Interface Engineered V-Zn Hybrids: Electrocatalytic and Photocatalytic CO₂ Reductions

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Abstract: V-Zn hybrids have widely been used as catalyst materials in the environment and as energy. Herein, V-Zn hybrid electrodes were prepared by the hydrothermal and sputter-deposition methods using a Zn foil support. Their electrocatalytic CO₂ reduction (EC CO₂ RR) performances were tested under various applied potentials, different electrolytes, and concentrations before and after thermal treatment of the demonstrated electrode. Gas and liquid products were confirmed by gas chromatography and nuclear magnetic resonance spectroscopy, respectively. For V-Zn electrode by hydrothermal method produced mainly syngas (CO and H₂) with tunable ratio by varying applied potential. Minor products include CH₄, C₂H₄, and C₂H₆. A liquid product of formate showed a Faradaic efficiency (FE) of 2%. EC CO₂ RR efficiency for CO, CH₄, and formate was best in 0.2 M KHCO₂ electrolyte condition. CO and formate were further increased by photoradiation and Nafion-treated electrode. Formate and CH₄ productions were significantly increased by thermal treatment of the V-Zn electrode. CO production was diminished for the V-Zn electrode by sputter deposition but was recovered by thermal treatment. Photocatalytic CO₂ RR was tested to find that RR products include CH₃OH, CO, CH₄, C₂H₄, and C₂H₆. Interestingly long-chain hydrocarbons (CₙH₂n+2, where n = 3–6) were first observed under mild conditions. The long-chain formation was understood by Fisher-Tropsch (F-T) synthesis. Alkenes were observed to be more produced than alkanes unlike in the conventional F-T synthesis. The present new findings provide useful clues for the development of hybrid electro- and photo-catalysts tested under various experimental conditions in energy and environment.

Keywords: V-Zn hybrids; electrocatalytic CO₂ reduction; photocatalytic CO₂ reduction; formate; syngas; Fisher-Tropsch synthesis

1. Introduction

Hybrids of different metal elements and their oxides have extensively been employed in catalyst application areas for energy and environments [1–5]. Among them, V-Zn hybrids with diverse compositions and morphologies have been developed and applied to photocatalysts, electrocatalysts, and energy storage materials [6–18]. In photocatalytic catalyst application of a V-Zn hybrid, it was theoretically found that photogenerated carriers are efficiently separated at the interface of V₂O₅/ZnV₂O₆, where the O 2p state is highly contributed near the Fermi level in the valence band structure [13]. Li et al. synthesized V₂O₅/ZnV₂O₆ nanosheets by the solvothermal method and the post thermal treatment (300–500 °C) [14]; they tested photocatalytic CO₂ reduction activities for V₂O₅/ZnV₂O₆ nanosheets, V₂O₅, and ZnV₂O₆, and found that the V₂O₅/ZnV₂O₆ showed the highest CO production activity; 2.2 × and 1.9 × higher than those observed in V₂O₅ and ZnV₂O₆, respectively. The enhanced activity was attributed to charge transfer from ZnV₂O₆ to

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V\textsubscript{2}O\textsubscript{5} at the interface and enhanced adsorption of CO\textsubscript{2} on the surface. Similarly, in the photocatalytic CO\textsubscript{2} RR over ZnV\textsubscript{2}O\textsubscript{5}/g-C\textsubscript{3}N\textsubscript{4}, CH\textsubscript{3}OH, CO, and CH\textsubscript{4} were reported to be more produced than in ZnV\textsubscript{2}O\textsubscript{5} and g-C\textsubscript{3}N\textsubscript{4}, attributed to the synergistic interfacial hybrid effect [15]. In the case of photocatalytic CO\textsubscript{2} RR over ZnO, V\textsubscript{2}O\textsubscript{5}, ZnO/V\textsubscript{2}O\textsubscript{5} composite, and ZnV\textsubscript{2}O\textsubscript{5} nanosheets [16], Bafaqueer et al. reported that ZnV\textsubscript{2}O\textsubscript{5} nanosheets showed the highest performance on CH\textsubscript{3}OH production by CO\textsubscript{2} RR. The activity of ZnV\textsubscript{2}O\textsubscript{5} was 3.4× higher than that of the ZnO/V\textsubscript{2}O\textsubscript{5} composite. In this experiment, formic acid and acetic acid were newly reported; they also found that the CO\textsubscript{2} RR activity was poorly degraded upon calcination at 550 °C; this indicates that many factors are involved in the mechanism, including surface and interface engineering. Tahir also reported a similar observation that hierarchical 3D ZnV\textsubscript{2}O\textsubscript{4} microspheres showed higher CO\textsubscript{2} RR performance than ZnO/V\textsubscript{2}O\textsubscript{5} composite [17]. In this experiment, CO\textsubscript{2} RR products include CO, CH\textsubscript{3}OH, CH\textsubscript{4}, and C\textsubscript{2}H\textsubscript{6}. As discussed above, the interface plays a significant role in CO\textsubscript{2} RR efficiency and it needs to be further elucidated in other developed catalyst systems.

Although there are several works of literature on the photocatalytic CO\textsubscript{2} RR [11–17] no studies have been reported on EC CO\textsubscript{2} RR over V-Zn hybrids although it shows electrochemical activity on water oxidation and hydrogen production [18,19]. From a practical point of view, EC CO\textsubscript{2} RR is more feasible in the production of value-added products from CO\textsubscript{2} than photocatalytic CO\textsubscript{2} RR [20]. In EC CO\textsubscript{2} RR over V-Zn hybrids and their oxides, CO and H\textsubscript{2} (called syngas) are expected to be produced because Zn is known to produce CO by EC CO\textsubscript{2} RR [3,4,21–23] and the Zn-V hybrid has shown EC activity on hydrogen production [19]. Guzman et al. prepared CuZnAl-oxide nanomaterials and demonstrated that H\textsubscript{2}/CO ratio could be tuned by applying potential [24]. Therefore, the syngas production performance needs to be tested for V-Zn hybrids. CH\textsubscript{4}, formate/formic acid, alcohols, and multi-carbon (C\textsubscript{n}≥2) products are also included in CO\textsubscript{2} reduction products [3,4,25–29]. Therefore, EC CO\textsubscript{2} RR products and efficiencies are needed to be newly examined by modifying the V-Zn interface.

