Solar-driven methanogenesis with ultrahigh selectivity by turning down H₂ production at biotic-abiotic interface

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Integration of methanogens with semiconductors is an effective approach to sustainable solar-driven methanogenesis. However, the H₂ production rate by semiconductors largely exceeds that of methanogen metabolism, resulting in abundant H₂ as side product. Here, we report that binary metallic active sites (namely, NiCu alloys) are incorporated into the interface between CdS semiconductors and Methanosarcina barkeri. The self-assembled Methanosarcina barkeri-NiCu@CdS exhibits nearly 100% CH₄ selectivity with a quantum yield of 12.41 ± 0.16% under light illumination, which not only exceeds the reported biotic-abiotic hybrid systems but also is superior to most photocatalytic systems. Further investigation reveal that the Ni-Cu-Cu hollow sites in NiCu alloys can directly supply hydrogen atoms and electrons through photocatalysis to the Methanosarcina barkeri for methanogenesis via both extracellular and intracellular hydrogen cycles, effectively turning down the H₂ production. This work provides important insights into the biotic-abiotic hybrid interface, and offers an avenue for engineering the methanogenesis process.

Effective conversion of carbon dioxide (CO₂) to value-added low-carbon biofuels is an important strategy for alleviating energy shortages and offsetting global carbon emissions via industrial CO₂ capture that displaces fossil fuel or natural gas use¹. It is estimated that over 0.5 gigatonnes of CO₂ can be utilized annually via the CO₂-to-fuel pathway and the value increases every year, which significantly improves the CO₂ emission-reduction potential globally with the significant technological and societal importance²–⁵. Elegant advances have achieved for CO₂ reduction via biocatalytic, electrocatalytic and photocatalytic approaches; however, these processes still face formidable challenges, mainly related to the limited solubility of electron carriers in water, low catalyst activity and product selectivity, and high energy barriers for reactions³–⁵. The limitations become more prominent when methane (CH₄), which has a high calorific value of 890 kJ mol⁻¹ and can be integrated into the existing energy infrastructure, is chosen as the target product⁶. The conversion of CO₂ to CH₄ is a kinetically complex and energetically intensive process that involves multiple proton-coupled electron transfer steps and requires to finely tune activation energy for promoting the forward reaction⁷. Solar-driven CO₂-to-CH₄ conversion is an ideal approach in terms of energy input, and yet is largely limited by unsatisfactory reaction activity and product selectivity.

Biotic-abiotic hybrid systems, which have been developed by integrating biological whole-cell bacteria with man-made semiconductor materials in recent years, offer new opportunities for the solar-driven CO₂-to-CH₄ conversion by taking advantage of both photocatalysis and biocatalysis⁸–¹³. In a typical hybrid system, methanogens can sustainably harness the reducing equivalents from biocompatible semiconductors with broadband light harvesting efficiency to realize effective solar-driven CO₂-to-CH₄ conversion¹². In most cases, the electron transfer and utilization across the biotic-abiotic interface govern the methanogenesis performance¹⁴.
Nevertheless, it is worth pointing out that direct interspecies electron transfer (DIET) is not the exclusive process for supplying reducing equivalents. H$_2$ is a preferred reducing equivalent that dominates the electron transport chain in biotic-abiotic hybrid systems at large timescales and conserves substantially more energy in CO$_2$-to-CH$_4$ conversion$^{15,16}$. Photocatalysis by the semiconductor materials can generate H$_2$ from water medium, providing the H$_2$ reducing equivalents for methanogens. However, high energy conservation can only be achieved at the compensation of high H$_2$ threshold concentration, particularly for methanogens with cytochromes such as Methanosaeta barkeri (M. b)$^{17}$. The metabolism of methanogens becomes significantly slower near the H$_2$ threshold concentration$^{18}$, whose rate would be substantially lower than that of H$_2$ production from photocatalysis. This circumstance inevitably leaves abundant H$_2$ in the system, resulting in relatively low CH$_4$/H$_2$ selectivity (typically about 50%)$^{19}$. To achieve ultrahigh product selectivity for CH$_4$, it is imperative to develop an approach by engineering the biotic-abiotic interface that can harness the hydrogen atoms from photocatalytic reduction to avoid H$_2$ production and directly transfer them to methanogens for successive biocatalytic reactions.

Here, we report the use of nickel-copper (NiCu) alloys as binary active sites for incorporation into the interface between M. b and cadmium sulfide (CdS) nanoparticles, designing an M. b–NiCu@CdS biotic-abiotic hybrid system (Fig. 1) to address this challenge. Ni and Cu are chosen for the interface engineering owing to their suitable work functions and binding strength for H atoms$^{20,21}$. The well-designed hybrid system demonstrates the dramatically enhanced hydrogen and electron flow from semiconductor to binary active sites and finally to archaea, coupled with CO$_2$ for methanogenesis. As a proof of concept, M. b–NiCu@CdS achieves nearly 100% CH$_4$ selectivity with a rate of 79.38 ± 2.83 μmol (gcat)$^{-1}$ h$^{-1}$ and a quantum yield of 12.41 ± 0.16%. This work provides important insights into the design of biotic-abiotic interface for harnessing element and electron flow in hybrid photocatalytic systems, and opens an avenue for achieving sustainable and scalable conversion of CO$_2$ to biofuels with ultrahigh product selectivity.

