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Theoretical efficiency limits of photoelectrochemical CO₂ reduction: A route-dependent thermodynamic analysis

Evangelos Kalamaras^[a], Huizhi Wang^[b], M. Mercedes Maroto-Valer^[a], John M. Andresen^{*,[a]} and Jin Xuan^{*,[c]}

Abstract: Solar fuel formation via photoelectrochemical (PEC) routes using water and CO₂ as feedstock has attracted much attention. Most PEC CO₂ reduction studies have been focused on the development of novel photoactive materials; however, there is still a lack of understanding of the key limiting factors of this process. In this study, the theoretical limits of Solar-to-Fuel (STF) efficiencies of single- and dual-junction photo-absorbing materials are illustrated for single-step multi-electron CO₂ reduction into fuels including HCOO⁻, CO, CH₃OH and C₂H₅OH. It is also highlighted that STF efficiency depends on the route of two-step PEC CO₂ reduction process using CH₃OH as a model fuel. Finally, it is illustrated the beneficial role of alternative strategies such as dual-junction photo-absorbing electrodes, externally applied bias and subsequent reactor chambers on the maximum theoretical efficiencies of PEC CO₂ reduction.

Introduction

The production of renewable fuels from CO₂ using sunlight as energy source is considered as a very promising energy generation technology enabling storage of solar energy into chemical form.^[1] Hydrocarbon fuels generated through this approach are known as solar fuels.^[2] The interest in using photoelectrochemical (PEC) devices for solar fuel generation has significantly increased over the last two decades, as PEC systems rely on the synergy of solar energy and external bias combining the advantages of both electrochemical and photocatalytic processes.^[3] So far, most studies in PEC systems have been focused on water-splitting

reaction,^[4] yet the PEC cells for CO₂ conversion are getting more attention because they can produce hydrocarbons which is more adaptable to existing fuel infrastructures while reduce CO₂ at the same time.^[5]

Fundamentally, the operation of a PEC cell for CO₂ reduction is based on photo-absorbing materials that convert incident photons, with energy equal to or greater than the width of its band gap, into electron-hole pairs. Then, photogenerated electron-hole pairs on the surface of the photo-absorbing material drive the water oxidation^[6] and CO₂ reduction half-cell reactions^[3b]. Although a large number of experimental studies has been conducted since Halmann^[7] first demonstrated the PEC CO₂ conversion into several products, theoretical STF efficiency limits for different solar fuel products has not been extensively analyzed. Finding the maximum theoretical STF efficiencies is of great importance to evaluate the PEC CO₂ reduction experimental data and assess the technological viability of PEC prototype devices. As evidenced by the photovoltaic (PV) counterparts when Shockley and Queisser in 1961 calculated theoretical efficiency limits of PV devices as a function of the semiconductor band gap, a thermodynamic analysis can be used to address such a challenge.^[8] Similar to PV devices, band gap of photo-absorbing material is the most important factor in thermodynamic efficiency limits of PEC cells. The optimal band gap of a semiconducting photo-absorber for CO₂ reduction should maximize the PEC efficiency and simultaneously minimize optical losses of the absorbance of solar light.^[9] Therefore, 'mapping' thermodynamic efficiency limits using an analogous strategy for CO₂ reduction in PEC cells can provide guidance for the development of very efficient photoelectrodes.

So far, a lot of research groups have developed modelling tools for estimation of thermodynamic limitations of PEC water splitting systems,^[6a, 10] while only a few studies have been focused on estimation of PEC CO₂ reduction theoretical efficiencies.^[11] PEC cells for CO₂ reduction and water splitting and CO₂ reduction share the same working principles, however, the former systems face a lot of challenges including limited solubility of CO₂ in liquid solutions and complexity of multi-electron reactions occur on the surface of the electrodes.^[5b, 12] These are the main reasons that PEC hydrogen generation demonstrator devices have shown significantly higher STF efficiency in laboratory scale than that of PEC CO₂ conversion devices. Specifically, the highest ever recorded STF efficiency for PEC water splitting reached 19%^[13] while only 1.2% STF efficiency is the highest ever obtained STF efficiency for PEC CO₂ reduction devices.^[14] On the other hand, thermodynamic studies have illustrated comparable maximum STF efficiencies for both PEC processes.^[9, 11, 15]

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Electronic Supplementary Information (ESI) available: Tables of assumptions, input parameters and standard potentials for half-cell electrochemical reactions, Figure of maximum theoretical STF efficiency vs band gap of several commonly used semiconducting materials, Tables with route-dependent half-cell reactions and calculated electrochemical potentials.