Motivated by this and the potential application of V-Zn hybrids to EC CO\textsubscript{2} RR, we have directly prepared diverse interface-engineered V/Zn electrodes using Zn foil support. The hydrothermal method and sputter-deposition method were both employed, and the prepared electrodes were tested before and after thermal annealing. Zn sputter deposition was also performed on V support to examine the difference between V/Zn and Zn/V before and after thermal treatment. On the basis of CO\textsubscript{2} RR products and Faradaic efficiencies tested over the systematically prepared electrodes, the roles of the V/Zn interface were further deeply discussed. The oxidation states of the diverse V-Zn hybrid electrodes were examined by X-ray photoelectron spectroscopy (XPS) before and after EC CO\textsubscript{2} RR. The stability of the electrodes was found to be dependent on the preparation methods. Thus, the present unique results provide clues on the interface engineering of V-Zn hybrids for improving CO\textsubscript{2} RR performance and stability, and strategy for the development of hybrid catalysts for energy and environment.

2. Materials and Methods

For the preparation of V-Zn hybrids by the hydrothermal method, a Zn foil (30 mm × 5 mm, 2 mm thick) was polished and cleaned by sonication in deionized water. A solution of 1 mM vanadium (V) was prepared by dissolving Na\textsubscript{3}VO\textsubscript{4} (99.9%, Thermo Scientific, Waltham, MA, USA) in deionized water. 60 mL of 1 mM V solution was taken into a 100 mL-size Teflon-lined stainless autoclave and a pre-cleaned Zn foil was dipped in the solution. After that, the autoclave was tightly capped and placed in an oven set at 180 °C for 24 h. After completion of the reaction, and the autoclave was naturally cooled to laboratory temperature the Zn foil was removed, cleaned with deionized water, and dried under an infrared lamp. The V-Zn hybrids prepared by the hydrothermal method were abbreviated as V-Zn(H). The V-Zn(H) sample was thermally treated at 400 °C for 1 h, and abbreviated as V-Zn(H-h). Vanadium (V) was sputter-deposited on a Zn foil support using an SPT-20 ion sputter coater (COXEM Co., Daejeon, Korea) at an ionization current of 5 mA for 600 s and 2400 s, and abbreviated as V(600 s)/Zn(S) and V(2400 s)/Zn(S), respectively.
Their thermal treated (at 400 °C for 1 h) samples were abbreviated as V(600 s)/Zn(S-h) and V(2400 s)/Zn(S-h), respectively. Zn was also sputter-deposited on a V foil support at 5 mA for 600 s and 2400 s, and abbreviated as Zn(600 s)/V(S) and Zn(2400 s)/V(S), respectively. Their thermal treated (at 400 °C for 1 h) samples were abbreviated as Zn(600 s)/V(S-h) and Zn(2400 s)/V(S-h), respectively.

The crystal phases of the V-Zn(H) sample were examined using a X-ray (Cu Kα radiation) diffractometer (MiniFlex II, Rigaku Corp., Tokyo, Japan) in CNU Chemistry Core Facility. The surface morphologies of the demonstrated samples were examined before and after EC CO₂ RR using a scanning electron microscope (SEM, model S-4800, Hitachi Ltd., Tokyo, Japan) setting at 10.0 keV. For Raman spectra of V-Zn(H) sample before and after EC CO₂ RR, a LabRAM HR-800 UV-Visible-NIR Raman spectrometer (Horiba Jobin Yvon, Kyoto, Japan) was used with experimental conditions of 514 nm laser light, a 100× objective, and the monochromator 1800 grating. For UV–visible absorption spectrum for V-Zn(H), a NeoSys-2000 double beam UV–visible spectrophotometer (SCINCO Co., Ltd., Seoul, Korea) was used with a diffuse reflectance mode. The oxidation states and the surface compositions of the demonstrated electrodes before and after EC CO₂ RR were examined by taking X-ray photoelectron spectra (XPS) using a K-Alpha+ XPS spectrometer (Thermo-VG Scientific, Waltham, MA, USA) equipped with a hemispherical energy analyzer and a monochromated Al Kα X-ray (1486.6 eV) light.

Electrocatalytic CO₂ reduction reaction (EC CO₂ RR) experiments were conducted in a conventional three-electrode system; a 1 mm thick Pt counter electrode, an Ag/AgCl (3.0 M KCl) reference electrode, and a V-Zn hybrid electrode (30 mm × 5 mm) working electrode. The electrodes were connected to a ZIVE SP1 compact type Potentiostat/Galvanostat (WonAtech Co., Ltd., Seoul, Korea). Electrolytes were KHCO₃, K₂CO₃, NaHCO₃, Na₂CO₃, and KH₂PO₄/K₂HPO₄ buffer with the desired concentration. A volume of 50 mL electrolyte was taken in a 100 mL size glass cell. Pure CO₂ gas (99.999%) was fully bubbled in the electrolyte and charged in a tightly closed EC cell. Amperometry experiments were conducted at a fixed applied potential (vs. Ag/AgCl) under dark, photoirradiation (365 nm, 3000 mW/cm²), and thermal irradiation (830 nm, 250 mW) conditions.

Photocatalytic CO₂ RR experiment was conducted in a closed stainless-steel chamber with a quartz window (47 mm) on top for UVC (200–290 nm) light irradiation (5.94 mW/cm²) to a V-Zn disc inside (45 mm diameter). Before the experiment, 20 µL of deionized water was placed beside the sample and the chamber was fully flushed and charged with CO₂ gas (99.999%). After that, UVC light was irradiated for 6 h on the disc sample through the quartz window.

After the EC and photocatalytic CO₂ RR experiments, gas and liquid products were examined by gas chromatography (GC) and nuclear magnetic resonance spectroscopy (NMR), respectively. For gas products, 0.5 mL volume of gas was taken from the EC cell (or the photocatalyst closed reactor) and injected into a GC system (YL 6500 GC, Young In Chromass Co., Ltd., Seoul, Korea). Diverse gas products were separated using two different columns of 40/60 Carboxen-1000 (Sigma-Aldrich, St. Louis, MO, USA) and HP-Plot Q PT (Agilent Technologies, Inc., Santa Clara, CA, USA). The GC system was equipped with a thermal conductivity detector, a flame ionization detector, and a Ni catalyst methanizer assembly. For the analysis of liquid products, an NMR spectrometer (600 MHz FT-NMR, AVANCE III, Bruker Corp., Billerica, MA, USA) was employed with 0.5 mL electrolyte and 0.1 mL of DMSO/D₂O (v/v = 1:20,000) internal standard.