**Fig. 1** Schematic illustration for the approach to solar-driven methanogenesis with M. b–NiCu@CdS. In other words, the produced protons (H$^+$) and photoexcited electrons (e$^-$) with CdS under light illumination can transfer to the NiCu alloy, and then be harvested by M. b for efficient CO$_2$-to-CH$_4$ conversion via turning down the H$_2$ production.

### Results

**System design and characterization**

The NiCu alloys are synthesized by the galvanic replacement reaction of corresponding metal ions. X-ray diffraction (XRD) patterns of NiCu alloys with different compositions show the typical face-centred cubic (fcc) crystal phase with a similar diffraction pattern between the standard JCPDS # 04–0850 for NiO and JCPDS # 04–0836 for CuO (Supplementary Fig. 1a), consistent with the previously reported NiCu alloys$^{22}$. For the optimized Ni$_2$Cu$_8$ (demonstrated in the following part), high-resolution transmission electron microscopy (HRTEM) image shows an interplanar distance of 0.210 nm, which matches well with the d-spacing value of the metallic NiCu(111) plane. The selected area electron diffraction (SAED) pattern identifies the monoclinic nature of as-prepared Ni$_2$Cu$_8$, demonstrating that no any new phases are formed (Supplementary Fig. 1b). The energy-dispersive X-ray spectroscopy (EDS) mapping images also show the relatively homogeneous distribution of introduced copper atoms (Supplementary Fig. 1c–f). These results can be attributed to the similar atom radius and electronegativity of Ni and Cu that prompt the formation of alloy$^{23}$. The formed NiCu alloys were then bound to M. b via electrostatic interactions based on zeta potential (Supplementary Fig. 2), followed by further integration with CdS via surface self-precipitation (Fig. 2a). The designed M. b–50%Ni$_2$Cu$_8$@CdS with noncovalent cysteine (Cys) is chosen as the main model for biotic-abiotic hybrid systems (denoted as M. b–NiCu@CdS), given its highest CH$_4$ yield among various composition configurations (Supplementary Fig. 3 and Supplementary Fig. 4). The combination of scanning electron microscopy (SEM, Fig. 2b), TEM (Fig. 2c), EDS mapping (Fig. 2d–g) and X-ray photoelectron spectroscopy (XPS, Supplementary Fig. 5) demonstrates the deposition of smaller nanoparticles composed of Cd, S, Ni and Cu for the encapsulation of M. b. Confocal laser scanning microscopy (CLSM) further confirms that the location of CdS nanoparticles, indicated by bright yellow fluorescence (a typical colour of metal chalcogenides), perfectly matches the shape of M. b (Fig. 2h). Further analysis reveals that the Ni/Cu ratios in the resulted biotic-abiotic hybrid system are close to the theoretical values (Supplementary Table 1), and the deposited nanoparticles are crystalline CdS and NiCu alloys (Supplementary Fig. 6).

To gain more information for interfacial binary active sites, the atomic structure of NiCu in the hybrid system is further examined by Ni and Cu K-edge X-ray absorption near edge structure (XANES) spectroscopy. The high similarity of the measured spectra to Ni and Cu foil references, which however greatly differ from those of NiO, CuO and Cu$_2$O references, indicates the metallic nature of the NiCu alloy (Fig. 2i). The radial structure function obtained by the Fourier transform (FT) of extended X-ray absorption fine-structure (EXAFS) spectra (Fig. 2j) shows profound peaks located at ~2.3 Å and ~2.4 Å, associated with Ni–Ni and Cu–Cu bonds, respectively. In particular, the intensities of both peaks are lowered along with the coordination numbers reduced from Ni (~12.00) to NiCu (~9.08) and from Cu (~12.00) to NiCu (~8.63), representing the formation of Ni–Cu bonds upon alloying Ni and Cu. This argument is supported by the length of the formed Ni–Ni and Cu–Cu bonds between those of typical Ni–Ni and Cu–Cu bonds (Fig. 2k, Supplementary Fig. 7, and Supplementary Table 2). As such, the formation of Ni–Ni/Cu bonds results in unique binary active sites at the biotic-abiotic interface, which can improve the capability of CO$_2$ adsorption (Supplementary Fig. 8). While the CO$_2$ adsorption takes place over the catalysts via either O–O or C–M interaction (M represents the metal active site), bimetallic atomic sites may offer both O–M and C–M interaction to enhance CO$_2$ adsorption$^{24}$. As a result, compared with CdS (E$_{ads}$ = −0.16 eV), a lower CO$_2$ adsorption energy (E$_{ads}$ = −0.61 eV) with NiCu@CdS is observed (Supplementary Fig. 9), indicating a stronger adsorption capacity of CO$_2$ on the Ni–Ni/Cu sites. Similar results were reported previously$^{25}$, in which the paired Cu-Pd...
sites in Pd$_2$Cu$_1$ alloys were demonstrated to enhance CO$_2$ adsorption and activation.

