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RESEARCH ARTICLE

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Unassisted photoelectrochemical CO₂ reduction by employing III–V photoelectrode with 15% solar-to-fuel efficiency

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Abstract

Solar-driven carbon dioxide reduction reaction (CO₂RR) provides an opportunity to produce value-added chemical feedstocks and fuels. However, achieving efficient and stable photoelectrochemical (PEC) CO₂RR into selective products is challenging owing to the difficulties associated with the optical and the electrical configuration of PEC devices and electrocatalyst properties. Herein, we construct an efficient, concentrated sunlight-driven CO₂RR setup consisting of InGaP/GaAs/Ge triple-junction cell as a photoanode and oxidederived Au (Ox-Au) as a cathode to perform the unassisted PEC CO₂RR. Under one-sun illumination, a maximum operating current density of 11.5 mA cm⁻² with an impressive Faradaic efficiency (FE) of ~98% is achieved for carbon monoxide (CO) production, leading to a solar-to-fuel conversion efficiency of ~15%. Under concentrated intensity of 10 sun, the photoanode records a maximum current density of ~124 mA cm⁻² and maintains ~60% of FE for CO production. The results demonstrate crucial advancements in using III–V based photoanodes for concentrated PEC CO₂RR.

KEYWORDS

3 J photoanode, CO2 reduction, high STF, unassisted PEC

Karthik Peramaiah, Vinoth Ramalingam, and Purushothaman Varadhan contributed equally to this study.

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1 | INTRODUCTION

Solar-powered carbon dioxide reduction reaction (CO₂RR) is one of the promising methods to convert CO₂ into valueadded chemicals and fuels using renewable solar energy.¹⁻⁵ In comparison to other energy conversion approaches, such as photocatalytic (PC) and electrocatalytic (EC), the photoelectrochemical (PEC) approach has gained significant attention due to the combined advantages of EC and PC processes. The PEC approach combines a light-harvesting system and electrochemical components into a single device. This approach has gained considerable attention for $CO_2 RR^{6-10}$ and various other PEC applications, such as water splitting and nitrogen reduction reactions.^{11–13} Among the wide range of CO₂ reduction products, carbon monoxide (CO) is a viable product due to its extensive applications in various industrial processes. Additionally, CO formation requires only two proton-electron transfer reactions, making it a kinetically favorable choice compared to other products, such as CH₃OH, C₂H₄, C₂H₅OH, and so forth, which require more than two proton-electron transfers to form.^{5,14-16} Intensive efforts are underway to produce cost-competitive CO and syngas $(CO + H_2)$ through an electrochemical approach for the industrial Fischer-Tropsch process.8,17,18 Besides, designing and developing an efficient PEC CO₂RR system can also lead to the cost-competitive production of CO and syngas. In addition, different ratios of syngas mixtures can also be produced in the PEC approach due to the competitive H_2 evolution reaction.^{19–21}

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To design an efficient solar-driven system for CO₂ reduction, highly selective electrocatalysts are necessary to facilitate the CO₂RR, preferentially at low overpotential levels.^{22,23} Metals including Au, Ag, Cu, and Sn have been widely used as the catalyst for CO2RR to achieve selective products in an aqueous electrolyte.^{24,25} The catalytic activity of metals can be significantly improved through precise control of crystal facets, grain boundaries, and nano- and mesostructures, as well as oxidation states.²⁶⁻²⁹ In particular, electrochemical anodization of metals is found to help achieve highly selective end-products by having controlled oxidation states of the catalysts with a porous surface.^{28,29} Furthermore, anodized metal catalysts can have different shapes and grain boundaries, which can improve catalytic performance at low potential. In our study, we employed the pulsed anodization strategy to prepare the oxide-derived Au (Ox-Au) electrocatalyst and used it as the cathode. This significantly reduced the CO₂RR onset potential compared to bare Au foil and demonstrated an unassisted PEC approach.

Various semiconductor photoelectrodes, including Si and III–V, have been investigated for solar-driven CO_2 reduction into CO, usually in conjunction with metal catalysts for selective reduction (e.g., Au, Ag, and derivatives). However, designing a PEC CO_2RR system with self-solar powered or

unassisted configurations for redox couple reactions could be a promising approach as it reduces the resistive losses due to the external wiring between electrocatalytic parts and solarpowered devices.^{30,31} An unassisted PEC system with a twoelectrode configuration, in which photoelectrodes are attached with redox reaction catalysts, facilitates long-term effective solar-energy utilization at a low cost. However, it is still challenging to develop an efficient and stable unassisted PEC CO₂RR system due to the difficulty in the prerequisite of sufficiently high photovoltage-producing semiconductor system, as most of the electrocatalysts have higher overpotential than hydrogen evolution reaction catalysts.³² To build an unassisted CO2RR system, tandem III-V photoelectrodes are commonly used.33,34 While tandem III-V photoelectrodes can generate the required photovoltage for an unassisted PEC approach, their instability in aqueous electrolytes poses a significant challenge for long-term stability. The low stability of the photoelectrode is due to photocorrosion and chemical instability in aqueous electrolytes, which needs to be prevented using suitable protection layers. In addition, using III-V semiconductors as a photoelectrode under one-sun intensity is not practically viable for solar fuel production as they cannot reach the industrial-level current density. Thus, addressing these challenges necessitates establishing a photoabsorber with optimal photovoltage, longterm stability, and a low-onset potential catalyst for a promising self-sustained PEC CO₂RR.