3. Results and Discussion

Figure 1a shows amperometry i-t curves over V/Zn(H) electrode obtained at various applied potentials of −1.6 V, −1.8 V, −2.0 V, and −2.2 V (vs. Ag/AgCl) for EC CO₂ RR. The current density (CD) was increased with increasing the negative potential as expected. The CD was observed to be approximately 1.5 mA/cm² and 6.5 mA/cm² at −1.6 V and −2.0 V, respectively. The gas and liquid products were examined by taking GC and NMR profiles shown in Figure 1b,c, respectively. Major gas products were detected to be H₂ and...
were small; e.g., lower than 0.04% for CH$_2$ (Figure 2(a,a1,a2)). All the FEs were observed to be highly dependent on the electrolyte. This reflects that the syngas ratio could be controlled from 2.5 to 0.4 by applying applied potential. In Figure 1e, CH$_4$ was very meaningfully produced and increased with applied potential; 1.8 ppm at $-1.6$ V and 10.3 ppm at $-2.0$ V. Although their amounts were only below 1 ppm the productions of C$_2$H$_6$ and C$_2$H$_4$ were not negligible. Figure 1f shows the Faradaic efficiency (FE) of the detectable products with applied potentials. The FE of H$_2$ was maximized to be 38.8% at $-2.0$ V, but the FE of CO was minimized to 15.4% at this applied potential. The maximum FE of CO was 30.9% at $-1.8$ V. The FE of formate was observed to be between 1.2% (at $-1.6$ V) and 2.4% (at $-1.8$ V). The FEs of other products were small; e.g., lower than 0.04% for CH$_4$. For minor liquid products at $-1.6$ V, acetate and acetone were weakly detectable with FEs of 0.5% and 0.1%, respectively; however, these were not clearly observed at higher applied potentials. In Figure 1h, the image depicts the CO$_2$ reduction process with major products of CO, formate, and CH$_4$ over V-Zn hybrid material.

![Figure 1. Amperometry i-t curves over V-Zn(H) hybrid electrodes at applied potentials of $-1.6$ V, $-1.8$ V, $-2.0$ V, and $-2.2$ V (vs. Ag/AgCl) (a). GC profiles after the amperometry tests (b). NMR spectra for liquid products after the amperometry tests (c). CO and H$_2$ production amount with applied potentials (d). CH$_4$, C$_2$H$_4$, and C$_2$H$_6$ amounts with applied potentials (e). Corresponding FEs including liquid products (f) and (g), respectively. Scheme for CO$_2$ reduction process over V-Zn hybrid material (h).](image)

The V/Zn(H) electrode was further tested in diverse different electrolytes of KHCO$_3$, K$_2$CO$_3$, NaHCO$_3$, Na$_2$CO$_3$, and KH$_2$PO$_4$/K$_2$HPO$_4$ buffer with a concentration of 0.1 M (Figure 2(a,a1,a2)). All the FEs were observed to be highly dependent on the electrolyte.
The FEs of H\textsubscript{2} and CO were all decreased in K\textsubscript{2}CO\textsubscript{3} (28.9\% and 10.4\%, respectively) and NaHCO\textsubscript{3} (30.9\% and 13.8\%, respectively) electrolytes, compared with those (38.8\% and 15.4\%, respectively) in 0.1 M KHCO\textsubscript{3} electrolyte (Figure 2a). The FE of H\textsubscript{2} was increased in Na\textsubscript{2}CO\textsubscript{3} (69.2\%) and KH\textsubscript{2}PO\textsubscript{4}/K\textsubscript{2}HPO\textsubscript{4} buffer (41.5\%) electrolytes, but the FE of CO was decreased in the electrolytes with FEs of 1.2\% and 6.3\%, respectively. The FEs of formate were all decreased to 1.2\%, 0\%, 0\%, and 0.3\% in K\textsubscript{2}CO\textsubscript{3}, NaHCO\textsubscript{3}, Na\textsubscript{2}CO\textsubscript{3}, and KH\textsubscript{2}PO\textsubscript{4}/K\textsubscript{2}HPO\textsubscript{4} buffer, respectively (Figure 2(a1)). Formate was not produced in NaHCO\textsubscript{3} and Na\textsubscript{2}CO\textsubscript{3} electrolytes; this indicates that Na\textsuperscript{+} plays a negative role in formate production, due to interaction between solvated cations and the adsorbed species [30]. CH\textsubscript{4} production was commonly dependent on H\textsubscript{2} production (Figure 2(a2)). The FE of CH\textsubscript{4} was maximized to be 0.05\% in 0.1 M Na\textsubscript{2}CO\textsubscript{3} electrolyte where the FE of H\textsubscript{2} was shown to be maximum. The production of C\textsubscript{2}H\textsubscript{6} was higher than that of C\textsubscript{2}H\textsubscript{4} and was observed to be between 0.002\% (corresponding to 0.3 ppm) and 0.01\% (corresponding to 0.7 ppm).

Figure 2. FEs of CO\textsubscript{2} RR products over V-Zn(H) electrode tested in various electrolytes (a,a1,a2). FEs tested in KHCO\textsubscript{3} electrolyte with different concentrations of 0.1 M, 0.2 M, and 0.5 M (b,b1,b2). FEs in 0.1 M KHCO\textsubscript{3} electrolyte tested under dark, photoirradiation, thermal irradiation, photothermal irradiation, Nafion-treated electrode, and H-cell condition (c,c1,c2).

The V/Zn(H) electrode was tested in different concentrations of 0.1 M, 0.2 M, and 0.5 M KHCO\textsubscript{3} electrolytes (Figure 2(b,b1,b2)). In 0.2 M concentration, CO\textsubscript{2} RR performance was significantly improved, compared with the result in 0.1 M concentration. The FEs of CO
and formate were dramatically increased to 23.2% by 1.5× and 6.0% by 2.9×, respectively, compared with those in 0.1 M concentration. The FE of H\(_2\) was instead decreased from 15.4% to 6.1%. In 0.5 M concentration, the FEs of CO and formate were observed to be only 6.1% and 1.9%, respectively, much smaller than those in 0.1 M and 0.2 M concentrations (Figure 2(b,b1)). The CH\(_4\) production amount (ppm) was linearly increased with increasing the concentration; 6.7 ppm, 20.0 ppm, and 30.7 ppm in 0.1 M, 0.2 M, and 0.5 M, respectively (inset in Figure 2(b2)). The FE of CH\(_4\) was maximized to be 0.07% in 0.2 M (Figure 2(b2)). C\(_2\)H\(_4\) and C\(_2\)H\(_6\) were not detected at all in these conditions.