**Light-driven methanogenesis performance**

To assess the validity of our design, we first examine the essentially key side reaction—H$_2$ production in 50 mL of sterilized autotrophic medium with CO$_2$ as the sole carbon source under irradiation of 395 ± 5 nm LEDs (0.8 ± 0.1 mW cm$^{-2}$). The H$_2$ production of different Cds-based materials without M. $b$ is first investigated (Fig. 3a). After 5 days of irradiation, the H$_2$ yield by NiCu@Cds, originating from photocatalytic reduction, reaches 64.26 ± 4.42 mmol g$_{\text{cat}}^{-1}$, which is 2.28-, 12.50- and 5.35-fold higher than that of Ni@Cds, Cu@Cds and Cds, respectively. This indicates that the synergistic cooperation of Ni and Cu metallic sites contributed to the enhanced photocatalytic H$_2$ production. Among the Cds-based materials without M. $b$, Cu@Cds exhibits the lowest H$_2$ yield because copper ions (Cu$^{2+}$) can be easily generated in the Cu@Cds system via a Fenton-type reaction (2H$_2$O + 2h $^+$ → 2H$^+$ + O$_2$, Cu$^{2+}$ + h $^+$ → Cu$^+$, Cu$^+$ + H$_2$O $\rightarrow$ Cu$^{2+}$ + OH$^-$ + OH$^-$). Then the formed Cu$^{2+}$ may react with the sulfhydrils in cysteine (RSH) (2Cu$^{2+}$ + 2RSH $\rightarrow$ 2Cu$^+$ + RSSR + 2H$^+$), and reduce the function of cysteine as a sacrificial reducing agent$^{21}$. In addition, Cu$^{2+}$ can be transformed to CuS ($K_{\text{sp}}$ of Cds: 8.0 $\times$ 10$^{-27}$, $K_{\text{sp}}$ of CuS: 1.27 $\times$ 10$^{-36})^{22,27}$, which has been confirmed by XPS and XRD (Supplementary Fig. 10). This feature for Cu@Cds reduces the efficiency of generating and transferring photoexcited electrons, significantly limiting the photocatalytic H$_2$ production. As M. $b$ is added into the system of NiCu@Cds without direct interaction of M. $b$ with NiCu (namely, NiCu@Cds$+$M. $b$, similarly to planktonic cells), we observe an obviously decrease in H$_2$ concentration to 38.36 ± 1.63 mmol g$_{\text{cat}}^{-1}$. This demonstrates that the produced H$_2$ can indeed be consumed by M. $b$ for CO$_2$ reduction; however, apparently the H$_2$ cannot be depleted by the metabolism of M. $b$ due to the H$_2$ threshold concentration for M. $b$. As a result, the H$_2$ utilization efficiency is only 40.13% resulting in a low CH$_4$ selectivity of 11.85% (Supplementary Table 3). In sharp contrast, dramatically lower H$_2$ concentration can be detected in the biotic-abiotic hybrid systems, particularly with M. $b$-NiCu@Cds (Fig. 3b). This suggests that the intimate contact between M. $b$ and NiCu@Cds through our interface engineering can effectively transfer the hydrogen atoms, formed through photocatalytic reduction, to M. $b$ for methanogenesis, effectively suppressing H$_2$ production as a side reaction. Moreover, almost no CO is detected with M. $b$-NiCu@Cds, most likely as CO can serve as a potential source for CO$_2$ reduction;

Leveraging the efficient hydrogen transfer, an impressive CH$_4$ yield of 9.50 mmol g$_{\text{cat}}^{-1}$ is obtained with M. $b$-NiCu@Cds, along with nearly 100% CH$_4$ selectivity (99.04%, Fig. 3c). The product selectivity and production rate (79.38 ± 2.83 mmol g$_{\text{cat}}^{-1}$ h$^{-1}$) not only exceed the reported biotic-abiotic hybrid systems (Supplementary Table 4), but...
that cysteine only acts as a reducing agent for methanogenesis, rather than an effective carbon source for *M. b*. Furthermore, the formation of CH3D (21.79%), CH2D2 (30.06%), CHD3 (20.96%) and CD4 (15.21%) with D2O as a solvent demonstrates the participation of water molecules, in addition to free protons, during methanogenesis with *M. b-NiCu@CdS*. A prominent quantum yield of 12.41 ± 0.16% is achieved during CO2-to-CH4 conversion with *M. b-NiCu@CdS* (Supplementary Fig. 15). It is worth noting that such a value is substantially higher than the year-long averages determined for crops and forests (0.2–0.4%)3 and those of the reported biotic-abiotic hybrid systems, even for more kinetically favourable two-electron reactions such as H+ to H2 and NO3 to NO2 reduction (Fig. 3e and Supplementary Table 4). Meanwhile, the energy efficiency of *M. b-NiCu@CdS* for CO2-to-CH4 conversion is evaluated as the ratio of the product free-energy change to the input solar energy. The calculated value is -0.7%, comparable to the energy efficiency of most plants3. Moreover, the overall energy efficiency of *M. b-NiCu@CdS* could be higher when considering the Gibbs free energy gains (ΔrGo) from CO2 to biomass due to the significant increase of cell concentration with a high live/dead ratio (Supplementary Fig. 4). The excellent CH4 yield obtained with *M. b-NiCu@CdS* remains stable over three 5-day cycles (i.e., 15 days in total, Supplementary Fig. 16), suggesting the potential for practical application.