This study employs III–V-based triple-junction (TJ) In-GaP/GaAs/Ge cell for unassisted CO_2RR using an Ox-Au as a cathode catalyst. To enable the unassisted CO_2RR at low applied potential, we integrated RuO_{x} -deposited thin Ti-foil with the InGaP/GaAs/Ge TJ cell, which served as the photoanode. This integrated system exhibited significant stability under aqueous electrolytes by preventing direct InGaP/GaAs/Ge contact with the electrolytes. Moreover, the two-electrode unassisted system achieved a ~98% Faradaic efficiency for CO production and an impressive solar-to-fuel (STF) efficiency of 15%. Notably, we demonstrated a more practical application of the III–V photoanode system by using concentrated sunlight to drive CO_2RR , resulting in a maximum current density of ~124 mA cm⁻² without an external bias.

2 | RESULTS AND DISCUSSION

2.1 | Anodized Au electrocatalyst

Ox-Au porous structure with excellent CO_2RR catalytic performance was achieved by an electrochemical pretreatment method.^{29,35} The pretreatment includes vigorous pulsed anodization followed by gentle reduction, which develops Ox-Au porous structures on the surface of a 3×3 cm² Au foil.²⁹ Pulsed anodization was initially employed to generate Au oxide on a thin Au film, applying potentials ranging from 1.2 to 2.7 V versus a reversible hydrogen electrode (RHE) in a KHCO₃ solution (0.5 M, pH = 7.2). This process was conducted in a two-compartment cell using a three-electrode configuration (Figure 1A), where Pt, Ag/AgCl, and Au foil served as the counter, reference, and working electrodes, respectively. The two-compartment cell was separated by a bipolar membrane (BPM) to minimize the deposition of impurities during the anodization process. Following pulsed anodization, we subsequently electrochemically reduced the anodic Au₂O₃ layer in the same electrolyte under a constant current density ranging from -0.1 to $-0.5 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ until the electrode potential stabilized (Figure 1B). Post-treatment, the gold color of the Au thin film transformed to a dark brown hue, indicating the formation of Au nanostructures on its surface.³⁵

Before integrating the Ox-Au catalyst with the PEC system, the electrocatalytic CO_2 reduction performance was evaluated in an H-type electrochemical cell (Figure S1) under a CO_2 -saturated 0.5 M KHCO₃ solution. After anodizing, the cyclic voltammetry (CV) profile of Ox-Au (Figure 1C) exhibits an apparent increase in total current density (j_{tot}) related to the CO_2RR .

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Moreover, compared to the as-obtained Au-foil, the Ox-Au exhibits a positive shift in onset potential of ~0.2 V versus RHE, revealing the importance of the anodization process. The shift in the onset potential of Ox-Au toward a positive direction is due to better CO₂ reduction in the presence of porous nanostructures, which not only enhance the CO₂ adsorption but also improve the CO₂RR activity.³⁶ Next, the applied potentials-dependent selectivity of the Ox-Au catalyst was evaluated by chronoamperometry (CA), and the Faradaic efficiencies for CO (FE_{CO}) and H_2 (FE_{H2}) production were quantified by online gas chromatography. Figure 1D,E shows the CA curves and FE_{CO}/FE_{H2} values at different applied potentials for the production of CO and H₂ using the Ox-Au in CO_2 -saturated 0.5 M KHCO₃. The initial FE_{CO} is observed to be ~55% at an applied potential of -0.3 V versus RHE. With increasing applied potentials, the production of CO increases and H₂ decreases as consistent with the higher j_{tot} at higher applied potentials. A maximum FE_{CO} of ~98% is achieved at an overpotential of -0.5 V versus RHE. Moreover, the FE_{CO} remains steady at >92% over a broad range of potentials from -0.6 to -1.0 V versus RHE. However, the FE_{CO} begins to drop at lower applied potentials, possibly due to changes in the local pH of the electrolyte.^{29,35,37} The partial current



FIGURE 1 (A) Current density as a function of time for polycrystalline Au foil during pulsed anodization process for 30 min under 0.5 M KHCO₃ electrolyte; (B) electrochemical reduction on Ox-Au at different constant current densities; (C) CV curves of as-obtained polycrystalline Au foil, anodized Au foil, and Ox-Au (reactivated Au foil) under CO₂ saturated 0.5 M KHCO₃ electrolyte at a scan rate of 20 mV/s; (D) CA curves at different applied potentials; (E) CO and H₂ Faradaic efficiencies at different applied potentials; and (F) CO and H₂ partial current densities at different applied potentials.