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The formation of intermediate chemicals prior to final products is a plausible scenario^[16] that can explain the significantly lower observed STF efficiency in experimental studies than that of theoretical studies. So far, many experimental PEC CO₂ reduction reports have presented formation of a mixture of products,^[16a, 17] indicating that multi-step CO₂ reduction is a realistic approach. Therefore, a route-dependent analysis is necessary to 'map' maximum theoretical efficiency of multi-step PEC CO₂ conversion into fuels assessing future economical sustainability of such devices.

In this study, a thermodynamic efficiency on route-dependent CO₂ thermodynamic analysis is illustrated, highlighting the efficiency limits of multi-step PEC CO₂ reduction. This thermodynamic analysis investigated for the first time the effect of intermediate product formation prior to final products on maximum theoretical efficiencies of CO₂ reduction highlighting the importance of reaction route and reactor design. Finally, we illustrated the beneficial role of alternative strategies such as dual-junction photo-absorbers, subsequent reactor chambers and externally applied bias on the maximum theoretical efficiencies of PEC cells for CO₂ reduction.

Results and Discussion

Single-step PEC CO₂ reduction

Maximum theoretical STF efficiencies of a single-junction photo-absorber (Figure 1a) electrode were estimated for CO₂ conversion into several possible products such as C1, C2 and C3 hydrocarbons (Equations 1-6). Here, PEC CO₂ reduction was considered as a single-step multi-electron transfer process without any intermediate fuel production.

The products that require low thermodynamic potential achieved higher maximum theoretical STF efficiency at smaller band gap values.^[18] Specifically, Figure 1b illustrates maximum theoretical STF efficiencies of several products under ideal standard conditions (Table S1) reached 17.9 % at 2.00 eV for HCOOH, 19.4 % at 1.92 eV for CO, 21.2 % at 1.80 eV for CH₃OH, 22.3 % at 1.68 eV for CH₄, 22.2 % at 1.72 eV for C₂H₆, 21.9 % at 1.76 eV for C₂H₅OH and C₂H₄ and 22 % at 1.76 eV for C₂H₆O and C₃H₈O.

The curve of each product illustrates a peak (maximum theoretical STF efficiency) at different band gap values because a different electrochemical potential is required for the performance of each reduction reaction. If the electrochemical potential needed for CO₂ reduction is low, a photo-absorber with low band gap can be used leading to generation of high photocurrents. As illustrated in Equation 4, PEC devices with high photocurrents result in high STF efficiency and therefore high CO₂ conversion rates. PEC conversion of CO₂ into CH₄ presented the highest theoretical efficiency because this reaction requires the lowest electrochemical potential (1.06 V) among all investigated products. On the other hand, HCOOH, that requires the highest thermodynamic potential (1.43 V), achieved the lowest optimal overall efficiency. In addition, it was illustrated that semiconductors with band gap lower than 1.40 eV cannot drive PEC CO₂ reduction. Even for the case of CO₂ reduction to CH₄, only photo-absorbers that possess a band gap higher than 1.42 eV enable such a reaction.

Figure S1 shows a screening of several potential candidate materials with conduction band and valence band that straddle the electrochemical potentials of both CO₂ reduction and water oxidation reactions (Table S4). Comparing STF efficiency of materials with different band gap, it was observed that materials with a range between 1.9 eV to 2.1 eV shown the best performance for

Figure 1. Schematic illustration of a single photo-absorber PEC cell. b) Maximum theoretical STF efficiency vs band gap for a single multi-electron transfer step of CO₂ reduction into several fuels.