**Function of interfacial binary active sites**

The electron transfer and capture at the biotic-abiotic interface are a key process in the methanogen-semiconductor hybrid system. Due to the fast recombination of electron-hole pairs in CdS and slow extracellular electron uptake by *M. b* metabolism3, significant energy losses and side reactions occur in the *M. b*-CdS-based hybrid systems, resulting in a poor CH4 selectivity. To elucidate the role of binary

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**Fig. 3** Light-driven methanogenesis performance. a, b H2 yields by various *M. b*-absent CdS-based materials (a) and biotic-abiotic *M. b*-CdS-based hybrid systems (b). c CH4 yields in various biotic-abiotic hybrid systems. d Mass spectrometric analysis of headspace gas with NaH13CO3 and D2O as carbon source and water medium, respectively, using *M. b-NiCu@CdS* as catalyst. e Comparison of the quantum yields of *M. b-NiCu@CdS* and the reported biotic-abiotic hybrid systems.
To gain insight into the methanogenesis in our system, we investigate the response of the complex energy-transferring networks of \( M. b \) to the hydrogen transfer through NiCu@CdS, using transcriptomic analyses. Principal component analysis (PCA) shows two distinct groups in the score plots for \( M. b \)-CdS and \( M. b \)-NiCu@CdS, indicating that the NiCu alloy remarkably influences the physiological state of \( M. b \) under light irradiation (Fig. 5a). A total of 124 genes are significantly upregulated (fold change > 1.20 and \( p < 0.05 \)), while 56 genes are significantly downregulated (fold change < 1.20 and \( p < 0.05 \)) in response to the introcorporation of NiCu alloy (Fig. 3b). These genes encode various processes and characteristics, such as biological processes, molecular functions and cellular components (Fig. 5c). In particular, the Hsp70 (DnaK-DnaJ-GrpE chaperone system) and Hsp60 (GroEL) systems have been reported to serve as indicators of environmental stress in \( M. b \). Surprisingly, the related genes of the Hsp70 and Hsp60 systems are not significantly regulated in our case, implying that our biotic-abiotic hybrid system maintains a suitable environment for the cell growth and metabolism of \( M. b \) after the involvement of NiCu. This feature could be attributed to the significantly increased excretion of extracellular polymeric substances (EPS) with the higher fluorescence intensities after the introduction of NiCu (Supplementary Fig. 19). Specifically, these EPS components, including proteins, polysaccharides and lipids, can bind with cells through complex interactions to form a vast net-like structure that protects cells against the harm of external stress. Meanwhile, the increased EPS concentration, particularly the proteins as the most prominent EPS component, could effectively bind with metal cations (i.e., Cu\(^{2+}\) and Ni\(^{2+}\)) to act as a permeability barrier to hinder the intracellular penetration of excessive metal ions and potential DNA damage. This argument is further confirmed by a higher concentration of membrane-bound protein in the \( M. b \)-NiCu@CdS hybrid system (Supplementary Fig. 20). In addition, many components of EPS are redox-active or electrically conductive, and as such, their combination with NiCu is beneficial for the extracellular electron transfer from NiCu into the cell for the growth and metabolism of \( M. b \) in the \( M. b \)-NiCu@CdS hybrid system. This finding is further verified by the insignificant change in the transcription level of DNA-binding protein from starved cells (Dps), which is known to protect cells against various types of stressors such as starvation, oxidative stress, metal toxicity, thermal stress and salt stress. In addition, the nickel transport proteins (CbiN and CbiM, \( p < 0.05 \)) in \( M. b \)-NiCu@CdS are significantly upregulated, which could be evidence of an effective interaction between the surface of \( M. b \) and Ni atoms. In fact, the living cells still maintain highly similar overall morphology to that of bare \( M. b \) after integrated NiCu@CdS, and remain close contact with the NiCu@CdS after light irradiation (Supplementary Fig. 21), demonstrating the stability of the self-assembled structure.

Furthermore, the transcriptional levels of the energy-converting ferredoxin-dependent hydrogenase (EcH), \( \text{F}_{\text{ad}} \)-reducing hydrogenase (Frh) and membrane-bound methanophenazine-dependent hydrogenase (Vht) are significantly upregulated with \( M. b \)-NiCu@CdS (Fig. 5d). This contributes to enhanced hydrogenotrophic methanogenesis, with the transferred H atoms (and possibly a small amount of produced \( \text{H}_2 \) below the threshold concentration) as electron donors, through the extracellular hydrogen cycle. These hydrogenases are also
involved in the intracellular hydrogen cycle, in which the cooperative activity of Vht and HdrDE generates a proton gradient across the cell membrane. As such, the released energy in this gradient is captured by ATP synthase, resulting in the increased transcriptional levels. These results provide a further explanation for the superior methanogenesis performance of *M. b-NiCu@CdS* where all methanogenesis genes show upregulated expression patterns, particularly the unique and ubiquitous *Mcr* genes in methanogens encoding the terminal step of CH₄ generation (Fig. 5d). Moreover, it should be noted that no significant change is detected in the expression of different subunits of the membrane-bound F₄₂₀, which is generally considered to be responsible for the transfer of photoexcited electrons via the DIET pathway for the generation of reduced F₄₂₀. This indicates that hydrogen atom is the preferred and main intermediate for methanogenesis with *M. b-NiCu@CdS*.