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density of CO is shown in Figure 1F, which indicates that most of the j_{tot} is contributed to producing CO. Furthermore, the Ox-Au catalyst demonstrated stable FE_{CO} of ~90% at -1.0 V versus RHE, maintaining 80% current density retention after 30 h of continuous operation, highlighting the excellent stability of the Ox-Au catalyst (Figure S2). A plausible CO₂ reduction mechanism on the Ox-Au surface is proposed and illustrated in Figure S3. First, CO₂ is adsorbed onto the electron-rich porous Ox-Au surface, forming the *COO⁻ intermediate, which plays a crucial role in CO selectivity. The further addition and removal of electrons and protons in the *COO⁻ intermediate facilitate CO selectivity.³⁸

2.2 | Surface characterizations before and after CO₂RR

After the anodization reaction followed by the reduction process, the X-ray diffraction (XRD) pattern indicates that the crystallinity of the Au remains unchanged (Figure S4). This suggests that the anodization and reduction processes contribute to forming a porous nanostructure without affecting the crystal structure, which is beneficial for CO₂RR. Similar XRD results were reported in the literature for the Au film after the anodization process,²⁹ and field-emission scanning electron microscopy (FE-SEM) confirms the

formation of porous nanostructures due to this (Figure S5). Transmission electron microscopy (TEM) was employed to probe the nanostructures of Ox-Au before and after CO₂RR.

Figure 2A,B depicts TEM images of the Au foil after the anodization process, revealing the formation of porous nanostructures on the surface. The high-resolution TEM image (Figure 2C) reveals the discontinuity of the crystal lattice fringes with the d-space value of 0.24 nm and grain boundaries with different orientations (marked in different colors).^{39,40} The fast Fourier transform (FFT) pattern (inset of Figure 1B) displays the ring patterns, indicating the formation of single Au crystallites consistent with XRD crystal planes.⁴¹ Furthermore, a high-resolution TEM image was obtained for Ox-Au after 25 h of continuous PEC CO₂RR, showing no signs of etching or corrosion even after prolonged operation (Figure 2D and inset). The visible grain boundaries and sub-grains indicate that the anodized Au nanostructures remain stable during extended CO₂RR.

X-ray photoelectron spectroscopy (XPS) was utilized to examine changes in the oxidation states of an Au foil before and after pulsed anodization, followed by a reduction reaction. Figure S6 shows the survey scan XPS spectra of Ox-Au before and after the PEC CO_2RR for 25 h, indicating the presence of Ox-Au after anodization and subsequent reduction. Figure 2E displays the high-resolution Au 4f XPS spectra of the bare Au foil, after the anodization process, and after PEC CO_2RR . The high-resolution Au 4f XPS spectra of



FIGURE 2 (A) Low-resolution TEM image of Ox-Au nanostructures before CO_2RR (scale bar: 50 nm). The top layer of the Au-foil has been anodized and converted into porous nanostructures. (B) High-resolution TEM images of the nanostructures reveal the different grain boundaries and sub-grains obtained from the pulsed anodization and reduction process. (scale bar: 5 nm). The inset of (B) shows the ring FFT pattern, demonstrating the formation of single Au crystallites. (C) High-resolution TEM image of Ox-Au nanostructures with crystal lattice fringes in different orientations (scale bar: 2 nm). (D) High-resolution TEM image of Ox-Au nanostructures after 25 h of continuous CO_2RR (scale bar: 10 nm). The inset of (D) shows crystal lattice fringes in different orientations (scale bar: 2 nm). (E) High-resolution Au 4f XPS spectra of as-obtained Au-foil, and Ox-Au before and after CO_2RR .

bare Au foil exhibit peaks at 84.0, and 88.2 eV, respectively, correspond to Au $4f_{7/2}$ and Au $4f_{5/2}$, indicating that Au is in a metallic state.^{36,37} After the pulsed anodization step, the Au $4f_{7/2}$ peaks are shifted to the high binding energies side, suggesting electron depletion in the Au foil after the oxidation reaction. This electron deficiency is crucial for adsorbing CO₂ reduction intermediates on the catalyst surface.⁴² As Ox-Au is electron-deficient, it can efficiently adsorb and stabilize CO_2^{-} intermediates compared to the bare Au foil, creating favorable conditions for the CO₂RR.²⁹ The linear sweep voltammerty results (Figure 1C) well support this, showing that Ox-Au has a higher current density at a lower onset potential than the bare Au foil. However, the Au surface is mostly reduced to Au⁰ after 25 h of CO₂RR, where the Au $4f_{7/2}$ peak is shifted back to $84.2 \,\text{eV}$ but not to the original position of 84.0 eV.^{37,43} These results confirmed that a thin layer of anodized Au is formed on the surface of Au foil during the pretreatment, which is reduced to Au⁰ during the CO₂RR.