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photoelectrosynthesis of all different fuels. Photo-absorbing materials with band gap higher than 2.8 eV such as TiO_2 achieved very low STF efficiency for CO_2 conversion into fuels. Another interesting finding is that semiconducting materials with a band gap of 1.5 eV such as CuInS_2 theoretically allows CO_2 conversion into CH_4 and C_2H_6 . However, experimental studies have reported that PEC CO_2 reduction occurs only on photo-absorbing materials with a band gap equal to or higher than 1.8 eV due to the presence of overpotential losses.^[19]

Route-dependent PEC CO_2 reduction to CH_3OH

In this section, we attempt to explore the viability of a multi-step PEC CO_2 conversion route into fuels with high energy density such as CH_3OH from a thermodynamic point of view. With insights into PEC CO_2 reduction pathway as a guiding principle for photo-absorber design, Figure 2a shows different proposed routes and Figures 2b-d illustrate the optimal band gap of photo-absorbing materials for one-step and several two-step multi-electron routes for PEC CO_2 conversion into CH_3OH .

For the conversion of CO_2 into $\text{CO}_2^{\cdot-}$,^[20] an electrochemical potential of 2.72 V is required. This is possible only if the semiconducting photocatalyst has an energy band gap greater than 3.3 eV as illustrated in Figure 2b. Additionally, this step can be achieved on a photocatalyst only if its conduction band edge is more negative than the $\text{CO}_2/\text{CO}_2^{\cdot-}$ redox potential, while at the same time, its valence band edge is located lower than the standard redox potential of water oxidation to O_2 . However, the most common semiconducting photocatalysts in CO_2 reduction literature do not satisfy these criteria.^[20b, 21] Therefore, from thermodynamics point of view the formation of $\text{CO}_2^{\cdot-}$ as an intermediate product of CO_2 conversion is a questionable step and needs further investigation for the clarification of this reaction route.^[3a] On the other hand, formation of both HCOO^- and CO via a 2-electron step CO_2 reduction reaction presented significantly higher maximum theoretical STF efficiency than that of $\text{CO}_2^{\cdot-}$ case because lower electrochemical potential is needed. More specific, maximum theoretical STF efficiency reached 18.9 % and 16.1% for CO and HCOO^- respectively (Figure 2b). PEC conversion of CO_2 into CO shown higher maximum theoretical STF efficiency

Figure 2. a) Plausible pathways for PEC CO_2 reduction. b) Maximum theoretical STF efficiency vs band gap for CO_2 reduction for three proposed intermediates, HCOO^- (blue line), CO (black line) and $\text{CO}_2^{\cdot-}$ (red line). c) Maximum theoretical STF efficiency vs band gap via further reduction of intermediates (HCOO^- and CO) into CH_3OH d) Comparison of single-step CO_2 conversion to CH_3OH (green line) with two-step CO_2 conversion to CH_3OH following HCOO^- and CO pathways.

As illustrated in Figure 2c, 4-electron step of HCOO^- reduction to CH_3OH illustrated theoretical STF efficiency of 23.8 % for a photo-absorber with 1.56 eV band gap which is higher than that of 4-electron step of CO reduction to CH_3OH . Specifically, maximum STF of CO conversion into CH_3OH reached 22 % for a photo-absorber with band gap of 1.84 eV. Maximum theoretical STF efficiency of single-step CO_2 conversion to CH_3OH was compared to two-step CO_2 conversion into CH_3OH following HCOO^- and CO pathways as shown in figure 2d. Maximum theoretical STF efficiency of 2% were recorded for CH_3OH formation via HCOO^- route ($\text{CO}_2 \rightarrow \text{HCOO}^- \rightarrow \text{CH}_3\text{OH}$) for a photo-absorber of 1.84 eV. On the other hand, the maximum theoretical STF efficiency of the 2-step PEC process following CO route ($\text{CO}_2 \rightarrow \text{CO} \rightarrow$