The ultrafast transient absorption (TA) spectroscopy is further employed to examine the photoexcited electrons transfer in the *M. b-NiCu@CdS* hybrid system. Similarly to the typical spectra of CdS-related systems, a visible band peaking at 430–500 nm is observed for the NiCu@CdS-related systems after excitation, which is absent in the NiCu@CdS-free *M. b* system (Supplementary Fig. 22). Fitting of the TA data sets to a biexponential decay reveals that the transfer of photoexcited electrons in the *M. b-NiCu@CdS*-related hybrid systems is governed by the multiple processes (Supplementary Table 7). Compared with the NiCu@CdS system, an accelerated decay kinetics of photoexcited electrons is observed after the introduction of *M. b*-NiCu@CdS compared with *M. b*-CdS. (1) EchA-F hydrogenases, (2) *Fmd*-dependent hydrogenases (*Fpo*), (3) *Ffi*-dependent hydrogenases (*Frh*), (4) MP-reducing hydrogenases (*VhtACGM*), (5) Heterodisulfide reductases (*HdrDE*), (6) Formylmethanofuran dehydrogenases (*Fmd*), (7) Formylmethanofuran-tetrahydromethanopterin N-formyltransferase (Frt), (8) Methylenetetrahydromethanopterin cyclohydrodrolase (*Mch*), (9) Methylenetetrahydromethanopterin dehydrogenase (*Mtd*), (10) S10-methylenetetrahydromethanopterin reductase (*Mer*), (11) Methyl-CoM reductases (*MtrA-H*), (12) Methyltransferases (*MtrA-H*), (13) ATP synthase. Source data are provided as a Source Data file.
intimate contact, a Fermi level equilibrium (~0.76 V) can be achieved in the NiCu@CdS. Under light irradiation, electrons are first photoexcited from the valance band (VB, 1.68 V) to the conduction band (CB, ~1.00 V) of CdS, and then transferred to NiCu alloy (~0.76 V) across the interface. As the reduction potential of the NiCu alloy is higher than that of the \( \text{H}_2 \)-ase and cytochrome \( \beta \)\(^{41} \), the efficient electron transfer is subsequently conducted from the NiCu alloy to the acceptor sites on the surface of \( M. b \) for methanogenesis. This electron transfer channel can effectively hinder the backflow of photoexcited electrons to recombine with holes, and then improve the efficiencies of charge separation and utilization. Meanwhile, the hydrogen at the NiCu@CdS interface, produced via the interaction between the electrons and protons from the oxidation of \( \text{H}_2 \text{O} \) and cysteine, can be harvested by \( M. b \) to significantly improve the \( \text{CH}_4 \) production through the extra-cellular and intracellular hydrogen cycling.

**Discussion**

A quantum yield of \( 85 \pm 12\% \) was observed with the \( M. \text{thermoacetica-CdS} \) hybrids for the photosynthesis of acetic acid from \( \text{CO}_2 \) in a previous work\(^{42} \). However, it should be pointed out that the value was achieved under the very low photon flux (the order of magnitude of \( > 10^3 \text{ cm}^{-2} \text{ s}^{-1} \)) that tried to reduce losses from charge recombination, along with the high hybrid loading (four times). When the photon flux increased to \( 1.6 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1} \), the quantum yield dramatically dropped to \( \pm 4 \% \). In particular, the peak quantum yield further decreased to only \( 2.44 \pm 0.62\% \) under low-intensity simulated sunlight with a light-dark cycle of 12 hour each, which was order-of-magnitude lower than that in our work (12.41 ± 0.16, 1.6 × 10\(^{15} \text{ cm}^{-2} \text{ s}^{-1} \)). Therefore, this study addresses the long-standing challenge via the bimetallic alloy strategy to achieve a high quantum yield under relatively high photon flux. More importantly, these results demonstrate the potential of \( M \cdot b \)-NiCu@CdS hybrid system for indoor application that has the similar light intensity (~1 mW cm\(^{-2} \)) to that reported in this study (0.8 mW cm\(^{-2} \)). To this end, energy harvesting for hybrid system from the indoor light sources, such as light emitting diodes (LEDs), fluorescent lamps or halogen lamps, not only brings opportunities to directly supply the high-grade biogas for daily life without the complex transmission pipeline system, but also meets the demand of zero net energy (ZNE) building in the future. To further evaluate the practicability of the hybrid system, we illuminate \( M \cdot b \)-NiCu@CdS under simulated sunlight (AM 1.5 G, 20 mW cm\(^{-2} \)) with a light-dark cycle of 12 h. A quantum yield of 1.01% of total incident simulated sunlight is observed after 3-day operation, which is order-of-magnitude comparable to the year-long averages determined for plants and algae (~0.2 to 1.6)%\(^{43} \). With the further increasing light intensity, the methanogenesis performance dramatically decreases. The quantum yield is only 0.05% under 100 mW cm\(^{-2} \) after 3-day operation, most likely due to the photodamage of cells such as destruction of the cell membrane under a higher light intensity\(^{11} \). However, such a limitation does not affect the application of biobr id system outdoors, because the shading technology, such as the use of optical glasses, shading nets and green house, becomes more and more mature.