2.3 | Photoabsorber design

It is important to have a photoabsorber with sufficient photovoltage to achieve high efficiency in standalone CARBON ENERGY-WILEY-

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solar-driven fuel production reactions. When designing a photoabsorber, it is crucial to consider several factors. This includes the overpotentials of the CO₂RR-cathode catalyst and the oxygen evolution reaction (OER)-anode catalyst, as well as the overall system resistance (iR), and the thermodynamic potential required to reduce CO_2 into CO. Here, we employed the InGaP/GaAs/Ge TJ cell as a photoanode to drive unassisted PEC CO₂RR to CO production with high current densities. The structure of the TJ cell is illustrated in Figure 3A, and detailed fabrication information is available in the Supporting Information.⁴⁴ To study the structure and composition of the TJ cell photoabsorber, we conducted TEM and highangle annular dark-field scanning transmission electron microscopy (HAADF-STEM) along with cross-sectional elemental mapping (Figure 3B,C). The results demonstrate a tandem arrangement of the top GaInP cell, middle GaAs sub-cell, and bottom Ge sub-cell, respectively.⁴⁵ Further, the photovoltaic characteristics of TJ cells under AM 1.5 G simulated sunlight illumination are shown in Figure 3D. Under AM 1.5 G simulated sunlight, the TJ cell demonstrates a short-circuit current density $(J_{\rm SC})$ of 13.5 mA cm⁻², an open-circuit voltage (V_{oc}) of 2.5 V, and a fill factor (FF) of 0.83. Importantly, in tandem cells, the photovoltages of the sub-cells are additive.



FIGURE 3 (A) Schematic architecture of InGaP/GaAs/Ge TJ solar cell. (B) Low-resolution TEM image of the InGaP/GaAs/Ge TJ cell (scale bar: $2 \mu m$). (C) HAADF-STEM images and elemental mapping images. (D) J-V characteristics of the InGaP/GaAs/Ge TJ photoabsorber under 1 sun AM 1.5G irradiation. (E) External quantum efficiency studies of the Ge/InGaAs/InGaP TJ photoabsorber. (F) OER performance of RuO_x, NiO_x and Pt in 0.5 M KOH electrolyte with a scan rate of 20 mV s⁻¹.

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Consequently, the Voc achieved with the TJ cell exceeds the potential required to drive unassisted CO₂ reduction (~2.3 V). To study the light absorption properties of TJ cells, we have performed the external quantum efficiency measurement (EQE) with the absorption edge of each sub-cell. As shown in Figure 3E, the top GaInP cell with a band gap of 1.85 eV harvests photons in the 300-600 nm range. The middle GaAs sub-cell with a band gap of 1.40 eV facilitates photon absorption in the 600-900 nm range. Finally, the bottom Ge sub-cell with a band gap of 0.67 eV absorbs the photons ranging between 900 and 1800 nm. The EQE and J_{SC} studies of TJ cells reveal the efficient light absorption capability and charge carrier separation properties. Furthermore, to protect and drive the unassisted PEC CO₂RR in the aqueous electrolyte, RuO_x-deposited Ti-foil was integrated on the back side of the TJ photoabsorber for OER at low onset potential.

2.4 | Cell configuration and unassisted PEC CO₂RR

To achieve an efficient PEC CO₂RR approach, parameters such as OER catalysts, membranes, and electrolytes must be optimized before CO₂RR. This is due to several challenges, including the low solubility of CO₂ in alkaline environments and the competitive hydrogen production in acidic environments, which can impede the PEC CO₂RR performance.^{16,27,45-51} The common OER electrocatalysts, such as Ni, Fe, and Co, can be used. However, obtaining the required potential for unassisted PEC is difficult because these catalysts can show high onset potentials for OER.²⁷ As a result, to date, precious metal OER catalysts, such as Pt and IrO₂, have been typically used to carry out coupled electrochemical water oxidation due to their stability in a neutral environment.³³ Despite using such precious metals for OER, the combination of reduction and oxidation still requires a total bias of at least ~3 V to produce a selective product at a significant yield $(>10 \text{ mA cm}^{-2})$.⁵² To match the independently optimized CO₂RR and OER catalysts and to eliminate any contamination, a BPM membrane is used.^{8,33,53} BPM can provide favorable pH conditions for alkaline OER (KOH) and neutral CO₂RR (KHCO₃), leading to a significant reduction in the potential to drive CO₂RR. A tri-potentiostat study was conducted to optimize the BPM potential for the unassisted PEC CO₂RR reaction under different anolyte and catholyte pH conditions (Figure S7). When selecting highly acidic and alkaline pH conditions for the anolyte and catholyte, respectively, such as 1 M KOH and 1 M H₂SO₄, the membrane potential was determined to be >0.7 V.