The V/Zn(H-h) electrode was further tested at −2.0 V in 0.1 M KHCO\(_3\) electrolyte under other various conditions of dark, photoirradiation (365 nm), thermal irradiation (830 nm), photothermal irradiation (365 nm + 830 nm), Nafion-treated electrode, and H-cell condition (Figure 2(c,c1,c2)). The FE of CO was distinctly increased to 27.6% by 1.8× under photoirradiation (365 nm), compared with that under dark conditions (Figure 2c). The increase in CO under photoirradiation was in good consistent with the literature [3]. The FE was also increased to 23.2% by 1.5× when the electrode was treated with Nafion. The FE in the other conditions showed no dramatic effect and decreased to 9.0% in the H-cell condition. In the H-cell condition, the FE of H\(_2\) was instead increased to 42.1%. For the formate production (Figure 2(c1)), the FE was somewhat increased under photoirradiation and thermal irradiation conditions. The FE of formate was more significantly increased to 6.4% by 3.0×, compared with that under dark conditions. For the FE of CH\(_4\) production (Figure 2(c2)), CH\(_4\) production was enhanced under photoirradiation but decreased in Nafion-treated electrode and H-cell conditions. On the basis of the results, it was concluded that the CO\(_2\)/RR performance was highly dependent on the experimental conditions.

The V/Zn(H) electrode interface was modified by thermal annealing at 400 °C. The consequent V/Zn(H-h) electrode was tested in 0.1 M KHCO\(_3\) electrolyte with various applied potentials of −1.6 V, −1.8 V, −2.0 V, and −2.2 V (vs. Ag/AgCl). In the amperometry i-t curves (Figure 3a), the final CD value at 3600 s was increased with increasing the potential; 1.0 mA/cm\(^2\), 2.3 mA/cm\(^2\), 4.6 mA/cm\(^2\), and 5.7 mA/cm\(^2\) at −1.6 V, −1.8 V, −2.0 V, and −2.2 V (vs. Ag/AgCl), respectively; however, for the initial and final CD values the i-t curve showed different behaviour at an applied potential of −2.2 V; this indicates that the V/Zn(H-h) electrode was oxidized after thermal annealing and more significantly altered during the initial EC at the highest applied potential. The gas and liquid products were examined by GC and NMR profiles shown in Figure 3b,c, respectively. Major gas products were detected to be H\(_2\) and CO that were increased with applied potential. Minor products include CH\(_4\), C\(_2\)H\(_4\), and C\(_2\)H\(_6\) (Figure 3b). A major liquid product was formate and others were unassignable (Figure 3c).

The H\(_2\) production was drastically increased with increasing potential; 2250 ppm and 29,115 ppm at −1.6 V and −2.2 V, respectively (Figure 3(d1)). CO production was sharply increased from 2693 ppm to 8952 ppm when the potential was increased from −1.6 V and −1.8 V; however, the CO production showed a sluggish increase above −1.8 V. As a consequence, CO production amount was higher than H\(_2\) production at −1.6 V and −1.8 V, but lower at −2.0 V and −2.2 V. In other words, the CO/H\(_2\) ratio was estimated to be 1.2 and 1.3 at −1.6 V and −1.8 V, respectively, but 0.84 and 0.41 at −2.0 V and −2.2 V, respectively. The syngas ratio was consequently tuned from 1.3 to 0.4. CH\(_4\) was only detected to be 0.4 ppm at −1.6 V, but detected to be 32–35 ppm at −1.8 V and −2.0 V. At a higher potential of −2.2 V, the CH\(_4\) amount was decreased to 8.1 ppm. As shown in Figure 3e, the FE of H\(_2\) was increased with applied potential and reached 28.0% at −2.2 V. The FE of CO at −1.8 V was maximized and observed to be 22.0%. The FE of CO decreased to 15.6% and 11.6% at higher potentials of −2.0 V and −2.2 V, respectively. The FE of formate was shown to be a maximum of 12.9% at −2.0 V. In Figure 3(e1), the FEs of CH\(_4\), C\(_2\)H\(_4\), and C\(_2\)H\(_6\) were observed to be maxima at −1.8 V.

The (FE\(_V/Zn(H-h)\) − FE\(_V/Zn(H)\))/FE\(_V/Zn(H)\) ratios were estimated, where FE\(_V/Zn(H-h)\) is the FE of the thermal-treated sample and FE\(_V/Zn(H)\) is the FE of the as-prepared sample at an applied potential. In Figure 3f, the ratios for H\(_2\) and CO commonly showed negative
values, indicating that the thermal-treated sample showed smaller FEs for H₂ and CO productions. For the formate production, the ratios showed high values between 1.6 and 5.2, indicating that the thermal-treated sample showed higher performance for formate production. In Figure 3(f1), the ratios for CH₄ production showed high positive values at −1.6 V and −2.0 V, but small negative values at −1.6 V and −2.2 V.

Figure 3. Amperometry i-t curves over V-Zn(H-h) electrode at various applied potentials of −1.6 V, −1.8 V, −2.0 V, and −2.2 V (vs. Ag/AgCl) in 0.1 M KHCO₃ electrolyte (a). Corresponding GC (b) and NMR (c) profiles for gas and liquid products, respectively. Measured H₂ and CO product amounts (d1). CH₄, C₂H₄, and C₂H₆ amounts (d2). Corresponding FEs of gas and liquid products (e,e1). (FEV/Zn(H-h)−FEV/Zn(H))/FEV/Zn(H) ratios for H₂, CO, and formate productions (f). (FEV/Zn(H-h)−FEV/Zn(H))/FEV/Zn(H) ratios for CH₄ production (f1).

