Photoelectrochemical CO$_2$ Reduction Products Over Sandwiched Hybrid Ga$_2$O$_3$:ZnO/Indium/ZnO Nanorods

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Recycled valuable energy production by the electrochemical CO$_2$ reduction method has explosively researched using countless amounts of developed electrocatalysts. Herein, we have developed hybrid sandwiched Ga$_2$O$_3$:ZnO/indium/ZnO nanorods (GZO/In/ZnONR) and tested their photoelectrocatalytic CO$_2$ reduction performances. Gas chromatography and nuclear magnetic spectroscopy were employed to examine gas and liquid CO$_2$ reduction products, respectively. Major products were observed to be CO, H$_2$, and formate whose Faradaic efficiencies were highly dependent on the relative amounts of overlayer GZO and In spacer, as well as applied potential and light irradiation. Overall, the present study provides a new strategy of controlling CO$_2$ reduction products by developing a sandwiched hybrid catalyst system for energy and environment.

Keywords: ZnO nanorod, electrochemical CO$_2$ reduction, indium, Ga$_2$O$_3$, sandwiched hybrid

1 INTRODUCTION

Producing recycled energy products using abundant CO$_2$ is another challenging project for future solutions for energy and environment (Sohn et al., 2017; Wang et al., 2019; Prabhu et al., 2020; Song et al., 2020; Bellardita et al., 2021; Chen et al., 2021; da Silva Freitas et al., 2021; Ješić et al., 2021; Ochedi et al., 2021; Sun et al., 2021). Electrochemical CO$_2$ reduction is a promising method, and the development of electrodes is a major goal for approaching practical application in the industry. Among many materials such as pure metals and metal oxides, ZnO, indium (In), and Ga$_2$O$_3$ show very unique CO$_2$ reduction products after electrochemical reaction (Sekimoto et al., 2016; Tatsumi et al., 2017; Kikkawa et al., 2018; Lu et al., 2018; Qin et al., 2018; Yamamoto et al., 2018; Zhang et al., 2018; Liu et al., 2019; Murali et al., 2019; Zhang et al., 2019; Akatsuka et al., 2020; Daiyan et al., 2020; Hou et al., 2020; Luo et al., 2020; Tan et al., 2020; Yang et al., 2020; Deng et al., 2021; Li et al., 2021; Liang et al., 2021; Ma et al., 2021; Teng et al., 2021; Wang et al., 2021; Wei et al., 2021; Wu et al., 2021; Xiao et al., 2021; Yoon et al., 2021).

ZnO (and metallic Zn) is known to predominantly produce CO with a high Faradaic efficiency by electrochemical CO$_2$ reduction (Lu et al., 2018; Qin et al., 2018; Zhang et al., 2018; Liu et al., 2019; Daiyan et al., 2020; Luo et al., 2020; Tan et al., 2020; Deng et al., 2021; Wang et al., 2021). Thereby, Zn-based materials have been chosen for CO and syngas (CO and H$_2$) production. Because of optical band gaps near 400 nm, it has been used extensively as good photo(electro)catalysts (Ansari et al., 2013; Choi et al., 2015; Kang et al., 2019; Yu et al., 2020). For metallic In, it has been used for formate (or CO) production by the electrochemical method (Ma et al., 2019; Murali et al., 2019; Zhang et al., 2019; Hou et al., 2020; Yang et al., 2020; Li et al., 2021; Ma et al., 2021; Teng et al., 2021; Wei et al., 2021; Wu et al., 2021; Xiao et al., 2021), where two major reaction channels include 1) forming
surface CO (from HOOC\textsubscript{ad}) and 2) surface OCHO (Li et al., 2021). Desirable CO\textsubscript{2} reduction products have been obtained by modification of In surface that include hybridization (metal/metal and metal-nonmetal), defects, core-shells, and synthetic methods (Ma et al., 2019; Murali et al., 2019; Zhang et al., 2019; Hou et al., 2020; Yang et al., 2020; Li et al., 2021; Ma et al., 2021; Teng et al., 2021; Wei et al., 2021; Wu et al., 2021; Xiao et al., 2021). For Ga\textsubscript{2}O\textsubscript{3} as a catalyst for CO\textsubscript{2} reduction, CO and H\textsubscript{2} productions are competitively occurring and dependent on the crystallinity (Akatsuka et al., 2020; Yoon et al., 2021).

Motivated by the current electrocatalysts development, herein sandwiched hybrid GZO/In/ZnO\textsubscript{NR} electrodes were developed, and their photoelectrochemical CO\textsubscript{2} reduction activities were examined. ZnO was chosen as a support and metallic In was used as a spacer material. GZO was used as the topmost layer and sputter-deposited to obtain a hybrid property of both Ga\textsubscript{2}O\textsubscript{3} and ZnO. GZO (Ga\textsubscript{2}O\textsubscript{3}:ZnO) is known to be a good candidate material for transparent conducting electrode (Beckford et al., 2021). For this reason, it was first introduced as an electrode material in electrochemical CO\textsubscript{2} reduction if there were any new performances. Moreover, we examined if these sandwiched hybrid materials showed any differences, compared with those for ZnO support, In/ZnO, and GZO/ZnO electrode materials.