However, these conditions are not suitable for cathodic CO₂ reduction since acidic electrolytes can promote the HER. Whereas the BPM exhibits a low membrane potential of <0.4 V in near-neutral pH conditions on the anode and cathode sides but OER rate can be sluggish in such conditions. Nevertheless, maintaining a nearneutral (0.5 M KHCO₃) and alkaline (1 M KOH) pH at the cathode and anode sides shows a more favorable membrane potential than creating extremely highly acidic and alkaline conditions, which could favor CO₂ reduction. Finally, we analyzed the electrocatalytic overpotentials for the OER catalyst using RuO_x , NiO_x , and Pt catalysts at 1 M aqueous KOH to construct the unassisted PEC device. As shown in Figure 3F, the OER overpotentials of RuOx, NiOx, and Pt catalysts to reach 1 mA cm^{-2} are 300, 410, and 640 mV, respectively. These results show that RuO_x at 1 M KOH combined with 0.5 M KHCO₃ separated by BPM can drive the CO₂RR at ~2.3 V; hence, the TJ photoanode employment here is justified.

Solar-driven PEC CO2RR was carried out in a customized H-cell reactor separated by a BPM membrane (Figure S8).³³ The photoanode consisted of a tandemjunction III-V photoabsorber a thin Ti-foil (0.05 mm) surface protection layer, and a 25 nm of RuO_x deposited by atomic layer deposition method to facilitate the OER, whereas the Ox-Au nanostructures were used as a dark cathode to drive the CO₂RR. Details of the fabrication of the photoanode and the reactor setup are described in the Supporting Information, and the fabricated photoanode image is shown in Figure S9. The oxidation behavior (Figure 4A) of the photoanode in 1 M aqueous KOH was investigated using CV without correcting for uncompensated resistance in a three-electrode electrochemical measurement setup under simulated one-sun illumination. The photoanode exhibited a light-limited photocurrent density of $\sim 12.5 \text{ mA cm}^{-2}$ and an equivalent V_{oc} of ~2.5 V in accordance with the photovoltaic characteristics of the TJ cell. The CV characteristics of the photoanode under pH 7 and the Ox-Au nanostructures are also shown in Figure 4A. The results show that in pH, 7 the photovoltage delivered by the photoanode is insufficient to drive the unassisted CO₂RR as the current densities cross over at $<1 \text{ mA cm}^{-2}$. However, at pH 14, the photoanode delivers sufficient photovoltage for CO₂RR. This reveals the necessity of the BPM and the requirement of different catholytes and anolytes to drive the unassisted CO₂RR.

Further, it is essential to analyze the CO_2RR catalyst at commercially required current densities, to minimize the capital expenditure of a conversion unit to economically compelling levels. To achieve this, here we have done concentrated solar-driven CO_2RR in which the InGaP/GaAs/Ge/Ti/RuO_x photoanode is capable of



FIGURE 4 (A) Photoelectrochemical characteristics of InGaP/GaAs/Ge TJ photoanode measured at 1 sun intensity at pH 7 (green line) and pH 14 (blue line), and at 10 sun intensity at pH 14 (gray line). The current density matches the cathodic characteristics of Ox-Au nanostructures measured under 0.5 M KHCO₃ with CO₂ saturation. (B) Behavior of InGaP/GaAs/Ge TJ photoanode under varying sun intensity (up to 10 sun) and its total current densities matching the cathodic characteristics of Ox-Au. (C) Total current densities and corresponding FE_{CO} by varying sun intensity. (D) Schematic of the unassisted device configuration for CO₂ to CO conversion. Unassisted two-electrode solar-driven CO₂RR by short-circuiting the InGaP/GaAs/Ge TJ photoanode with the dark cathode (Ox-Au). (E) j_{tot} partial current density (J_{CO}), and STF conversion efficiency as a function of time.

working under >100 sun concentrated illumination. However, due to the PEC H-cell reactor's limitations and the diffusion limit of CO_2 in the electrolyte, we carried out the reaction at 10 sun intensity. Under concentrated 10 sun illumination, the oxidation behavior of the photoanode in 1 M aqueous KOH has been characterized by the CV in a three-electrode electrochemical measurement setup (Figure 4B). Here, three-electrode measurements are used due to the higher overpotential of RuO_x catalyst at higher j_{tot} compared to the 1 sun illumination. Subsequently, a chronoamperometry study was carried out for concentrated sunlight experiments at the potential of 0 V versus RHE in a typical H-cell, and the photoanode exhibited a light-limited photocurrent density of ~124.8 mA cm⁻². In addition to this, the j_{tot} was stable over 25 h; however, the FE_{CO} reduced over time and reached as low as 60% within 1 h with simultaneous enhancement in the FE_{H2} (Figures S10 and S11). The reduced FE_{CO} can be explained by kinetic limitations of CO₂ saturation in a typical H-cell reactor with higher current densities.

