. The error bars represent the standard deviation of four measurements.



Figure S14: Stability test of WSe₂ NFs in 50 vol% IL at potential of -0.364 V (0.254 V overpotential). The chronoamperometry (CA) experiment indicate 10% decay after 27 h.



Figure S15: Schematic of the Photochemical Chamber with two PV cells in series connected by a copper tape.



Figure S16: Photographs A and B of the photochemical chamber with 50 vol% EMIM BF₄/water solution under one sun simulated sunlight illumination



Figure S17: The mechanism of artificial leaf (A) transient state and **(B)** steady state after reaching a pH of 3.35.



Time (hour)





Figure S19. The optical images of PV-a-si-3jn cell before (A) and after (B) 5 hours photochemical process. (C) The zoom in image of corroded region using scanning electron microscopy (SEM) (scale bars, 250 µm).



Figure S20. SFE (%) with respect to time. The error bars represent the overall uncertainty of the calculations, as discussed in details in section S14.6 and Table S5.



Figure S21. Electrochemical Impedance Spectroscopy (EIS) measurement for WSe₂ NFs inside ionic liquid at different overpotentials (150-500 mV).



Figure S22: Experimental Work function measurement for Ag nanoparticles (Ag NPs) and TMDC NFs. The error bars represent the standard deviation of three measurements.



Figure S23: Scanning Transmission Electron Microscopy images of WSe₂. (A) STEM image of WSe₂ (scale bar, 2 nm) and (B) Intensity profile of the flake before electrochemical experiment (C) STEM images of WSe₂ nanoflake (scale bar, 2 nm) and (D) Intensity profile of the flake after 27 hours chronoamperometry experiment.



Figure S24: X-ray photoelectron spectroscopy (XPS) spectra of WSe₂ NFs. (A and B) XPS spectra of W 4f before and after 27 h of chronoamperometry experiments. The Spectra shows standard W $4f_{7/2}$ (~32.6 eV) and $4f_{5/2}$ (~34.7 eV) peaks consistent with the presence of W⁺⁴ in WSe₂ structures. (**C and D**) XPS spectra of Se 3d before and after 27 h of CA experiments. The Spectra shows standard Se $3d_{5/2}$ (~54.57 eV) and $3d_{3/2}$ (~54.7 eV) peaks consistent with the presence of Se⁻² in WSe₂ structures.



Figure S25: Optimized geometries of the COOH* and CO* intermediates for the TMDCs at 1ML coverage of COOH and CO (bond lengths are in Å)



Figure S26: Calculated partial density of states (PDOS) of the d band (spin up) (**A-C**) surface bare metal edge atom (Mo and W) of the MoSe₂, MoS₂ and WSe₂ NFs, respectively, and (**D**) the surface Ag atom of bulk Ag(111)



Figure S27: Theoretical Work function calculations for TMDC monolayers.

Water volume	pH	Water volume	pН
fraction		fraction	
0 % H2O	6.54	65% H2O	3.78
5 % H2O	4.87	75% H ₂ O	3.98
10% H2O	4.54	85% H ₂ O	4.82
25% H ₂ O	4.14	90 % H ₂ O	5.30
50% H2O	3.20	95 % H2O	5.98

Table S1: pH value with respect to water volume fraction (measured by pH meter)

Table S2: Number of active sites for Ag NPs, bulk MoS₂ and WSe₂ NFs

Catalyst	flat standard capacitor $(23, 51, 52) (\mu F.cm^{-2})$	double layer capacitor (mF.cm ⁻²)	Roughness factor	# active sites
WSe ₂ NFs	60	2.6	44	5.1×10^{16}
Bulk MoS ₂	60	2.23	37	4.3×10^{16}
Ag NPs	25	3.71	148	4.44×10^{17}

Table S3: The molar quantities of CO and H₂ produced during 100 hours of the artificial leaf operation.

Time	CO	H ₂	Time	CO	H ₂
(hour)	(mmol)	(mmol)	(hour)	(mmol)	(mmol)
4	3.9588	0.4468	56	3.9690	0.4098
8	3.9469	0.4069	60	3.9471	0.4315
12	4.0263	0.3969	64	3.9006	0.4237
16	3.9985	0.4348	68	4.0302	0.4189
20	3.9548	0.3985	72	3.9982	0.4205
24	3.9311	0.4039	76	3.9487	0.4349
28	4.0858	0.3981	80	3.8882	0.4017
32	4.0580	0.3965	84	4.0302	0.4251
36	4.0520	0.4348	88	4.0501	0.4234
40	4.0719	0.3973	92	4.0144	0.4191
44	3.9628	0.3981	96	3.8859	0.4278
48	4.0144	0.4269	100	3.9714	0.4338
52	3.9349	0.3881			

#sun	CO (mol/s)	Water	Water (mL/h)
Illumination		(mol/s)	
0.5	1.32x10 ⁻⁷	1.32x10 ⁻⁷	0.00855
1	2.75x10 ⁻⁷	2.75x10 ⁻⁷	0.0178
1.5	4.08x10 ⁻⁷	4.08x10 ⁻⁷	0.0264
2	5.21x10 ⁻⁷	5.21x10 ⁻⁷	0.0338

Table S4: The amount of produced water at different sun illumination using stoichiometric Eq. S1.

Table S5: The uncertainty analysis in the SFE calculation for one sun illumination.

Input	Units	x _i (values)	u _{xi} /x _i	Sensitivity	$c_i = S_i \times u_{xi} / x_i$	$(c_i)^2 / \Sigma(c_i)^2$
N_1	mol/s	2.75×10 ⁻⁷	0.07	0.952643	0.0667	0.00445
N ₂	mol/s	2.78×10 ⁻⁸	0.09	0.047357	0.0043	1.8×10^{-5}
E_1	Kj/mol	283.24	0	0.952643	0	0
E ₂	Kj/mol	140	0	0.047357	0	0
Ug	W/cm ²	100	0.035	0.98039	0.0343	0.0012
A _{cat.}	Cm ²	18	0.05	0.98039	0.049	0.0024

Table S6: SFE of the artificial leaf during 100 hours operation via replacing PV-a-si-3jn with a time interval of four hours

Time (hour)	SFE%	Time (hour)	SFE%	Time (hour)	SFE%	Time (hour)	SFE%
4	4.570	32	4.651	60	4.549	88	4.657
8	4.535	36	4.665	64	4.494	92	4.616
12	4.617	40	4.667	68	4.633	96	4.480
16	4.607	44	4.548	72	4.599	100	4.577
20	4.539	48	4.620	76	4.553		
24	4.516	52	4.512	80	4.468		
28	4.682	56	4.561	84	4.636		

Table S7. Binding energies (eV) of CO on the TMDC metal edges at different coverages (θ_{CO}). For $\theta_{CO} = 1/6$ and 1ML, the values are average binding energies per CO molecule; for $\theta_{CO} = 1.25$ and 2ML, the values are the average binding energies per second CO on the metal atom.

CO Coverage	1/6ML	1ML	1.25ML	2ML
MoS ₂	1.27	0.85	0.80	0.27
MoSe ₂	1.20	0.81	0.82	0.31
WS ₂	1.55	1.14	0.88	0.28
WSe ₂	1.42	1.05	0.90	0.48

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