Improving the maximum theoretical STF efficiency with dual-junction photo-absorber

As shown in Figures 3a-b, a strategy to enhance the efficiency of PEC cells is the utilization of photoelectrodes consisting of two photo-absorbers with different band gaps for

Figure 3. a) Schematic illustration of photon absorption on a single and dual-junction photo-absorber. b) Schematic illustration of a dual-junction photo-absorber PEC cell approach. Maximum theoretical STF efficiency vs band gap for CO₂ reduction into c) HCOOH, d) CH₃OH e) CH₄ f) C₂H₅OH or C₂H₄ g) C₂H₆ f) and h) C₂H₆O or C₃H₈O on dual-junction photo-absorber.

extended light absorption. For all cases, the optimal combination of a dual-junction configuration (Figures 3c-h) illustrated a much higher maximum theoretical STF efficiency than that of the optimal single photo-absorber system (Figure 1b). In other words, higher efficiencies can be achieved with a dual-photo-absorber configuration, in which each photocatalyst absorbs a different part of the solar spectrum. This study was confined to single and dual-junction photo-absorbers because the addition of more than two junctions have not led to increased theoretical efficiencies for either water splitting or CO₂ reduction.^[11a, 19, 22] So far, modelling studies have shown that dual-junction photo-absorbers are more efficient than triple-junction photo-absorbers for electrochemical reactions that require a thermodynamic potential lower than 1.5 V.^[11a, 19] The dual photo-absorber system works in series by connecting the wide band gap and low band gap photo-absorbing materials enabling a higher total voltage at the expense of current density which is a crucial factor for STF efficiencies, as presented in Equation 4.

All contour plots present a sharp turn-on of maximum theoretical STF efficiency for band gaps just large enough to provide the CO₂ reduction potential and a gradual decline of efficiency beyond that peak due to decreased light absorption. In the case of CH₃OH, the maximum STF efficiency of 30.3 % is obtained with top and bottom photo-absorber's band gaps of 1.48 eV and 0.76 eV, respectively. A similar behaviour was also observed for CO₂ conversion into both C₂H₅OH and C₃H₆O due to the fact that the required electrochemical potential is 1.15 V and 1.13 V, respectively.

On the other hand, CO₂ conversion to HCOOH requires a much higher electrochemical potential of 1.43 V which allow a larger increase of STF efficiency using a dual-junction photo-absorber in comparison with that observed in the case of a single photo-absorber. Specifically, the maximum STF efficiency was 32.2% with top and bottom photo-absorber's band gaps of 1.6 eV and 0.95 eV, respectively. Apart from the highest value, the dark red area which represents STF efficiency higher than 30% is significantly larger in the case of HCOOH than that of the other fuels. This is an indication that a dual-junction photo-absorber has an increased impact on a reaction that requires a higher electrochemical potential.^[19]

It is also interesting to observe that the maximum theoretical efficiency for CO₂ into all investigated fuels shown that top photo-absorber has a larger band gap (e.g. 1.5 eV) than the bottom photo-absorber (e.g. 0.8 eV). The main reason is that photoactive materials can absorb photons of energy equal to or greater than the band gap energy, while photons with lower energy than the energy band gap of the photo-

absorbing material interact only weakly with the material passing through it (Figure 3a). Finally, it is highlighted that semiconductors with band gap between 0.6 and 0.8 eV can significantly increase the efficiency of a dual-junction photo-absorbing systems. Therefore, an interesting strategy for future research is the utilization of narrow band gap semiconductors as bottom photo-absorbers.