While cysteine has been selected as a representative sacrificial hole scavenger (i.e., electron donor) in our study, we can potentially use other electron donors, including the low-value organic compounds such as lactic acid, formic acid and methanol\(^{44} \), and the universal inorganic electron donors such as sodium sulfide (Na\(_2\)S) and sodium sulfide/sodium sulfite (Na\(_2\)S/Na\(_2\)SO\(_3\)) to enable similar scenarios\(^{45,46} \). For instance, an excellent methanogenesis performance is achieved with the \( M \cdot b \)-NiCu@CdS hybrid system after the replacement of cysteine with KI (~0.35 V vs. SHE at pH 7, Supplementary Fig. 14). Furthermore, the abundant wastes such as the lignocellulose and plastics may also be used as the potential electron donors\(^{47,48} \). As such, there is a broad electron donor spectrum to support the \( M \cdot b \)-NiCu@CdS hybrid system, offering the possibility of realizing both high quantum efficiency and energy conversion efficiency that may play an important role in scalable energy-storage systems of the future\(^{49} \). In this sense, a different autotrophic way has been established for \( M \cdot b \) methanogens via direct hydrogen transfer through interface engineering, differently from the traditional chemoheterotroph using organic carbon sources and chemoautotrophic using \( \text{H}_2 \). In addition, compared with *Moorella thermoacetica*-CdS, an increased acetate yield is also observed in the *Moorella thermoacetica*-NiCu@CdS hybrid system (Supplementary Fig. 24). For this reason, it can be predicted that such a promising alloy strategy is able to improve the \( \text{CO}_2 \) conversion to various value-added products, not limited to \( \text{CH}_4 \), which would open an avenue for achieving effective and scalable conversion of \( \text{CO}_2 \) to biofuels.

**Methods**

**Synthesis of nanoparticles**

Ni\(_x\)Cu\(_y\) alloys (where \( x \) and \( y \) refer to the molar ratio of Ni and Cu) were prepared through a galvanic replacement reaction. For instance, 0.8 mmol NiSO\(_4\)·6H\(_2\)O was dissolved in 150 mL of ultrapure water. Then Ni\(_x\) was completely reduced to Ni\(_y\) after dropwise addition of potassium borohydride (KBH\(_4\), 0.4 M) until the bubbles and green colour disappeared under a mechanical stirring speed of 200 rpm at 25 °C. Afterward, 0.64 mmol CuSO\(_4\)·5H\(_2\)O was added dropwise into the mixture to partially replace Ni\(_x\). After 20 min of reaction, the typical blue colour of Cu\(_x\) disappeared. Subsequently, the mixture was centrifuged at 5000 × g for 10 min, washed six times with ultrapure water, and freeze-dried for 48 h to obtain Ni\(_x\)Cu\(_y\) alloy. To investigate the effect of hydrogen on methanogenesis performance, the produced Ni\(_x\)Cu\(_y\) alloy was immersed in 100 mM 1,4-diphenylbutadiyne (DPB) solution for 12 h to form a layer of hydrogen scavenger before use\(^{45} \).

The CdS semiconductor was synthesized according to the following protocols\(^{46} \), where 3-mercaptopropionic acid (MPA) was used to control the particle size of CdS nanoparticles. Briefly, 10 mmol of CdCl\(_2\) and 17 mmol of MPA were dispersed in 200 mL of water. The solution pH was adjusted to 10.0 by 5.0 mol L\(^{-1}\) of NaOH, and transferred into a 250 mL three-necked flask. Then the air in the headspace of the flask was replaced with Ar, and 0.5 mmol of freshly prepared Na\(_2\)S solution was dropwise added under stirring. Subsequently, the mixture was heated to 100 °C with a condenser, and the observed bright-yellow, transparent solution was continually stirred at 100 °C for 30 min. After naturally cooled to room temperature, the CdS semiconductors were isolated through precipitation with alcohol, dispersed in water, and freeze dried for further use.

**Construction of biotic-abiotic hybrid system**

\( M \cdot b \) (DSM 800) was obtained from DSMZ (Braunschweig, Germany) and inoculated into 50 mL of heterotrophic medium at 37 °C with a ratio of 1:5 (Table S8). When the growth of \( M \cdot b \) reached the logarithmic phase (OD\(_{600}\)~0.2), 2.16 mg Ni\(_x\)Cu\(_y\) alloy and 4.32 mg CdS semiconductor were added in turn over a time interval of 12 h according to the preliminary experiments. After a total of 24 h of cultivation at a mechanical stirring speed of 180 rpm, the suspension of \( M \cdot b \)-Ni\(_x\)Cu\(_y\)CdS (denoted as \( M \cdot b \)-NiCu@CdS hereafter) was sequentially centrifuged, washed and resuspended in 5 mL of 0.9% NaCl solution three times for further use. As controls, \( M \cdot b \)-Cu@CdS, \( M \cdot b \)-Ni@CdS and \( M \cdot b \)-CdS were prepared by the same method, except that NiCu@CdS was replaced with Ni@CdS, Cu@CdS and CdS, respectively. In addition, *Moorella thermoacetica*-CdS, was obtained from the Global Bioresource Center ATCC, and inoculated into 50 mL of heterotrophic medium at 52 °C with a ratio of 1:5 (Table S9). Then \( M \cdot t \)-CdS and \( M \cdot t \)-NiCu@CdS were prepared by the same method, except that \( M \cdot b \) was replaced with \( M \cdot t \).
Characterization