Another V/Zn interface was prepared by sputter-deposition of V on Zn foil support and also inversely sputter deposition of Zn on V foil support. Figure 4(a,a1) shows FEs of detectable gas and liquid products for as-sputtered V(2400 s)/Zn(S) electrode with various applied potentials of −1.6 V, −1.8 V, −2.0 V, and −2.2 V (vs. Ag/AgCl). The FEs of H₂, CO, and formate were measured to be 20.9%, 15.5%, and 6.3% at −1.6 V, respectively (Figure 4a). The FE of H₂ was increased at higher potentials, but those of CO and formate were decreased at higher potentials. The FE of formate at −1.6 V was approximately three times higher than those at higher applied potentials (Figure 4b). The FEs of CH₄ and C₂H₆ are shown in the inset of Figure 4a. The (FEV/Zn(S)−FEV/Zn(H))/FEV/Zn(H) ratios were estimated (Figure 4(a2)), where FEV/Zn(S) is the FE of the sample by sputter deposition and FEV/Zn(H) is the FE of the sample by hydrothermal method at an applied potential. The ratios for H₂, CH₄, and formate showed positive value, indicating that the V/Zn
The thickness of V and thermal treatment (400 °C for 1 h) effects were examined for the V/Zn(S) electrodes prepared by sputter deposition. As shown in Figure 4b, the FE of H₂ was increased upon thermal treatment for V(600 s)/Zn electrode. On the other hand, the FE of H₂ was increased upon thermal treatment for V(2400 s)/Zn electrode. For the FE of CO (Figure 4b1), the thermal treatment showed a negative effect for both V(600 s)/Zn(S) and V(2400 s)/Zn(S) electrodes. The as-sputtered V(600 s)/Zn(S) electrode showed an FE of 9.8%
for CO, but decreased to 7.6% upon thermal treatment. The as-sputtered V(2400 s)/Zn(S) electrode showed an FE of 15.5% for CO, but decreased to 4.1% upon thermal treatment. For the FE of formate, the V(600 s)/Zn(S) electrode showed enhancement upon thermal treatment from 0.8% to 1.8%, but the V(2400 s)/Zn(S) electrode showed diminishment upon thermal treatment from 6.3% to 0.8%. Interestingly, the FE of C2H6 showed a large enhancement with a FE of 1.6%, compared with other samples (Figure 4(b2)). In addition, the FE was larger than that of CH4. Although it is not clear whether the experimental observation was meaningful. The FE of CH4 showed the highest FE of 0.14% for the V(600 s)/Zn(S-h) electrode (inset of Figure 4(b2)).

When Zn was used as a support material the EC CO2 RR showed higher FE for CO and formate, as discussed above. Inversely, the Zn/V interface was prepared by sputter-deposition of Zn on V foil support and tested for EC CO2 RR. As shown in Figure 4c, H2 production was major, but CO production was dramatically diminished. The FE of formate was distinctly enhanced upon thermal treatment at 400 °C for 1 h. The FE of formate for Zn(600 s)/V(S) was increased from 0.6% to 4.7% (Figure 4(c1)). The FE of formate for Zn(2400 s)/V(S) was increased from 0.7% to 2.4%. The FE of CO was much lower than 1% (Figure 4(c2)). The FE of CO for Zn(600 s)/V(S) was increased from 0.1% to 0.3%. The FE of CO for Zn(2400 s)/V(S) was decreased from 0.4% to 0.06%. The FE of CO and CH4 showed the highest FE of 1.6%, compared with other samples (Figure 4(b2)). In addition, the FE was larger than that of CH4. Although it is not clear whether the experimental observation was meaningful. The FE of CH4 showed the highest FE of 0.14% for the V(600 s)/Zn(S-h) electrode (inset of Figure 4(b2)).

For direct comparison with the EC process, photocatalytic CO2 RR was tested for a selected sample of V/Zn(H) disc (Figure 5). The experiment was conducted in the gas (CO2 and H2O)-solid (catalyst) mode as depicted in the inset of Figure 5a [2,4]. Photocatalytic CO2 RR experiments over V-Zn hybrids in the literature have commonly been conducted in the liquid (bulk H2O with dissolved CO2)-solid (dispersed powder) mode [14–17]. Gas products were mainly detected because of the gas-phase mode. CO, CH4, C2H4, and C2H6 were clearly detected in the GC profiles separated by the Carboxene-1000 column (Figure 5(a,a1)). More interestingly, although the amounts were small Hydrocarbons (CnH2n and CnH2n+2, where n = 3–6) were detected in the GC profile separated by HP Plot Q PT column (Figure 5b), including CH3OH (MeOH). The production amounts of CO, CH4, and MeOH were measured to be 45.2 ppm, 9.4 ppm, and 15.6 ppm (Figure 5c). CO was more produced than CH4, in good with the literature using a similar catalyst system of V2O5/ZnV2O6 nanosheets [14]. The total amounts of C2-5 reached to approximately 3 ppm. In the photocatalytic CO2 RR, alkene (CnH2n) was produced more than alkanes (CnH2n+2). The C2H4/C2H6 ratio was observed to be 2.0. In the EC CO2 RR, the C2H6 production was more dominant than C2H4 (e.g., 6.7 ppm vs. 0.2 ppm at −2.0 V over V/Zn(H) electrode). The alkene/alkane ratios were estimated to be 1.7, 3.6 and 1.2 for C3, C4, and C5 hydrocarbons, respectively. The long-chain formation was understood by C-C coupling in the conventional Fisher-Tropsch synthesis [25,26], further discussed below.
photocatalytic CO$_2$ RR, alkene (C$_n$H$_{2n}$) was produced more than alkanes (C$_n$H$_{2n+2}$). The C$_2$H$_4$/C$_2$H$_6$ ratio was observed to be 2.0. In the EC CO$_2$ RR, the C$_2$H$_6$ production was more dominant than C$_2$H$_4$ (e.g., 6.7 ppm vs. 0.2 ppm at $-2.0$ V over V/Zn(H) electrode). The alkene/alkane ratios were estimated to be 1.7, 3.6 and 1.2 for C$_3$, C$_4$, and C$_5$ hydrocarbons, respectively. The long-chain formation was understood by C-C coupling in the conventional Fisher-Tropsch synthesis [25,26], further discussed below.

Figure 5. GC profiles separated by Carboxene-1000 column (a, a1) after photocatalytic CO$_2$ RR for 6 h under UVC irradiation. Inset is a schematic of a closed stainless-steel reactor. GC profile separated by HP Plot Q PT column (b). Consequent photocatalytic CO$_2$ RR product amounts (c).