The novelty of this study was to show the roles of spacer and the topmost layers in the developed sandwiched electrodes. Thereby, the present study provides new strategic information on the development of sandwiched hybrid electrodes for energy and environment.

## 2 EXPERIMENTAL SECTION

### 2.1 Preparation of ZnO\textsubscript{NR} and Sandwiched GZO/In/ZnO\textsubscript{NR} Electrodes

ZnO nanorods (ZnO\textsubscript{NR}) were directly grown on a Zn plate (99.9%, 2 mm thick) to use as an electrode support. For the ZnO\textsubscript{NR} support, a Zn plate (5 mm × 30 mm) was dipped in a mixed solution of 50 ml deionized water and 1 ml of NH\textsubscript{4}OH (30%) solution. The Zn plate-dipped solution in a Teflon-lined (100 ml) autoclave was tightly capped and placed in an oven. The oven temperature was slowly increased to 120°C and then kept for 12 h. After the reaction time and natural cooling to room temperature, the autoclave reactor was opened, and then, the plate was removed, washed with deionized water, and dried under an infrared lamp.

For the preparation of an In/ZnO\textsubscript{NR} electrode, indium was sputter-coated on an as-prepared ZnO\textsubscript{NR} plate (5 mm × 30 mm) using an indium sputtering target (99.99%, Made Lab Co.) and an SPT-20 ion sputter coater (COXEM Co., Korea). The experimental conditions were an ionization current of 3 mA and deposition times of 60, 120, 240, 480, and 960 s. For the preparation of a GZO/In/ZnO\textsubscript{NR} electrode, GZO (99.99%, Ga\textsubscript{2}O\textsubscript{3}:ZnO) was sputter-deposited to obtain a hybrid property of both Ga\textsubscript{2}O\textsubscript{3} and ZnO. GZO (Ga\textsubscript{2}O\textsubscript{3}:ZnO) is known to be a good candidate material for transparent conducting electrode (Beckford et al., 2021). For this reason, it was first introduced as an electrode material in electrochemical CO\textsubscript{2} reduction if there were any new performances. Moreover, we examined if these sandwiched hybrid materials showed any differences, compared with those for ZnO support, In/ZnO, and GZO/ZnO electrode materials.

The novelty of this study was to show the roles of spacer and the topmost layers in the developed sandwiched electrodes. Thereby, the present study provides new strategic information on the development of sandwiched hybrid electrodes for energy and environment.

![FIGURE 1](image-url)
ZnO = 7:3 at % ratio, Made Lab Co.) was sputter-coated on an In/ZnONR electrode described above. For GZO sputtering, the experimental conditions were an ionization current of 5 mA and deposition times of 10, 100, and 800 s. The consequent sandwiched electrode was abbreviated as GZO(deposition time)/In(deposition time)/ZnONR, for example, GZO(960s)/In(240s)/ZnONR.

2.2 Characterization of Electrodes
The crystal phases of prepared electrode samples were examined using an X-ray diffractometer (Rigaku MiniFlex II) with a Cu Kα X-ray radiation (CNU Chemistry Core Facility). The surface morphology was examined using a scanning electron microscope (SEM, Hitachi S-4800) at a 10.0 keV condition. Energy-dispersive X-ray spectroscopy (EDXS) was employed to examine elemental compositions and mapping images using an SEM (Merlin Compact, Carl Zeiss, Germany) coupled with an AZtec Energy X-MaxN EDXS (OXFORD, Oxford, United Kingdom). UV–visible (UV-Vis) absorption property was examined using a double beam UV–visible spectrophotometer (SCINCO NeoSys-2000) with a diffuse reflectance mode. Raman spectral profiles were recorded using a UV-Visible-NIR Raman spectrometer (Horiba Jobin Yvon LabRAM HR-800) with 514 nm laser line, 1800 grating monochromator, and a ×100 objective. For the surface analysis before and after electrochemistry, X-ray photoelectron spectroscopy (XPS) data were obtained using an XPS spectrometer (Thermo-VG Scientific K-Alpha) equipped with a hemispherical energy analyzer and a monochromated Al Kα X-ray (1486.6 eV) source.

2.3 Photoelectrochemical CO₂ Reduction and Product Analysis
Electrochemical experiments were performed in a three-electrode system using a WPG100 potentiostat/galvanostat (WonATech Co., Ltd.) instrument. The size of a working electrode was 30 mm × 5 mm, and a Pt coil (1 mm thick) and an Ag/AgCl (3.0 M KCl) were used as counter and reference electrodes, respectively. An airtight glass cell size was 100 and 50 ml of 0.1 M NaHCO₃ (or
0.1 M KHCO₃ electrolyte was used. Before the experiments, the electrolyte was fully bubbled with CO₂ gas (99.999%) for obtaining CO₂-saturated electrolyte. After that, amperometry was running at a fixed potential for 1 h under dark or 365 nm light (171.84 mW cm⁻²) conditions.