Externally applied bias for PEC CO₂ reduction

Application of external bias is necessary to enable PEC CO₂ reduction on photo-absorbers with narrow band. Figure 4 a-b shows a comparison of the maximum theoretical STF efficiency and n_{bias} (Equations 4 and 7) for PEC CO₂ reduction into CO and CH₃OH. For CO production (Figure 4a), maximum theoretical STF efficiency (without external applied bias) shown a similar behaviour with that of n_{bias} efficiency (with external applied bias) for photo-absorbers with a band gap greater than 1.9 eV. However, for single photo-absorbers with a band gap lower than 1.9 eV, it was calculated a significantly higher n_{bias} than maximum theoretical STF efficiency with a peak efficiency of 23.6% at 1.40 eV. A similar behaviour of n_{bias} was obtained for different products including CH₃OH (Figure 4b). This behaviour is highly related to the web-based model principles dictating

Figure 4. Maximum theoretical n_{bias} STF efficiency vs band gap for single multi-electron transfer of CO₂ reduction into a) CO b) CH₃OH with (red line) and without (black colour) external bias. Maximum theoretical (n_{bias}) STF efficiency vs band gap of dual-junction photo-absorbers for single multi-electron transfer of CO₂ reduction into c) CO and d) CH₃OH.

that external voltage is applied only when the photo-absorber cannot offer the necessary photovoltage to drive the desired electrochemical reaction.

As illustrated in Figures 4a-b, n_{bias} was drastically decreased for single photo-absorbers with narrow band gap (<1.30 eV). In the case of narrow band gap photo-absorbing materials, a large external applied voltage is needed to satisfy thermodynamic requirements of PEC CO_2 reduction leading to lower n_{bias} according to Equation 7. Therefore, if the photovoltage is not enough to drive PEC CO_2 reduction, external applied voltage is playing a beneficial role only for single photo-absorbers with band gap between 1.4 and 1.6 eV. In addition, as illustrated in Figures 4c-d, n_{bias} was significantly higher for the case of dual-junction photo-absorbers exceeding 30 % for CO_2 conversion into CO and CH_3OH . A PV module connected directly to a PEC cell can provide the required additional voltage comprising a promising hybrid solar-driven configuration (PV-PEC)^[23] for sustainable CO_2 reduction. As illustrated in Figures 4c-d, n_{bias}

illustrated an irregular profile for top photo-absorbers with band gap between 1.5 and 1.7 eV. In this band gap region, the web-based model allows the application of external voltage for the top photo-absorber which is leading to an increase of the total n_{bias} . It should also be mentioned that chosen theoretical approach of the program for the dual-junction case simply calculates a j-V curve for top and bottom photo-absorbers and the maximum photocurrent for the device is limited by whichever photo-absorber has the lowest maximum photocurrent. This maximum photocurrent is used to provide STF efficiency and n_{bias} .

A PEC reactor with two subsequent chambers using photoelectrodes with different band gaps

A reactor with two subsequent chambers offers the possibility to run each multi-electron step of CO_2 reduction process on two different photocatalysts as presented in Figure 5a. In addition, a comparison of maximum theoretical

Figure 5. a) Two subsequent chamber PEC reactor approach that allows to run each multi-electron step in different photo-absorbers. (Half reduction and oxidation reactions from Tables S5 and S6 were used to calculate maximum theoretical STF efficiency vs the energy gap of a single photocatalyst). Comparison of single and dual-junction photo-absorber approach b) for single-step CO_2 conversion to CH_3OH (green colour) and c) two-step CO_2 conversion to CH_3OH via CO pathway in a two subsequent chamber PEC reactor with (red colour) and without (black colour) external bias using optimal photo-absorbers.

STF efficiencies between a single-step (Figure 5b) and two-step (Figure 5c) CO₂ conversion into CH₃OH is illustrated for optimal single- and dual-junction photo-absorber cases. Maximum theoretical STF efficiency for optimal single photo-absorber system was 21.2 %, while for two-step CO₂ reduction via CO (Figure 5c) pathway a two subsequent PEC reactor approach achieved maximum theoretical STF efficiency of 4.3 %.