Figure 4C shows the sun intensity-dependent total current densities and FE_{CO} (from 0.5 to 10 sun). Increasing sun intensity increases the total current

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densities of the InGaP/GaAs/Ge/Ti/RuO_x photoanode. The NMR analysis ensures that no liquid product is formed during CO₂RR (Figure S12). Unassisted twoelectrode CO₂RR was also performed in the H-cell reactor by short-circuiting the InGaP/GaAs/Ge/Ti/RuO_x photoanode (0.8 cm^2) and ~1 cm² of Ox-Au catalyst as a counter electrode (Figure 4D). CV with a two-electrode setup showed a J_{SC} of ~11.5 mA cm⁻², which is ~1 mA $\rm cm^{-2}$ lower than that of the three-electrode setup, demonstrating the unassisted CO₂RR. This two-electrode measurement was utilized to calculate STF efficiency.³³ Corresponding to a current density of $\sim 11.5 \text{ mA cm}^{-2}$, a maximum STF of ~15% was achieved, considering the FE_{CO} of ~98%. In addition, we conducted a 25 h stability test in a two-electrode configuration to validate the claimed efficiency (Figure 4E). Over the entire measurement period of ~25 h, the j_{tot} was stable, and the FE_{CO} was ~96%. This results in the STF efficiency of ~15% over the entire period. It is worth mentioning that the achieved PEC performance of the present system outperforms that in many reported literature (Table S1). Furthermore, following the stability experiment, we conducted XRD and SEM studies on the cathode Ox-Au, which revealed no significant changes during stability studies (Figure S13).

3 | CONCLUSIONS

In summary, we report an efficient and stable solardriven CO_2RR system by integrating the Ox-Au as a cathode catalyst with the InGaP/GaAs/Ge/Ti/RuO_x photoanode that can drive the spontaneous CO_2RR . A BPM was employed to allow different pH electrolytes for the catholyte and anolyte, reducing the required overpotentials to drive the unassisted reaction. Under simulated AM 1.5 G, 1 sun illumination, the reactor yields an operating J_{tot} of 11.5 mA cm⁻², indicating an STF efficiency of ~15%. InGaP/GaAs/Ge/Ti/RuO_x system also allows one to use concentrated sunlight-driven CO_2 reduction up to 10 sun intensity, in which the efficiency scales up linearly with reduced FE_{CO} due to the diffusion limits of the H-cell reactor.

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CONFLICT OF INTEREST STATEMENT

The authors declare that there are no conflicts of interests.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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Unassisted Photoelectrochemical CO₂ Reduction by Employing III-V Photoelectrode with

15% Solar-to-Fuel Efficiency

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Characterizations Analyses

The transmission electron microscope (TEM) images were obtained from an FEI-ST Titan 80–300 kV instrument with an operating voltage of 300 kV. The X-ray photoelectron spectroscopy (XPS) analysis was done using an Axis Ultra DLD system (Kratos, U.K.) equipped with an Al Kα radiation source. BioLogic VMP3 potentiostat was used for the photoelectrochemical (PEC) and electrochemical measurements. High-angle annular dark-field imaging (HAADF)-STEM and mapping studies were carried out with a transmission electron microscope (Titan Themis Z, FEI).

Material details

The solvents, such as ethanol and isopropanol, were purchased from Merck and used without any further purification. The chemicals such as KOH, KHCO₃, Au-foil, Ti-foil, Ga-In eutectic, bis(ethylcyclopentadieny)ruthenium (II) were also purchased from Merck. In addition, the Pt electrode, carbon paper and bipolar membrane (BPM) (thickness 130 - 160 μ m) were obtained from fuel cell stores. The bipolar membrane (BPM) was activated by soaking it in a 1M KOH solution prior to its use. Moreover, the reference Ag/AgCl electrode was purchased from Metrohm.

Anodization of Au and preparation of oxide-derived Au (Ox-Au)

Au electrocatalyst was prepared by pulsed anodization process followed by gentle reduction. Au foil with an area of 3×3 cm² was pulsed between the potential range of 1.2 to 2.7 V vs. RHE using an H-type cell, consisting of the Pt, AgAgCl, and Au foil as the counter, reference, and working electrode, respectively. For this process, 0.5 M KHCO₃ electrolyte was used as the electrolyte.