Gas and liquid products were examined by gas chromatography (GC) and nuclear magnetic resonance (NMR) spectroscopy, respectively. For gas products in an airtight closed cell, 0.5 ml of gas was taken and injected into a GC system (Y.L. 6500, Young In Chromoss Co., Ltd.) equipped with 40/60 Carboxen-1000 column, HP-PLOT Q-PT column, an Ni catalyst methanizer assembly, a thermal conductivity detector, and a flame ionization detector. For liquid products, 0.5 ml of liquid electrolyte and an internal reference of 0.1 ml of DMSO/water solution were used in a 5-mm NMR Tube (WG-1241-7, Wilmad-Labglass), and then a 600-MHz FT-NMR (AVANCE III, Bruker Corp.) was employed with a water suppression method.

3 RESULTS AND DISCUSSION

3.1 Crystal Phases and Morphologies of ZnO NR and Sandwiched GZO/In/ZnO NR Electrodes

Figure 1A displays the XRD profiles for selected ZnO NR, GZO(100s)/In(960s)/ZnO NR, and GZO(800s)/In(240s)/ZnO NR electrode samples. It was shown that all the XRD profiles were very similar, indicating that the XRD signals were mainly due to ZnO NR support. The XRD signals were observed to be analyzed into two crystal phases of Zn and ZnO. For hexagonal phase ZnO (ref. # 98-002-9272), the corresponding peaks () were observed at 2θ = 31.8°, 34.5°, 36.3°, 47.7°, 56.7°, and 63.0°, assigned to the (010), (002), (011), (012), (110), and (013) crystal planes, respectively (Choi et al., 2015; Daiyan et al., 2020; Luo et al., 2020). For hexagonal metallic Zn (ref. # 98-065-3505) (Qin et al., 2018), the corresponding peaks (blue closed circles) were observed at 2θ = 36.4°, 39.1°, 43.3°, 54.5°, 70.3°, 70.8°, 70.8°, and 77.3°, attributed to the crystal planes of (002), (010), (011), (012), (013), (110), and (004). No significant XRD patterns of In and GZO were observed, indicating that In and GZO were ultrathin and/or amorphous and undetectable by XRD. This is discussed further below. The crystal projection of ZnO is shown with major crystal planes in Figure 1B.

Figure 1C shows the Raman spectra of the ZnO NR, GZO(100s)/In(960s)/ZnO NR, and In(240s)/ZnO NR electrode samples. All the Raman peaks were mainly assigned to those of wurtzite ZnO, where six Raman active modes are Γ = 2A₁ + E₁ + 2E₂. The E₁ and A₁ are polar modes with transverse optical (TO) and longitudinal optical (LO) components, while the E₂ modes are non-polar low and high modes. For bare ZnONR, the LO peaks were main and observed around 542 and 570 cm⁻¹, assigned to A₁(LO) and E₁(LO) modes, respectively (Russo et al., 2014). The TO and E₂ modes were observed to be weaker than those of LO components. Interestingly, upon sputter deposition of In on ZnO NR, the E₂ high mode was substantially increased at 438 cm⁻¹. The E₂ high and E₁(LO) modes are depicted in the inset of Figure 1C. The Raman profile of In(240s)/ZnO NR was the same as those of the GZO(100s)/In(960s)/ZnO NR sample. The peaks at 378 and 410 cm⁻¹ were assigned to A₁(TO) and E₁(TO) modes. The other at 332 cm⁻¹ was assigned to E₂ high – E₂ low combination (Russo et al., 2014; Luo et al., 2020).

Figure 1D displays UV-visible reflectance absorption spectra (after baseline correction) of ZnO NR, In(240s)/ZnO NR, and GZO(100s)/In(960s)/ZnO NR electrode samples. The absorption edge was commonly observed around 400 nm, an indication that the band gap showed no critical difference upon deposition of In and GZO. On the basis of inset plots of (ahv)² vs. hν (photon energy in eV), the band gap of bare ZnO NR was estimated to be 3.14 eV and slightly increased to 3.22 and 3.17 eV for In(240s)/ZnO NR, and GZO(100s)/In(960s)/ZnO NR electrode samples, respectively. Upon further increasing of GZO the band gap was not critically changed. This indicates that the band gap was mainly due to ZnO NR and the overlayers of In and GZO showed very minor effect (Supplementary Figure S1). This is in good consistency with the XRD and Raman results.

3.2 Morphologies and Compositions

SEM images of ZnO NR and GZO(100s)/In(960s)/ZnO NR are shown in Figure 2. For bare ZnO NR, the rods with thickness of 10–50 nm were observed to be vertically grown on the Zn plate (Figures 2A, A1). Upon deposition of In and GZO, the rods appeared to be fully coated by the sputter-deposited materials (Figures 2B, B1). It was commonly shown that the morphology appeared to be changed after electrochemical experiments as shown in Figures 2A2, B2. This morphology change was plausibly due to reduction of ZnO to metallic Zn during the CO₂ reduction at a high negative potential (Luo et al., 2020). Luo et al. (2020) observed the same and explained this behavior to be due to dissolution-reduction-crystallization process’ where ZnO was changed initially to soluble Zn(OH)₂⁻ ions followed by reduction to metallic Zn. The soluble product was observed during linear sweep voltammetry tests (Supplementary Figure S2). Surface composition elements of the prepared electrodes were examined by EDXS; Zn (0.884, 0.906, 1.012, 8.639, and 9.572 keV), O (0.525 keV), Ga (0.957, 0.984, 1.098, and 9.252 keV), and In (0.366, 2.904, 3.113, 3.287, 3.487, and 4.161 keV) (National Institute of Standards and Technology, 2021). Elemental mapping images are shown in Figures 2C–E for In(240s)/ZnO NR, GZO(100s)/ZnO NR, and GZO(800s)/In(240s)/ZnO NR, respectively. Zn and O were main elements, and In (e.g., 0.04 at%) for GZO(800s)/In(240s)/ZnO NR and Ga (e.g., 0.66 at% for GZO(800s)/In(240s)/ZnO NR) were very weakly detected in the EDXS profiles. The overlayer elements were further confirmed by XPS below.