Utilization of dual-junction photoelectrodes in a two-chamber PEC reactor approach increased maximum theoretical STF efficiency reaching 8.9 % for CO pathway as shown in Figure 5c. In other words, optimal dual-junction photo-absorbers for both reduction steps, CO₂ reduction into CO followed by CO reduction into CH₃OH, led to an increase of more than 100 % underlining the importance of reactor design on the performance limits of PEC systems. Application of external bias further increase the maximum theoretical η_{bias} of the optimal dual-junction dual-chamber PEC system achieving 9.2 %. Although this optimized strategy achieved high efficiencies for two-step PEC CO₂ reduction route, theoretical efficiency levels were below 10 % indicating that such devices are far from becoming commercially viable. For this reason, alternative strategies should be used in combination with two-chamber reactor approach in order to further improve the theoretical efficiency limits of two-step PEC CO₂ reduction process.

Conclusions

The main goal of this research study was to provide an insight of the performance limits on single or multi-step highly endothermic CO₂ reduction into several fuels. It was found that single-junction photo-absorbers with band gap lower than 1.40 eV are not able to provide the required total cell voltage for single-step PEC CO₂ reduction while photo-absorbing materials with a range between 1.9 eV to 2.1 eV obtained the highest STF efficiency for single-step CO₂ conversion into most of the fuels. However, photo-absorbers with narrow band gap can drive PEC CO₂ conversion into fuels with the aid of an external applied bias. Furthermore, it was emphasized that STF efficiency highly depends on CO₂ reduction route. Using CO₂ conversion into CH₃OH as case study, a single-step reduction route achieved significantly higher maximum theoretical STF efficiency than a two-step reduction route. It was also illustrated that application of additional voltage can increase maximum theoretical efficiency of single photo-absorbers with band gap between 1.4 and 1.6 eV. Finally, combination of strategies such as dual-junction photo-absorbers with complementary light absorption, external applied voltage and dual-chamber PEC reactors with different dual-junction photoelectrodes led to a much higher maximum theoretical STF efficiencies than that of the single photo-absorber systems providing a plausible direction for future development of new heterogeneous CO₂ photocatalysts and PEC reactors.

Methods

Analytical model for PEC efficiency

A photocatalytic reaction is possible only if the potential provided by the photo-absorbing material, E_{PEC} , is equal to or greater than the thermodynamic potential, E_{Therm} , plus any other losses. The following equation governs any photoelectrochemical reaction:^[10a, 22, 24]

$$\sum_i^n E_{PEC}(j) \geq E_{Therm} + \eta_{Red}(j) + \eta_{Ox}(j) + E_{Ionic,Res}(j) + E_{Elec,Res}(j) - E_{Bias}(j) \quad (1)$$

where E_{PEC} is the potential provided by the photo-absorbing material, n is the number of photo-absorbers, j is the current density (A cm⁻²), η_{Red} is the reduction overpotential (V), η_{Ox} is the oxidation overpotential (V), $E_{Ionic,Res}$ is the losses related to ionic resistance (V), $E_{Elec,Res}$ is the losses related to electric resistance (V), and E_{Bias} represents external bias that can be applied (V). Thus, n was equal to one for a single-junction photo-absorber, while n was equal to two for a dual-junction photo-absorber. To simulate the thermodynamic behaviour of semiconductor-liquid junction cells the calculation of photovoltage based on diode equation. Specifically, photodiode voltage is calculated as a function of current using the following two equations:

$$j = j_{Limit} - j_0 \times \left(\exp \left(\frac{q(V + j\Omega_{Series})}{kT} \right) - 1 \right) - \left(\frac{V + j\Omega_{Series}}{\Omega_{Shunt}} \right) \quad (2)$$

where j_0 is defined as:

$$j_0 = M_{user} \times qA \frac{2kT}{h^3 c^2} \times (E_g^2 + 2kTE_g + (kT)^2) \times \exp \left(\frac{-E_g}{kT} \right) \quad (3)$$