Figure 6 displays SEM images (a, a1, a2, a3, and a4) of V/Zn(H) electrodes before and after EC at various applied potentials of $-1.6$ V, $-1.8$ V, $-2.0$ V, and $-2.2$ V (vs. Ag/AgCl); it was commonly observed that the surface morphology became changed and the surface became more drastically changed with increasing the applied potential. The surface reconstruction has commonly been reported during EC CO$_2$ reduction at negative applied potentials, especially for oxide materials due to the reduction of surface oxide species [21,31]. XRD profiles (Figure 6b) were obtained for V/Zn(H) electrode and a ZnO/Zn reference electrode. XRD profiles of the two different samples were quite similar. Strong XRD patterns (closed squares, ■) were commonly observed at $2\theta = 36.7^\circ$, $39.4^\circ$, $43.7^\circ$, and $54.7^\circ$, attributed to the (002), (010), (011), and (012) crystal planes of metallic Zn [32–34]; these signals were from the Zn support material. The other XRD signals (closed circles, ●) were also commonly observed at $2\theta = 32.0^\circ$, $34.7^\circ$, $36.5^\circ$, $47.7^\circ$, and $56.9^\circ$, attributed to the (010), (002), (011), (012), and (110) crystal planes of hexagonal phase wurtzite ZnO [21,27,32]; this indicates that ZnO phase was commonly formed during the hydrothermal synthesis using metallic Zn support. No significant XRD profiles of V oxide and Zn-V oxides were observed, indicating that these species were ultrathin and/or amorphous; however, V species were clearly observed by XPS, discussed below. In Figure 6c, the Raman profile of the V/Zn(H) electrode showed mainly characteristics of
ZnO [31]. The peaks around 435 cm\(^{-1}\) and 570 cm\(^{-1}\) were assigned to \(E_2\) high and \(E_1\) (LO) modes, respectively [31]. The peaks were weakened after EC, due to surface reduction of V-Zn oxide species. SEM images were obtained for other demonstrated samples of V/Zn(H-h), V(2400 s)/Zn(S), V(2400 s)/Zn(S-h), and Zn(2400 s)/V(S-h) before and after EC in Figure 6(d,d1),(e,e1),(f,f1),(g,g1), respectively. The morphologies were different from those of V/Zn(H) electrodes as expected for different electrode materials.

Figure 6. SEM images of V/Zn(H) electrode before (a) and after EC at various applied potentials (a1–a4). XRD profiles (b) of V/Zn(H) and ZnO/Zn (reference). Raman spectra of V/Zn(H) electrode before and after EC at \(-2.0\) V (c). V/Zn(H-h) (d,d1), V(2400 s)/Zn(S) (e,e1), V(2400 s)/Zn(S-h) (f,f1), and Zn(2400 s)/V(S-h) (g,g1) electrodes before and after EC.

XPS spectra were obtained to examine oxidation states, stability before and after EC, and differences in surface electronic structures before and after thermal treatment for the interface engineered V/Zn electrodes. Figure 7(a–a3) display Zn 2p, V 2p, O 1s, and VB XPS profiles, respectively for V/Zn(H) electrodes before and after EC CO\(_2\) RR at \(-1.6\) V, \(-1.8\) V, \(-2.0\) V, and \(-2.2\) V. For the Zn 2p XPS of as-prepared V/Zn(H) electrode before EC (Figure 7a), Zn 2p\(_{3/2}\) and Zn 2p\(_{1/2}\) peaks were observed at binding energies (BEs) of
1021.9 eV and 1044.9 eV, respectively with a spin-orbit (S-O) splitting energy of 23.0 eV; this is plausibly due to Zn(II) oxide species [14,35–38]. In Figure 7(a1), V 2p_{3/2} peaks could be resolved into two peaks at 517.1 eV (major) and 515.8 eV (shoulder), attributed to V^{5+} and V^{4+}, respectively [6,7,14,37]. The V 2p_{3/2} peak at 517.1 eV was predominant. For the O 1s XPS of the as-prepared V/Zn(H) electrode sample (Figure 7(a2)), two broad peaks were observed at 530.5 eV and 532.6 eV, commonly attributed to lattice oxygen (O_L) of Zn-V oxide species and surface oxygen species (e.g., O_{ad}: OH/H_2O, OH^−, and defects), respectively [7,14,15,39,40]. For the corresponding valence band (VB) profile (Figure 7(a3)), the VB edge was positioned at 3.0 eV below the Fermi level. The corresponding band gap was observed to be 3.1 eV (measured by UV-visible absorption spectrometer), indicating that the conduction band (CB) edge is positioned near the Fermi level. Two broad features were seen around 5.0 eV (A) and 8.0 eV, attributed to hybridizations of O 2p/Zn 3d/partially Zn 4p states and O 2p/Zn 3d/Zn 4s states, respectively [41]; it appears that O 2p state is highly contributed in the VB structure near the Fermi level [13].

Figure 7. Zn 2p, V 2p, O 1s, and VB XPS profiles for V/Zn(H) electrode before and after tested at various applied potentials ((a–a3), respectively), V/Zn(H-h) electrode before and after tested at various applied potentials ((b–b3), respectively), and V(600 s)/Zn(S-h), V(600 s)/Zn(S-h), V(2400 s)/Zn(S-h), V(2400 s)/Zn(S-h) electrodes before and after EC (shaded area) at −1.6 V in 0.1 M KHCO_3 electrolyte ((c–c3), respectively).

For the Zn 2p XPS after EC CO_2 RR at −1.6 V, −1.8 V, and −2.0 V, the Zn 2p_{3/2} peak position was observed at a higher BE position of 1022.8 eV. V 2p peaks were somewhat weakened, but their BE positions were slightly altered (Figure 7(a1)). More clearly, the O 1s peak for O_{ad} became dominant while the O 1s for O_L became weak (Figure 7(b1)). In the VB region, A and B peaks appeared to be merged one peak centred around 6 eV; it appears that the surface state changed to more like Zn(II)/V-OH species [35]. Upon applying the highest potential of −2.2 V, the Zn 2p_{3/2} peak was again shifted to a lower BE position of...
1022.1 eV. The corresponding V 2p peak disappeared, indicating that the surface V species were dissolved and diffused into the bulk electrolyte during EC. The O 1s and VB XPS peaks became critically different from others, due to mainly surface states of V-free reduced ZnO/Zn(OH)$_2$ [35–38].