3.3 Electrochemical CO₂ Reduction Tests

Electrochemical CO₂ reduction experiments were performed at various conditions of GZO thickness, In spacer thickness, applied potentials, electrolytes, concentrations, and light irradiation.

3.3.1 GZO Thickness Effects

In this experiment, the In spacer thickness was fixed and the thickness of the topmost GZO layer was changed. Figures
Figure 3A, A1, A2 display FE(%) ppm amounts of H$_2$ and CO, and the corresponding NMR data, respectively, obtained for ZnO NR, In(240s)/ZnO NR, and GZO/In(240s)/ZnO NR with GZO thicknesses of 10, 100, and 800 s at $-1.6$ V (vs. Ag/AgCl), FE (%) (B), ppm amounts of H$_2$ and CO (B1), and the corresponding NMR data (B2) for ZnO NR, GZO(100s)/ZnO NR, GZO(100s)/In/ZnO NR with In thicknesses of 60, 240, and 960 s at $-1.6$ V (vs. Ag/AgCl).

3A, A1, A2 display FE(%) ppm amounts of H$_2$ and CO, and the corresponding NMR data, respectively, obtained for ZnO NR, In(240s)/ZnO NR, and GZO/In(240s)/ZnO NR with GZO thicknesses of 10, 100, and 800 s at $-1.6$ V (vs. Ag/AgCl). For bare ZnO NR, major gaseous products were observed to be H$_2$ (1285 ppm) and CO (2179 ppm) with Faradaic efficiencies (FEs) of 9.3 and 15.8%, respectively, and a CO/H$_2$ ratio of 1.7. One minor species included CH$_4$ with 1.5 ppm. The CH$_4$ amount was not significantly dependent on the GZO thickness (Supplementary Table S1). No liquid products were observed. Total FE (%) was observed to be below 30%. Several reasons were plausibly proposed. In the present study, we used a 2 mm thick Zn plate different from those (e.g., powder in carbon paste) in the literature (Sekimoto et al., 2016; Tatsumi et al., 2017; Kikkawa et al., 2018; Lu et al., 2018; Qin et al., 2018; Yamamoto et al., 2018; Zhang et al., 2018; Liu et al., 2019; Ma et al., 2019; Murali et al., 2019; Zhang et al., 2019; Akatsuka et al., 2020; Daiyan et al., 2020; Hou et al., 2020; Luo et al., 2020; Tan et al., 2020; Yang et al., 2020; Deng et al., 2021; Li et al., 2021; Liang et al., 2021; Ma et al., 2021; Teng et al., 2021; Wang et al., 2021; Wei et al., 2021; Wu et al., 2021; Xiao et al., 2021; Yoon et al., 2021). Therefore, non-Faradaic current such as capacitive current might be significantly involved. As discussed previously in Figure 2, ZnO reduction occurred, and therefore ZnO reduction current was also added in the amperometry current. Further, the experiment was performed in a single cell and therefore evolved oxygen gas was present in the cell. Therefore, oxygen reduction reaction current was also plausibly involved (Zhou et al., 2020).

Upon deposition of In, drastic changes were observed; H$_2$ production was substantially decreased while formate was newly observed with a substantial amount. The NMR data (Figure 3A2) confirmed the formation of formate. The FEs (%) for H$_2$, CO, and formate over In(240s)/ZnO NR were estimated to be 2.1, 15.0, and 7.5%, respectively. The CO/H$_2$ ratio was substantially increased and estimated to be 7.2. Moreover, C$_2$H$_2$ was very meaningfully observed with an amount of 16.7 ppm (Supplementary Table S1). Upon deposition of a
small amount of GZO on In(240s)/ZnO NR for 10 s, the FEs(%) of H2, CO, and formate were observed to be decreased. After GZO deposition for 100 s, the FEs(%) of H2, CO, and formate were all increased. Upon further increasing GZO for GZO(800s)/In(240s)/ZnO NR, the FEs(%) of H2 and CO were increased by ×1.36 and ×1.14. On the other hand, the formate was decreased by ×0.71. The CO/H2 ratio was estimated to be 2.5. Conclusively, In was a key factor of producing formate and the GZO thickness was a control factor for controlling the amounts of three major products (H2, CO, and formate).