The hybrid materials were fixed with 2.5% glutaraldehyde for 12 h, and dehydrated in 25, 50, 75, 90 and 100% ethanol sequentially, the morphologies of the hybrid materials were observed with SEM (Hitachi S-8000) and high-resolution TEM (HRTEM, FEI Tecnai G2 F20 S-TWIN). Surface elemental compositions and states were analysed with EDS (X-MaxN, Oxford Instruments). XPS measurements were performed by Thermo ESCALAB 250 XPS spectrometer system using Al Kα (1486.6 eV) radiation (operated at 15 kV) in the constant analyzer energy mode. Fluorescence images were collected using confocal laser scanning microscopy (CLSM, Carl Zeiss LSM880). XRD patterns were obtained using an X-ray diffractometer (XRD-6000, Shimadzu) with Cu Kα radiation at 40 kV and 30 mA in a 2θ range of 5–80° at a scan speed range of 1° min⁻¹. X-ray absorption spectroscopy (XAS) measurements for the Ni and Cu K-edges were conducted in transmission mode (fluorescence mode) on beamline 12-BM at the Advanced Photon Source at Argonne National Laboratory. The XANES and Fourier transformed EXAFS spectra were analysed using Athena and Artemis software. The zeta potentials of the samples were measured using a Nanobrook Omni analyser (Nano-brook Omni, Brookhaven, US).

Electrochemical characterization was conducted in a three-electrode anerobic electrochemical quartz chamber connected to a CHI 660E electrochemical station (CH Instruments, TX, USA). The working electrode used was an indium tin oxide (ITO)−coated glass plate (radius: 1.5 cm) placed at the bottom of the chamber with 6.48 mg of self-precipitated samples. A platinum sheet (1×1 cm) and a saturated calomel electrode (SCE) mounted on the salt bridge were used as the counter and reference electrodes, respectively. The photocurrents (IP) were measured under a light on/off cycle of 60 s at a bias potential of ~300 mV versus SCE. Electrochemical impedance spectroscopy (EIS) experiments were conducted from 1000 kHz to 0.01 Hz with a sinusoidal perturbation amplitude of 5 mV under an open-circuit potential. Steady-state PL spectra and PL decay spectra were determined by a PL−UV spectrofluorometer (PerkinElmer LS55) with a 450 nm excitation source at room temperature. All PL spectra and PL decay spectra were measured under a light on/off cycle of 60 s at a bias potential of 300 mV versus SCE. Electrochemical impedance spectroscopy (EIS) experiments were conducted from 1000 kHz to 0.01 Hz with a sinusoidal perturbation amplitude of 5 mV under an open-circuit potential.

Product measurements

The H₂ and CH₄ concentrations were determined using an Agilent 7890 A Gas Chromatograph (GC) equipped with a flame ionization detector (FID). The gas products in the headspace of the hybrid system during the isotopic labelling experiments were determined by a Shimadzu GC-2010 equipped with a Shintadzu AOC-20i auto sampler system and interfaced with a Shimadzu QP 2010S mass spectrometer (DB-5 capillary column (30 m×0.25 mm × 0.25 μm), Helium (99.999%) as carrier gas with a flow rate of 1.2 mL min⁻¹). Acetate measurement was performed on a Shimadzu Nexis GC-2030 system equipped with a CP Wax 52 CB column and an FID detector. The metabolites of cysteine by M. b were characterized by Varian INOVA 600 MHz NMR spectroscopy (Varian, USA).

Both M. b-NiCu@CdS and M. b-CdS samples after light irradiation for 72 h were collected and centrifuged at 10,000 × g for 30 min at 4 °C for transcriptomic analysis. Total RNA was extracted with TRIzol reagent (Invitrogen, California, USA). Directional multiple libraries were prepared with the NEBNext® Ultra II™ Directional RNA Library Prep Kit (New England Biolabs Ltd., Beijing, China). rRNA was depleted using subtractive hybridization employing biotinylated rRNA probes. All reads matching 16S and 23S rRNA genes were removed, and the remaining reads were mapped against the published genome of M. b MS (NZ_CP009528.1). Mapped reads were normalized with FPKM (fragments per kilobase per million mapped reads) method. Multiple fluorescent staining was conducted with fluorescein-isothiocyanate (FITC) (proteins), concanavalin A (Con A, α-polysaccharide), calcein white (β-polysaccharide) and Nile red (lipids), and then observed with CLSM (Carl Zeiss LSM880). For the isolation of the extracellular membrane-bound proteins, the cell culture of M. b was subjected to shearing forces in a Waring blender at room temperature at a low speed for 1 min and measured with the BCA protein assay kit (Thermo Scientific Pierce). Cell viability were measured using the Live/Dead® BaLight™ Bacterial Viability Kit, observed with CLSM (Carl Zeiss LSM880) and then analysed with ImageJ software. The average quantum yield (QY) was defined by the ratio of the effective electrons used for CH₄ production to the total input photon flux as the following equation:

\[ QY(%) = \frac{\text{the number of electrons accepted for CH₄ production}}{\text{the number of incident photons}} \times 100\% \]  

where [CH₄] is the CH₄ concentration (mol L⁻¹), V is the volume of the reactor headspace (L), A is the area of irradiation (15.9 cm²), t is the illumination time, λ is the light wavelength (395 nm), h is the Planck constant (6.63 × 10⁻³⁴ J s⁻¹), c is the speed of light (3 × 10⁸ m s⁻¹), and P_light is the light intensity (0.8 mW cm⁻²).