Electrocatalytic CO₂ reduction reaction (CO₂RR)

The electrocatalytic CO₂ RR was performed in an H-type cell in which anode and cathode chambers were separated by the bipolar membrane (BPM). Ox-Au, Pt, and AgAgCl were the working counter, reference, and electrodes. Moreover, 1 M KOH and 0.5 M KHCO₃ solution were

utilized as the anolyte and catholyte for OER and CO_2RR . The CO_2 gas flow rate was maintained as 10 sccm. The formation of gaseous products was analyzed by Gas chromatography (GC) equipped with TCD and FID detectors. The liquid product formation in the electrolyte was authenticated by NMR analysis using D₂O and DMSO as the solvent and internal reference.

Faradaic efficiency (FE) calculation

The following equation calculated the FE for CO2RR

$$\eta = \frac{2nF}{Q} \times 100\%$$

Here, n - moles of the product; F- Faradaic constant (96485); Q- total charge passed through the system; 2 means the electron required for CO_2 to CO reduction

Fabrication of RuO_x layer for OER

The RuO_x-deposited Ti-foil was fabricated by the atomic layer deposition (ALD) technique (Oxford Instrument Plasma-ALD system). Firstly, 0.05 mm thin Ti-foil was sonicated to remove surface impurities and washed by isopropyl alcohol and deionized water. Then, the cleaned Ti-foil was securely fixed in the ALD chamber and vacuum-sealed. To deposit 25 nm of RuOx, the bis(ethylcyclopentadieny)ruthenium (II) (Ru(EtCp)₂ was used as the ALD precursor. Subsequently, Ru (EtCp)₂, Ar, and O₂ were deposited in the pulse cycle at 1, 10, and 5 sec, respectively. The temperature was fixed at 200 °C throughout the deposition process.

Ge/InGaAs/InGaP triple junction photoelectrode fabrication

The PEC device for CO_2RR was fabricated by taking the lead from the top surface of Ge/InGaAs/InGaP using a Cu strip and silver paste. The cell area was maintained to be 1 cm² in the electrolyte. Ga-In eutectic was used to achieve efficient ohmic contact, and the cell was covered with epoxy (Loctite Hysol 1 C) resin. Then, the out-contact Cu strip was threaded through

a glass tube, and the front surface was covered with a glass slide to avoid a short circuit in the electrolyte. RuOx-deposited (25 nm) thin Ti-foil (0.05 mm) was integrated on the cell's back side to protect the cell surface and drive a water oxidation reaction. Using thin Ti foil can increase carrier transport at semiconductor/electrolyte interfaces by changing the oxidation states.

Photoelectrochemical (PEC) CO₂ RR

The PEC CO₂RR was conducted in the H-type cell, separated by the BPM. The InGaP/GaAs/Ge/Ti thin foil/RuO_x photoelectrode was used as a photoabsorber as well as an anode. At the same time, Ox-Au nanostructures were used as the cathode for CO₂ to CO reduction. The anode and cathode sides were filled with 1 M KOH and 0.2 M KHCO₃ for water oxidation and CO₂ to CO reduction. Xe arc lamp (ABET Technologies) with AM 1.5 and IR filter is utilized as an illumination source for all PEC measurements. Moreover, the anolyte evaporation during the stability experiment was mitigated by regular refilling every five hours of the reaction. The formed products were analyzed by GC and NMR instrumentations.

Solar to fuel conversion efficiency (STF)

The solar conversion efficiency (Π) was calculated as per the below equation:

$$\eta_{\text{STF}} = \frac{J_{op} \times [1.23 \text{ V} - E^{\circ}] \times FE\%}{100 \text{ mW.cm}^{-2}}$$

 J_{op} operation current°; the thermodynamic potential of a selected product, *FE*; Faradaic efficiency. For our photoanode system, the calculation is as follows.

Here, the operating current density $(J_{op}) = 11.5 \text{ mA}$

Faradaic Efficiency of CO (FE) = 98%

The thermodynamic potential of CO product $(E^{\circ}) = (-0.11 \text{ V})$

Solar power = 100 mW.cm^2

$$\eta_{STF} = \frac{11.5 \text{ mA cm}^{-2} \times [1.34 \text{ V}] \times 98\%}{100 \text{ mW.cm}^{-2}} = 15.1\%$$

Solar to CO efficiency at 10 suns illumination

Here, the operating current density $(J_{op}) = 124 \text{ mA/cm}^2$

Faradaic Efficiency of CO (FE) = 60%

The thermodynamic potential of CO product $(E^{\circ}) = (-0.11 \text{ V})$

Solar power = $10 \times 100 \text{ mW.cm}^2$



Figure S1. Schematic design of H-cell with bipolar membrane (BPM) used reactor for CO_2 reduction experiment. The BPM was used to match the required potential for unassisted CO2RR under different pH conditions independently.