3.3.2 In Spacer Thickness Effects
For the electrodes in this experiment, the topmost GZO layer was fixed and the In spacer thickness was changed. Figures 3A, A1, A2 show FE(%), ppm amounts of H2 and CO, and the corresponding NMR data for ZnO NR, GZO(100s)/ZnO NR, and GZO(100s)/In/ZnO NR with In thicknesses of 60, 240, and 960 s at −1.6 V (vs. Ag/AgCl) in 0.1 M NaHCO3 electrolyte for 1 h. Upon deposition of GZO on ZnO NR for 100 s, formate was newly detected with an FE(%) of 2.8%. The formate enhancement was smaller than that (7.5%) after In deposition. This also confirms that In was more efficient for formate production, in good consistency with the literature (Ma et al., 2019; Murali et al., 2019; Zhang et al., 2019; Hou et al., 2020; Yang et al., 2020; Li et al., 2021; Ma et al., 2021; Teng et al., 2021; Wei et al., 2021; Wu et al., 2021; Xiao et al., 2021). The CO(%) was slightly decreased while that of H2 was substantially decreased by ×0.32, compared with those for bare ZnO NR. Therefore, the CO/H2 ratio was increased to 5.3 (Supplementary Table S2). One solid interesting observation was that the formate was continuously increased as the thickness of In spacer was increased, confirmed by NMR data in Figure 2B2. For CO production, when In was sandwiched, the FE(%) was observed to be somewhat decreased and lower than those of ZnO NR and GZO(100s)/ZnO NR. For H2 production, the FE(%) of H2 was maximum when In spacer thickness was 10 s, but the FEs(%) for other samples was observed to be lower than that of bare ZnO NR. The CH4 amount (with only 1.3–1.9 ppm) was also not significantly dependent on the applied potential. The CH4 amount with only 1.3–1.8 ppm was not significantly changed with applied potential (Supplementary Table S4). The CH4 amount with only 1.3–1.9 ppm was also not significantly dependent on the applied potential. The CO/H2 ratio was estimated to be 0.7 at −1.2 V. Upon increasing the potential to −1.4 V, formate was clearly increased with an FE(%) of 5.3%. The amount of formate was continuously increased with increasing the potential as seen in the NMR data. Upon further increasing the potential to −1.6 and −1.8 V FEs(%) were observed to be 25.8 and 22.9%, respectively. CO and H2 productions were also increased with increasing the potential and the amounts (ppm) were highest at −1.8 V. After considering the current density at each applied potential the FE(%) of CO at −1.4 V was obtained to be 14.9 and higher. The FE(%) became decreased with increasing the potential. The FE(%) of H2 at −1.4 V was minimum of 2.9 but increased with increasing the potential. In other words, when the FE(%) of CO was decreased the FE(%) of H2 was inversely increased.

3.3.3 Applied Potential Effects
A GZO(100s)/In(960s)/ZnO NR electrode sample was selected and tested at different applied potentials of −1.2, −1.4, −1.6, and −1.8 V (vs. Ag/AgCl) in 0.1 M NaHCO3 electrolyte for 1 h (Figure 4; Supplementary Table S4). At a low potential of −1.2 V, gaseous products (H2, CO, and C2H2) were mainly produced and no formate was observed as seen in the NMR spectrum. The CH4 amount (with only 1.3–1.8 ppm) was not significantly changed with applied potential (Supplementary Table S4). The CO/H2 ratio was estimated to be 0.7 at −1.2 V. Upon increasing the potential to −1.4 V formate was clearly increased with an FE(%) of 5.3%. The amount of formate was continuously increased with increasing the potential as seen in the NMR data. Upon further increasing the potential to −1.6 and −1.8 V FEs(%) were observed to be 25.8 and 22.9%, respectively. CO and H2 productions were also increased with increasing the potential and the amounts (ppm) were highest at −1.8 V. After considering the current density at each applied potential the FE(%) of CO at −1.4 V was obtained to be 14.9 and higher. The FE(%) became decreased with increasing the potential. The FE(%) of H2 at −1.4 V was minimum of 2.9 but increased with increasing the potential. In other words, when the FE(%) of CO was decreased the FE(%) of H2 was inversely increased.
3.3.4 Photoirradiation Effects

Light (365 nm) ON and OFF conditions were tested to examine photoirradiation effects on photoelectrochemical CO₂ reduction over a selected GZO(100s)/In(960s)/ZnOₙR electrode (Figure 5). The band gap edge was observed around 400 nm and therefore a shorter wavelength of 365 nm was chosen in this experiment. The amounts (ppm) of H₂ and CO were commonly increased upon irradiation of 365 nm light during amperometry (Figure 5A). The amount of H₂ was increased by ×1.93 and that of CO was increased by ×5.40 (Figures 5A,A1). However, as seen in the NMR spectra (Figure 5A2), the formate was decreased after light irradiation. The FE(%) of formate was drastically decreased by ×0.17 (Figure 5B). Based on the amperometry i-t curve (Figure 5C), the current density was increased by about ×1.7 upon irradiation of 365 nm light. In the FE(%) calculation, the total current (including photogenerated current) was used. The FE(%) of formate was drastically decreased by ×0.81 and that of H₂ was decreased by ×0.79 under 405 nm light. These diminutions were less compared with those (×0.17 for formate and ×0.79 for H₂) under 365 nm light. It was a common observation that CO production was enhanced under light, but formate production was negated by light irradiation. When light wavelength was shorter, this observation was more pronounced. For GZO(100s)/In(240s)/ZnOₙR electrode (Supplementary Figure S3), similarly CO production was increased and formate production was decreased under light. However, unlike the GZO(100s)/In(960s)/ZnOₙR electrode, the FE(%) of H₂ was also increased under light. This was due to a smaller amount of In spacer and the H₂ production was more or less affected by the overlayer GZO. For GZO(10s)/In(240s)/ZnOₙR electrode, the thickness of GZO was much less. Consequently, the production of H₂ was observed to be much less than those for other samples with GZO thickness for 100 s. Similarly, CO production was also increased under light. Conclusively, it was evident that CO was increased under light, and formate and H₂ were determined by the thicknesses of GZO and the In spacer.