The energetic efficiency (η) was calculated as the ratio of the product free-energy change to the input solar energy by the following equation:

\[ \eta = \frac{\Delta G^0}{\text{Energy Input}} = \frac{N \Delta G^0}{E_{\text{solar}}} \]  

where ΔG⁰ is the reaction Gibbs free-energy change, N is the number of moles of produced CH₄, and E_solar is the total incident photon energy from the simulated sunlight.

With the stoichiometry of photooxidation of I into I₃⁻ (3I²⁺ + 2H⁺ → I₃⁻), a maximum CH₄ yield of 0.075 mmol could be achieved, corresponding to 0.9 mmol KI. CH₄ efficiency was then defined as:

\[ \text{Efficiency}(\%) = \frac{C_{\text{CH₄}}}{0.075} \times 100\% \]
where $C_i$ is the CH$_i$ yield (mmol).

The ultrafast femtosecond transient absorption (fs-TA) measurements were conducted on a Helios spectrometer system (Ultrafast systems, USA) with a modelocked Ti:sapphire seed laser (Spectra Physics, Maitai) directed to a regenerative amplifier (Spitfire Pro, Spectra Physics) and a high power laser (Empower, Spectra Physics). Briefly, the samples were excited with $\sim 120$-fs laser pulses at a repetition rate of 1 kHz. A chopper that can modulate the pump pulses was employed to obtain fs-TA spectra with and without the pump pulses alternately, and an optics fibre coupled to a multichannel spectrometer with a CMOS sensor was used to record the pump-induced fluctuation in probe/reference beam intensity with adjusting the optical delay line (maximum $\sim 3$ ns). The obtained spectra were further processed by the Surface Xplorer, and fitted to a multieponential decay.

All culture and sampling manipulations were performed using the sterile technique in a Vacuum Atmospheres Nexus One glovebox with a Surface Xplorer, and in probe/reference beam intensity with adjusting the optical delay line with a CMOS sensor was used to record the pump-induced fluctuation in probe/reference beam intensity with adjusting the optical delay line (maximum $\sim 3$ ns). The obtained spectra were further processed by the Surface Xplorer, and fitted to a multieponential decay.

Computational details
All the calculations were performed in the framework of the density functional theory with the projector augmented plane-wave method, as implemented in the Vienna ab initio simulation package$^{30}$. The generalized gradient approximation proposed by Perdew, Burke and Ernzerhof was selected for the exchange-correlation potential$^{60}$. The cut-off energy for plane wave was set to 450 eV. The energy criterion was set to $10^{-3}$ eV in iterative solution of the Kohn-Sham equation. A vacuum layer of 15 Å was added perpendicular to the sheet to avoid artificial interaction between periodic images. The Brillouin zone integration was performed using a 3x3x1 k-mesh. All the structures were relaxed until the residual forces on the atoms had declined to less than 0.03 eV/Å.

The CO$_2$ adsorption energy ($\Delta E_{\text{ads}}$) and free energy changes ($\Delta G$) of reaction intermediates could be calculated by the following equations:

$$\Delta E_{\text{ads}} = E_{\text{ads}} - E_{\text{ads}} - E_{\text{slab}}$$

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S$$

where $E_{\text{ads}}$ is the energy of CO$_2$ adsorbed on the substrate, $E_{\text{ads}}$ and $E_{\text{slab}}$ are the energy of CO$_2$ and substrate, respectively. The $\Delta E$ is the adsorption energy on the cluster surface from DFT calculations. The $\Delta E_{\text{ZPE}}$ and $\Delta S$ are the difference for the zero-point energy and entropy. The zero-point energy and entropy were calculated at the standard conditions corresponding to the pressure of 101,325 Pa (1 bar) of H$_2$ at the temperature of 298.15 K ($T$).

Statistics and reproducibility
Each of the captured images presented in Fig. 2b–h, Supplementary Fig. 1b–f, Supplementary Fig. 4a, Supplementary Fig. 6b, Supplementary Fig. 19a and Supplementary Fig. 21 was measured independently for 5 times to confirm results reproducibility.

Reporting summary
Further information on research design is available in the Nature Research Reporting Summary linked to this article.

Data availability
The authors declare that all data supporting the findings of this study are available in the article and its Supplementary Information. Source data are provided with this paper.

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Acknowledgements
This work was supported by the National Science Fund for Distinguished Young Scholars (41925028, 21725102), the National Natural Science Foundation of China (42177206), and the National Natural Science Foundation of Fujian Province, China (2020J06017).

Author contributions
J.Y., S.Z. and Y.X. conceived the idea for this work. C.W. and T.F. prepared the NiCu alloy. C.Y., C.W. and C.G. performed the characterizations, catalytic measurements, DFT calculations and transcriptomic experiments. J.Y., C.W., C.G., T.F., G.R. and J.L. analyzed the data. J.Y., C.W., C.G., S.Z. and Y.X. wrote the manuscript. All the authors contributed to the interpretation of the data and preparation of the manuscript.
Competing interests
A patent application was submitted to China National Intellectual Property Administration (patent applicant: Fujian Agriculture and Forestry University; names of inventors: Jie Ye, Chao Wang, Shungui Zhou; application number: 202111327225.4; status of application: submitted; specific aspect of manuscript covered in the patent application: the preparation and application of biocatalyst with sandwich structure for photoelectrochemical methanogenesis). The remaining authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-022-34423-1.

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Peer review information Nature Communications thanks the anonymous reviewers for their contribution to the peer review of this work.

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