For the XPS of thermal treated electrode of V/Zn(H-h) (Figure 7(b–b3)), Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ peaks were observed at binding energies (BEs) of 1022.1 eV and 1045.2 eV, respectively with a S-O splitting energy of 23.1 eV (Figure 7b); this is plausibly due to Zn(II)/V oxide species [35–37]. For the Zn 2p XPS after EC CO$_2$ RR at $-1.6$ V, $-1.8$ V, $-2.0$ V and $-2.2$ V, the Zn 2p$_{3/2}$ peak position was observed at a higher BE position of 1023.1 eV, plausibly due to Zn(II)/V-OH species [35]. V 2p peaks were not seen (Figure 7(b1)), due to diffusion of V into the bulk state upon thermal treatment. For the O 1s XPS of V/Zn(H-h), two broad peaks were seen at 531.0 eV and 532.7 eV, attributed to lattice oxygen (O$_L$) of Zn-V oxide species and surface oxygen species (e.g., O$_{ad}$: OH/H$_2$O, OH$^*$, and defects), respectively, as mentioned above [7,39,40]. After EC CO$_2$ RR at $-1.6$ V, $-1.8$ V, $-2.0$ V and $-2.2$ V, a broad peak around 533.2 eV became dominant, attributed to an increase in surface oxygen species such as OH. In the VB XPS profiles (Figure 7(b3)), two broad features (A and B) became more distinct and appeared to be merged one after EC CO$_2$ RR, as mentioned above.

For the XPS profiles of sputtered V on Zn foil support before and after thermal treatment (Figure 7(c–c3)), a Zn 2p$_{3/2}$ peak was observed at 1021.8 eV, due to the more metallic nature of Zn. The BE position showed no critical change after thermal treatment, due to the protection of overlayer V. After EC CO$_2$ RR at $-1.6$ V, the BE position of the Zn 2p$_{3/2}$ peak was commonly shifted to 1021.3 eV. The Zn 2p XPS profiles of V(600 s)/Zn(S) and V(2400 s)/Zn(S) were qualitatively similar before and after EC. A V 2p$_{3/2}$ peak was dominantly seen at 516.9 eV, attributed to V$_{ad}^+$ of V$_2$O$_5$ [6,7,37]. The V 2p of V(2400 s)/Zn(S) was stronger than that of V(600 s)/Zn(S) as expected. V 2p peaks became disappeared (Figure 7(c1)), due to diffusion of V into bulk state upon thermal treatment. For the V 2p XPS after EC, the peak intensity was quite weakened, especially for V(600 s)/Zn(S); however, the V 2p signal of V(2400 s)/Zn(S) was quite stable and broadened after EC. The BE distribution around 515.5 eV was due to V$^{4+}$. The O 1s XPS profiles of V(600 s)/Zn(S) and V(2400 s)/Zn(S) were also qualitatively similar before and after EC (Figure 7(c2)). The O 1s XPS peaks of V(600 s)/Zn(S) and V(2400 s)/Zn(S) before thermal treatment were observed around 530.2 eV (530.0 eV) and 531.6 eV, due to lattice oxygen (O$_L$) and surface oxygen species, respectively. After thermal treatment for V(600 s)/Zn(S-h) and V(2400 s)/Zn(S-h), two O 1s peaks were observed around 530.8 eV and 532.0 eV, attributed to lattice oxygen (O$_L$) and surface oxygen species, respectively. After EC CO$_2$ RR at $-1.6$ V, the lattice O 1s peak was weakened while the surface O 1s peak became stronger, as discussed above. For the VB profiles, a broad feature was commonly seen around 6 eV, attributed to hybridized O 2p states with Zn/V. The thermally treated sample of V(600 s)/Zn(S-h) and V(2400 s)/Zn(S-h) showed more clearly two features around 5.0 (A) and 8.0 eV (B), as mentioned above; these two merged one after EC, also discussed above. On the basis of the products tested over diverse electrode samples, the CO$_2$ RR mechanism was discussed below and depicted in Figure 8. In an electrolyte, H$^+$, electrolyte cations/anions, and CO$_2$ are commonly present. In CO$_2$ RR, H$^+$ is consumed for producing organic compounds, and negatively and competitively used for H$_2$ production via H$^+$ + e$^-$ → H$_{ad}$ followed by H$_{ad}$ + H$_{ad}$ → H$_2$ or H$_{ad}$ + H$^+$ + e$^-$ → H$_2$ [3–5,39,40]. CO$_2$ is adsorbed on an electrode surface commonly with two different bindings via CO$_2$ + H$^+$ + e$^-$ → HCOO$_{ad}$ or HOOC$_{ad}$ [3,4]. The O or C of CO$_2$ is hybridized with surface metal orbitals as depicted in Figure 8. When HCOO$_{ad}$ is formed it may release into bulk electrolyte as formate. The hybridization forming HCOO$_{ad}$ was observed to be enhanced by thermal annealing of both V/Zn(H) and Zn/V(S). In other words, formate production was further improved by a more V-Zn hybridized state. The fate HOOC$_{ad}$ is transformed into OC$_{ad}$ via HOOC$_{ad}$ + H$^+$ + e$^-$ → OC$_{ad}$ + H$_2$O [3,4]. The OC$_{ad}$ is then released into free CO or converted into other surface species. For the productions of minor CH$_4$, C$_2$H$_4$, and C$_2$H$_6$,
it requires a surface reaction process of $\text{OC}_{\text{ad}} + H^+ + e^- \rightarrow \text{adCHO}$. The $\text{adCHO}$ species proceed surface $\text{adCH}_2$ and $\text{adCH}_3$ via $\text{adCHO} + 3H^+ + 3e^- \rightarrow \text{adCH}_2 + H_2O$ and $\text{adCHO} + 4H^+ + 4e^- \rightarrow \text{adCH}_3 + H_2O$, respectively [3,4]. The $\text{CH}_3$ associates with $H$ to form $\text{CH}_4$ via $\text{CH}_3 + H \rightarrow \text{CH}_4$ or $\text{CH}_3 + H^+ + e^- \rightarrow \text{CH}_4$ [42,43]. The surface $\text{CH}_x (x = 2, 3)$ may couple to generate free $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$. The productions of $\text{CH}_4$, $\text{C}_2\text{H}_4$, and $\text{C}_2\text{H}_6$ were significantly increased when V-Zn hybridization was increased by thermal annealing treatment. When the desorption of CO is easy the productions of $\text{CH}_4$, $\text{C}_2\text{H}_4$, and $\text{C}_2\text{H}_6$ are expected to be reduced, or vice versa.

Figure 8. Proposed CO$_2$ RR mechanism on the basis of the products.