3.3.5 Electrolyte and Electrolyte Concentration Effects

Electrolytes of 0.1 M KHCO₃ and a higher concentration of 0.5 M NaHCO₃ were also tested for a selected GZO(100s)/In(960s)/ZnOₙR electrode and provided in Supplementary Figure S4. When the electrolyte was changed from 0.1 M NaHCO₃ to 0.1 M KHCO₃, it was observed that the amounts (ppm) of H₂ and CO were increased from 496 to 804 ppm and from 1827 to 4,422 ppm, respectively. However, because of a current increase in 0.1 M NaHCO₃ compared with KHCO₃, the CO was increased from 3.7 to 10.3 and the H₂ was decreased from 1.3 to 4.9 ppm (Supplementary Table S5).

A longer wavelength of 405 nm light was also used, and the wavelength was near the band gap edge (Supplementary Figure S3). For GZO(100s)/In(960s)/ZnOₙR electrode, the FE(%) of CO was increased by a factor of ×1.47 under 405 nm irradiation. This was compared with ×1.95 for 365 nm light. This indicates that the 405 nm light showed less impact on producing CO. Inversely, similar phenomena were observed for formate and H₂.
KHCO₃, the FEs(%) of formate, CO and H₂ were decreased by ×0.81, ×0.91, and ×0.61, respectively. C₂H₂ and acetone were newly but very weakly detected (Supplementary Table S6). When the electrolyte concentration was increasing from 0.1 to 0.5 M NaHCO₃ the H₂ production was dramatically increased from 496 to 5,563 ppm by a factor of ×11.2. The CO production was increased from 1,827 to 4,695 ppm by a factor of ×2.57. When the current density was considered, the FEs(%) of formate and CO were decreased by ×0.24 and ×0.51, respectively. On the other hand, the FE(%) of H₂ was increased from 3.8 to 8.4% by a factor of 2.2. Consequently, the CO/H₂ ratio was observed to be 0.8. Further, C₂H₂ was detected with an amount of 12 ppm.

Although similar sandwiched samples have not been reported, some literature was summarized and discussed in Supplementary Table S7. Although the FE(%) was somewhat less, compared with those in the literature, the present study showed very unique information on sandwiched structures under various experimental conditions.

3.4 X-Ray Photoelectron Spectroscopy Before and After CO₂ Reduction Tests

3.4.1 XPS With GZO Thickness

Figure 6 displays Zn 2p, In 3d, valence band (VB), Ga 2p, O 1s XPS profiles, and the consequent interfacial energy levels for ZnOₙRN, In(240s)/ZnOₙRN, GZO/In(240s)/ZnOₙRN with GZO thicknesses of 10, 100, and 800 s. The interfacial energy level alignments for ZnOₙRN, In(240s)/ZnOₙRN, and GZO/800s/In(240s)/ZnOₙRN samples.
no critical change and the width of Zn 2p peak became slightly narrower. As the GZO was deposited and the thickness was increased Zn 2p BE became shifted to a higher BE position. For GZO(800s)/In(240s)/ZnO NR electrode, Zn 2p <sub>3/2</sub> and Zn 2p <sub>1/2</sub> peaks were shifted by +0.2 eV and observed at 1021.4 and 1044.7 eV, respectively (Naumkin et al., 2012; Ansari et al., 2013; Choi et al., 2015; Kang et al., 2019). For In(240s)/ZnO NR electrode, the In 3d <sub>5/2</sub> and In 3d <sub>3/2</sub> XPS profiles were observed at 444.6 and 452.1 eV, respectively with an S-O splitting energy of 7.5 eV (Naumkin et al., 2012; Li et al., 2021). The BEs were shifted to lower BE positions by −0.2 eV, and observed at 444.4 and 451.9 eV, respectively, for GZO(800s)/In(240s)/ZnO NR electrode. Conclusively, Zn 2p XPS peaks were shifted to higher BE positions while In 3d and Ga 2p BEs were shifted to lower BE positions. GZO (Ga<sub>2</sub>O<sub>3</sub> and ZnO) was sputter-deposited on top of In(240s)/ZnO NR for a very long time of 800 s. During this time, Ga, Zn, and In reacted, and consequently Zn 2p was shifted to a higher BE position while In 3d and Ga 2p were shifted to lower BE positions.