where j_{Limit} represents the maximum theoretical photocurrent for a given amount of absorbed photons (mA cm⁻²), j_0 is the dark saturation current density (mA cm⁻²), q is equal to elementary charge (1.60218 × 10⁻¹⁹ C), V is the photovoltage (V), Ω_{Series} and Ω_{Shunt} represent the series and the shunt resistance respectively (Ohm cm⁻²), M_{user} represents a factor equal to multiple of the minimum theoretical dark saturation current, A is an indicator of the number of the emitted surfaces of a material ($A=2$ for a material because it has two sides), k is the known Boltzmann's constant (8.61733 × 10⁻⁵ eV K⁻¹), T is the temperature (K), h is the constant of Planck (4.13567 × 10⁻¹⁵ eV s), c is the speed of light (3 × 10⁸ m s⁻¹) and E_g is the band gap (eV). To sum up, the overall electrochemical reaction occurs only when the PEC voltage is greater than or equal to the potential needed to drive half-cell reduction and oxidation reactions, as presented in Eq. 1. This means that maximum efficiency takes place when E_{PEC} is equal to the required electrochemical potential for the desired chemical reaction because this leads to maximum current density, j_{max} , of PEC device. As it can be clearly seen from the following equation, j_{max} is proportional to the STF efficiency:^[19, 25]

$$STF(E_g) = \frac{j_{max} \times E_{Therm} \times FE}{P_{in}} \times 100\% \quad (4)$$

STF represents the total chemical energy produced at a given band gap (E_g) divided by the incident solar power density. FE is the faradaic efficiency and it can be calculated as follows:^[26]

$$FE = \frac{e_{out}}{e_{input}} \times 100\% \quad (5)$$

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where i_{output} is the current contributing to CO_2 conversion into chemical fuels and i_{input} is the produced current of PEC device. In addition, P_{in} for illumination of solar light with AM 1.5 G spectrum is derived from the following equation:^[25, 27]

$$P_{\text{in}} = q \times \int_0^{\infty} \text{AM 1.5G}(E) dE \quad (6)$$

Efficiency for PEC devices that require an external bias to drive electrochemical reactions differ from STF efficiency and it is defined by the following equation^[19]:

$$\eta_{\text{bias}}(E_g) = \text{STF}(E_g) = \frac{j_{\text{max}} \times (E_{\text{Therm}} - E_{\text{Bias}}) \times FE}{P_{\text{in}}} \times 100\% \quad (7)$$

where E_{bias} is the external bias applied to PEC cell. All the calculations were performed using a web-based modelling tool.^[28] In all cases, theoretical STF efficiency limits obtained from Equation 4 using the maximum current density that achieved for the optimized band gap. For route-dependent calculations the same tool was used taking into account the assumption that initial reaction ($\text{CO}_2 \rightarrow$ intermediate product) occur on the irradiated active sites of the photocatalyst and subsequently the second step of the reaction (intermediate product $\rightarrow$ final product) should take place after the complete conversion of CO_2 into intermediate product. In addition, it was assumed that all incident photons above the band gap of photoactive material were absorbed. Furthermore, reduction and oxidation overpotentials losses were set as negligible which mathematically means infinite catalytic exchange current densities. This assumption implies that ideal catalysts with very high catalytic exchange current densities and high-surface area were used to model catalytic overpotentials. All standard conditions and parameters are summarized in Table S1.

Route-dependent model

In Table S2, a large variety of half-reactions related to CO_2 reduction and water splitting is presented. Thermodynamically, converting CO_2 into CH_3OH requires an electrochemical potential of 1.21 V. However, the reduction process can be broken up into several steps via formation of intermediate products such as $\text{CO}_2^{\cdot-}$, CO and HCOO^- (Table S3). So far, several mechanisms have been proposed and investigated in experimental and computational CO_2 reduction studies.^[12a, 29] Although there are still controversies regarding the mechanisms of CO_2 reduction into alcohols, the formation of the following three routes has been mainly proposed in the literature. The initial single or 2-electron steps and several possible pathways are shown in Scheme S3.

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Based on theoretical calculations, we determined maximum STF efficiencies of PEC CO_2 reduction examining different reaction routes and different cell configurations. Utilization of different strategies such as dual-junction photo-absorbers, external applied voltage and dual-chamber PEC reactor led to a much higher theoretical STF efficiencies.

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Theoretical efficiency limits of photoelectrochemical CO_2 reduction: A route-dependent thermodynamic analysis