In electrochemical CO$_2$ reduction, it is not easy to determine different active sites involved because of diverse surface species, electrode surface reconstruction, and the topmost element diffusion into a bulk electrolyte during electrochemical reaction [44,45]. For the different active sites, it needs to determine hydrogen adsorption, CO adsorption by the stripping method, and formate adsorption by the oxidation peak analysis [44,45]. For these V-Zn hybrids, the surface electronic structures are altered by different V/Zn ratios, the amounts and active site species become different, and thereby CO$_2$ reduction performances are expected to be different. In the present study, two different d-block transition metal elements of V and Zn were used to examine EC CO$_2$ reduction performances. To increase selectivity for a desired product, it is also necessary to employ different synthesis methods and other metal elements for hybrid systems; for example, Cu for C-C compounds, Au for CO, and p-block elements for formate [46–49].

For the CO$_2$ RR products by photocatalysis, CH$_3$OH and meaningful amounts of C$_{3-5}$ compounds were newly detected. CO, CH$_4$, C$_2$H$_4$, and C$_2$H$_6$ were common products as observed in electrocatalysis. In addition, the alkenes were more produced than the alkanes. For example, as discussed above, C$_2$H$_4$ was more produced than C$_2$H$_6$, unlike in electrocatalysis and conventional F-T synthesis. The alkene/alkane ratio has commonly been determined by the nature of a catalyst and the surface H/CO ratio at an experimental condition [50]. To confirm the alkene preference, we have also tested photocatalytic CO$_2$ RR experiments over other transition metal elements and found similar results (not shown here). On the basis of these results, intuitively, because the neighbouring surface H in photocatalysis is much less than in electrocatalysis (and conventional high-pressurized conventional F-T synthesis) unsaturated alkenes are expected to be more produced in
\[
\text{H}_2\text{O} + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g)
\]
photocatalysis. Otherwise, the V-Zn surface may not be active for hydrogenation reaction; it needs further study to confirm the mechanism.

\[
\text{CH}_3\text{OH} \text{ is expected to be produced via } \text{CH}_\text{ad} + 3\text{H}_\text{ad} \rightarrow \text{CH}_3\text{OH} \text{ (g). For the production of long-chain C}_{3-5} \text{ compounds, C-C coupling can be understood by (1) coupling}
\]
of surface \text{CH}_x \text{ and (2) CO insertion mechanism proposed in the conventional Fischer-Tropsch (F-T) synthesis [25,26]. In the coupling of surface CH}_2, the coupling of CH}_2 \text{ occurs via CH}_3(\text{CH}_2)_x\text{C}_\text{ad}H_2 + \text{H}_x \rightarrow \text{CH}_3(\text{CH}_2)_x\text{C}_\text{ad}H_2 \text{ followed by association with surface H to liberate alkenes and alkanes. The CO insertion mechanism occurs via CH}_3(\text{CH}_2)_x\text{C}_\text{ad}H_2 + \text{CO} + \text{H}_\text{ad} \rightarrow \text{CH}_3(\text{CH}_2)_x\text{C}_\text{ad}H_2 + \text{HO}_\text{ad}. As a consequence, longer chain hydrocarbons were formed.}

4. Conclusions

In summary, V-Zn hybrids were prepared by hydrothermal (H) and sputter-deposition (S) methods using a Zn foil support. For EC \text{CO}_2 \text{ RR over V/Zn(H) electrode in 0.1 M KHCO}_3, \text{CO (FE = 15–31%), H}_2 \text{ (FE = 11–39%), and formate (FE = 1.1–2.4%) were mainly produced with minor CH}_4, \text{C}_2\text{H}_4, \text{ and C}_2\text{H}_6. Syngas (CO/H}_2) ratio was tuned from 2.5 to 0.4 by applying applied potential from \text{−1.6 V to −2.2 V (vs. Ag/AgCl). The maximum FE of CO was 30.9% at \text{−1.8 V in 0.1 M KHCO}_3 electrolyte. The KHCO}_3 electrolyte showed the best performance in CO and formate production, compared with other demonstrated electrolytes. In 0.2 M KHCO}_3 \text{ electrolyte, the FEs of CO, CH}_4, \text{ and formate were increased by 1.5×, 2.3×, and 2.9×, respectively, compared with those in 0.1 M KHCO}_3 \text{ electrolyte. CO and formate were further increased under photoirradiation conditions and by using a Nafion-treated electrode. For EC \text{CO}_2 \text{ RR over V/Zn(H-h) electrode, formate production was dramatically increased by 160–520%, compared with those over the V/Zn(H) electrode, understood by an increased hybridization of V and Zn. CH}_4 \text{ production was increased by 450–1200%.}

For EC \text{CO}_2 \text{ RR over V/Zn(S) electrode in 0.1 M KHCO}_3, \text{the FEs of CO and formate at \text{−1.6 V were much higher than those at higher applied potentials. CH}_4 \text{ and formate were produced more in the V/Zn(S) electrode, compared with those in V/Zn(H) electrode. CO production was negated in the V/Zn(S) electrode by sputter deposition. CO production was negated by thermal treatment of the V/Zn(S) electrode. For Zn/V(S) electrodes, when V support was used CO production was drastically diminished and the FE of CO was much lower than 1%. The FE of formate was also lower than 1%. When Zn/V(S) electrode was thermally treated the FE of formate was increased to 2–5%, due to an increased hybridization of V and Zn; this is in good consistency with the V/Zn(H) electrode. The EC \text{CO}_2 \text{ RR mechanism was proposed by two different initial bindings via CO}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{HCOO}_\text{ad} \text{ or HOOC}_\text{ad}. The hybridization between surface V/Zn and C and O may determine the production of CO, formate, and C}_2 \text{ compounds.}

In photocatalysis over V/Zn(H), CH}_3\text{OH, CO, and CH}_4 \text{ were mainly produced. Meaningful amounts of C}_{2-6} \text{ hydrocarbons were first observed to be produced. The long chain}
formation was understood by the coupling of surface \text{CH}_x \text{ and CO insertion mechanism in the F-T synthesis process. Alkenes were more produced than alkanes unlike in electrocatalysis and conventional F-T synthesis.}

Overall, the present unique results on electrocatalysis and photocatalysis over interface engineered V-Zn hybrid materials provide deeper information on the development of V-Zn hybrid materials producing value-added carbon products from \text{CO}_2 \text{ and H}_2\text{O by electrocatalyst as well as photocatalysis for energy and the environment.}

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