For the corresponding O 1s XPS profiles, two broad O 1s peaks were commonly observed at 530.2 and 532.0 eV that were attributed to lattice and surface oxygens, respectively. The surface oxygen peak at 532.0 eV was observed to be stronger for bare ZnO NR while the lattice O 1s peak at 530.2 eV was

![FIGURE 7](image-url) Zn 2p, In 3d, VB, Ga 2p, and O 1s XPS profiles for GZO(100s)/In/ZnO NR with In thicknesses of 60, 120, 240, 480, and 960 s. The interfacial energy level alignments for GZO(100s)/In(60s)/ZnO NR and GZO(100s)/In(960s)/ZnO NR samples.
stronger for the other samples. The O 1s peaks for GZO(800s)/In(240s)/ZnONR electrode were broader than those for In(240s)/ZnONR electrode. The broader O 1s signals were plausibly due to the topmost GZO layer. In other words, more different oxygen species were intuitively present in the GZO(800s)/In(240s)/ZnONR electrode, compared with the In(240s)/ZnONR electrode.

In the corresponding VB spectra of ZnONR, the VB edge appeared at 2.6 eV below the Fermi level (EF). Upon deposition of In, the VB edge was observed around 2.7 eV below the EF. The conduction band (CB) edge was similar based on the corresponding UV-Vis absorption spectra in Figure 1 and the VB spectra. By increasing the coverage of GZO, it appeared that the VB edge was shifted toward the Fermi level. For the GZO(800s)/In(240s)/ZnONR electrode, the VB edge was observed at 2.3 eV below the EF and the CB was observed at 0.95 eV above the EF. For the energy band diagram, we assumed the multilayer system to be a single well-hybridized system.

The overlayer thickness was roughly estimated using a well-known equation (Powell and Jablonski, 2000; Naumkin et al., 2012), $I = I_0 \exp(-d/\lambda)$, where $I$ and $I_0$ is the Zn 2p XPS intensities before and after overlayer deposition, $d$ is the overlayer thickness, and $\lambda$ is the electron inelastic mean free path (here $\lambda = 1.5$ nm used) (Naumkin et al., 2012), respectively. The overlayer thicknesses were calculated to be approximately 0.1 nm for In deposition of 240 s and approximately 0.4 nm for GZO deposition of 800 s, respectively (Powell and Jablonski, 2000).

3.4.2 XPS With In Spacer Thickness

Figure 7 displays Zn 2p, In 3d, VB, Ga 2p, O 1s XPS profiles, and the interfacial energy levels for GZO(100s)/In/ZnONR with In thicknesses of 60, 120, 240, 480, and 960 s. For GZO(100s)/In (60s)/ZnONR, Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ peaks were observed at 1021.2 and 1044.5 eV, respectively, with an S-O splitting of 23.3 eV. The BE positions were the same as those for bare ZnONR. As the sandwiched In thickness was increased to 200 nm, the Zn 2p BE became shifted to a higher BE position. For GZO(100s)/In(960s)/ZnONR, Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ peaks were shifted by +0.2 eV and observed at 1021.4 and 1044.7 eV, respectively (Naumkin et al., 2012; Ansari et al., 2013; Choi et al., 2015; Kang et al., 2019). For GZO(100s)/In (60s)/ZnONR, the In 3d$_{5/2}$ and In 3d$_{3/2}$ XPS profiles were observed at 444.6 and 452.1 eV, respectively, with an S-O splitting energy of 7.5 eV (Naumkin et al., 2012; Li et al., 2021). As the In thickness was increased, the In 2p intensity was increased as expected. The BE positions were shifted to lower BEs by ~0.3 eV, and observed at 443.3 and 451.8 eV, respectively, for GZO(100s)/In(960s)/ZnONR electrode. It appeared that In reacted with ZnONR support during the very long time of 960 s. Therefore, Zn 2p was shifted to a higher BE position while In 3d was shifted to a lower BE position. The Ga 2p$_{3/2}$ and Ga 2p$_{1/2}$ peaks were commonly observed at 1,117.6 and 1,144.4 eV, respectively, with a spin-orbit S-O splitting of 26.8 eV. The BEs showed no change with the In spacer thickness. It was expected that the topmost GZO layer thickness was the same for all the samples. This indicates that GZO was not critically reacted with In during the relatively shorter deposition time of 100 s.

Two broad O 1s peaks were commonly observed at 530.2 and 532.0 eV that were attributed to lattice and surface oxygens, respectively, as discussed above. As the In thickness was increased, the lattice O 1s peak was decreased while the surface oxygen peak was observed to be somewhat enhanced. On the basis of the lattice O 1s peak and Zn 2p XPS, the XPS signals from the ZnONR support were decreased as the thickness of the In spacer was increased as expected. For the corresponding VB spectra of GZO(100s)/In (60s)/ZnONR, the VB edge was observed at 2.7 eV below the EF. Upon increasing the thickness of the In spacer, the VB edge became slightly shifted toward the EF and observed around 2.5 eV below the EF for the GZO(100s)/In(960s)/ZnONR electrode. Based on a similar band gap, the interfacial energy level was depicted as shown in Figure 7.