Figure S2: Stability measurements of electrocatalyst measure at -1.0 V vs. RHE throughout 30 h. Overall 80% of the total current is retained during the measurements.



Figure S3. Schematic representation of CO₂ reduction to CO pathway



Figure S4: The X-ray diffraction pattern (XRD) of Au-foil and Ox-Au.



Figure S5: The scanning electron microscopy (SEM) images of (a) Au-foil (scale bar: $1 \mu m$) and (b, c) Ox-Au (scale bar: $1 \mu m$ and 100 nm).



Figure S6: XPS survey scans of (a) of Ox-Au and (b) after 25 h of electrochemical CO_2RR . The survey scan shows Au, oxygen, and carbon peaks, confirming a clean surface with no external contamination within the detection limits of XPS.



Figure S7: (a) schematic design of bipolar membrane used reactor for CO₂ reduction experiment,
(b) bipolar membrane characteristics under different electrolyte conditions. The membrane potential was studied by the tri-potentiostat method as reported in the literature¹.



Figure S8: Photograph of PEC reactor for CO₂ reduction reaction.



Front side (Illumination side)

Back side (OER side)

Figure S9: Photo of fabricated TJ solar photoanode using epoxy resin, Cu strip, and a glass tube for PEC CO₂ RR reaction.



Figure S10: (a) Single injection in-line chromatography data corresponding to the solar-driven CO_2RR measured at a two-electrode setup by short-circuiting the TJ (InGaP/GaAs/Ge/Ti/RuOx) photoanode and Ox-Au cathode in an H-cell reactor, separated by a BPM membrane with CO_2 saturated 0.5M KHCO₃ catholyte and 0.5M KOH anolyte. (b) Time-dependent CO production rate.



Figure S11: Concentrated sunlight-driven CO_2RR measured in a 3-electrode setup at 0 V vs. RHE. Here we have used a 3-electrode setup due to the higher overpotentials associated with the higher



J_{tot} in RuOx-based OER catalyst.

Figure S12: 1H NMR spectra data corresponding to the solar-driven CO₂RR measured at a twoelectrode setup by short-circuiting the TJ (InGaP/GaAs/Ge/Ti/RuOx) photoanode and Ox-Au.



Figure S13. The XRD and SEM I image of the Ox-Au catalyst after CO₂RR. (scale bar: 100 nm)

Table S1. Photoanode promoted CO₂ RR and its solar-to-fuel (STF) conversion efficiency comparison.

This comparison table includes PEC and PV-EC of two and three-electrode systems.

	Cathod		Current density	nt density		
Photoanode	e	Products	(mA.cm ⁻²)	FE (%)	STF (%)	Stability (h)
GaAs/InGaP ^a	Pd-C	HCOO-	8.5	94	10	32
III-V 4-Junction	Au	CO+H ₂	12	90	7	33
III-V 3-Junction	Au	CO+H ₂	12	94	15	174
a-SiGe 3-Junction	p- RuCP	HCOO-	1	93	4.6	6 ⁵
$Cu(In_xGa_{1-x})(SySe_{1-y})_2$	Au	CO	7.3	90	4.2	NA ⁶
3-Junction a-Si	Au	СО	1.5	95	2.0	27
Si IrOx	In-Cu	HCOO-	2.5-3.1	67	1.8	1.58
GaN/Si	Cu	HCOO-	1.58	35	0.046	19
Si NiFeZn	Cu-S	HCOO-	17.3	59.7	6.2	1010
3-jn-SiGe IrOx	RuCP	HCOO-	7.0	93	4.6	611
c-Si IrOx	RuCP	HCOO-	7.42	96.1	10.5	10 ¹²
InGaP/GaAs/Ge/Ni- RuOx	Ox-Au	СО	11.5	98	15	25 (This work)

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III-V 4-Junction	Au	CO+H ₂	12	90	7	3 ³
III-V 3-Junction	Au	CO+H ₂	12	94	15	174
a-SiGe 3-Junction	p- RuCP	HCOO ⁻	1	93	4.6	65
$Cu(In_xGa_{1-x})(SySe_{1-y})_2$	Au	СО	7.3	90	4.2	NA ⁶
3-Junction a-Si	Au	СО	1.5	95	2.0	27
Si IrOx	In-Cu	HCOO-	2.5-3.1	67	1.8	1.58
GaN/Si	Cu	HCOO-	1.58	35	0.046	19
Si NiFeZn	Cu-S	HCOO-	17.3	59.7	6.2	10 ¹⁰
3-jn-SiGe IrOx	RuCP	HCOO ⁻	7.0	93	4.6	611
c-Si IrOx	RuCP	HCOO ⁻	7.42	96.1	10.5	10 ¹²
InGaP/GaAs/Ge/Ni- RuOx	Ox-Au	CO	11.5	98	15	25 (This work)