On the basis of the CO$_2$ reduction of major products, the simplified CO$_2$ reduction mechanism is depicted in Figure 8 (Sohn et al., 2017; Wang et al., 2019; Song et al., 2020; Prabhu et al., 2020; Sun et al., 2021; da Silva Freitas et al., 2021; Jelić et al., 2021; Ochedi et al., 2021; Chen et al., 2021; Bellardita et al., 2021).
In an NaHCO₃ electrolyte saturated with CO₂, two processes are initially involved; H⁺ + e⁻ → H₂ via CO₂ + H⁺ + e⁻ → H₂O. The surface H₂ is released as gaseous H₂ via H₂ + H⁺ + e⁻ → H₂ or H₂ + H₂O → H₂ (Sohn et al., 2017; Wang et al., 2019; Prabhu et al., 2020; Song et al., 2020; Bellardita et al., 2021; Chen et al., 2021; da Silva Freitas et al., 2021; Ješić et al., 2021; Ochedi et al., 2021; Sun et al., 2021). This process became pronounced when the thickness of GZO was increased. The surface HOOCad is then transformed into formate or changed into surface O≡Cad via HOOCad + H⁺ + e⁻ → O≡Cad + H₂O (Lu et al., 2018; Qin et al., 2018; Zhang et al., 2018; Liu et al., 2019; Daiyan et al., 2020; Luo et al., 2020; Wang et al., 2021). The formate production was only observed when In and GZO (Ga₂O₃:ZnO) were present. Without In or GZO, no formate was produced. The formate production was more significantly dependent on In thickness. Ga and In have an electron configuration d¹0s²p¹, and it appeared that the partially filled p orbital may play a role in the formate production (Li et al., 2021). The surface O≡Cad is likely liberated as gaseous CO. In the initial stage over GZO/In, H₂O(2) and formate, and CO competitively occurred.

The CO production process became dominant when light was irradiated on the electrode surface. Inversely, the formate and H₂ production processes became reduced under light irradiation. CH₄ and C₂H₂ were minor products and the net reactions are written as CO₂ + 8H⁺ + 8e⁻ → CH₄ + 2H₂O and 2CO₂ + 10H⁺ + 10e⁻ → C₂H₂ + 4H₂O, respectively (Sohn et al., 2017; Wang et al., 2019; Song et al., 2020; Prabhu et al., 2020; Bellardita et al., 2021; Chen et al., 2021; da Silva Freitas et al., 2021; Ješić et al., 2021; Ochedi et al., 2021; Sun et al., 2021). Some surface O≡Cad species may transform into HOOCad and H₂Cad. Consequently, some CH₄ and C₂H₂ were expected to be produced. In the photoelectrochemical CO₂ reduction process, light was irradiated and therefore electrons (e⁻CB) and holes (h⁺VB) are generated in the conduction and valence bands, respectively (Choi et al., 2015; Yoon et al., 2021). Plausible processes under photoirradiation include 1) e⁻CB + adsorbed O₂ → •O₂, 2) OH + h⁺VB → •OH, 3) •O₂ + H⁺ → •OOH, 4) •OOH + e⁻ + H⁺ → H₂O and, 5) H₂O₂ + e⁻ → •OH + OH⁻. Oxygen was expected to participate in the process because the electrochemical test was conducted in a single cell and therefore evolved O₂ gas was present in the cell. The generated active species are also expected to play roles in CO₂ reduction process. H₂ production was neglected because of the side reactions. Surface H was consumed to be less under photoirradiation, and instead surface CO was facile to be liberated. Formate production was also observed to be diminished under UV irradiation. It was plausibly due to that formate reacted with •OH to return to •CO₂⁻ via the reaction of HCO₂⁻ (formate) + •OH → •CO₂⁻ + H₂O (Talu and Diynamandoglu, 2004).

4 CONCLUSION

Hybrid sandwiched GZO/In/ZnONR was prepared with various thicknesses of overlayer GZO and In spacer. Their electrochemical CO₂ reduction performances and products were evaluated by gas chromatography and nuclear magnetic resonance spectroscopy. GZO and In were not clearly detected by XRD and Raman spectroscopy, but the elements were detected by EDXS and XPS. This indicates that the overlayers of GZO and In were ultrathin and/or amorphous.

For bare ZnO NR, major products were observed to be H₂ and CO by electrochemical CO₂ reduction. Formate production was observed upon introducing the In layer and the amount was increased as the In spacer thickness was increased. When the In spacer layer was fixed and the GZO thickness was varied the FEs(%) of H₂, CO, and formate were relatively varied. For a GZO/In/ZnO NR electrode, the FE(%) of CO was decreased as the applied potential was increased from −1.4 to −1.8 V (vs. Ag/AgCl) while that of H₂ was inversely increased with potential. The FE(%) of formate showed the highest at −1.6 V (vs. Ag/AgCl). Upon 365 nm light irradiation, CO production was significantly increased while formate was dramatically diminished. CO and formate productions were decreased while H₂ was increased at a higher concentration of 0.5 M NaHCO₃. In 0.1 M KHCO₃ electrolyte, the FEs(%) of all the products were decreased, compared with those in 0.1 M NaHCO₃. Faradaic efficiencies were all highly dependent on the relative amounts of overlayer GZO and In spacer, as well as applied potential, light irradiation, and electrolyte.

Overall, the present study provides new strategic information on the development of sandwiched hybrid electrodes for energy and the environment.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

HJ: Conceptualization, methodology, data curation, software visualization, formal analysis. YJ: Methodology, data curation. MJ: Methodology, formal analysis. JM: Methodology, data curation. YK: Methodology, data curation. CR: Supervision, conceptualization, reviewing. YS: Project administration, supervision, conceptualization, validation, writing—original draft, writing—reviewing and editing, funding acquisition.

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SUPPLEMENTARY MATERIAL

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