Supporting Information

Enhanced CO_2 reduction and valuable C_{2+} chemical production by a CdS-Photosynthetic hybrid system

Bo Wang,‡[a,b] Zhifeng Jiang,‡[b,c,d] Jimmy C. Yu,*[a] Jianfang Wang,*[e] and Po Keung Wong*[bf]

[a] *Department of Chemistry, The Chinese University of Hong Kong, Shatin New Territories, Hong Kong, China*

[b] *School of Life Sciences, The Chinese University of Hong Kong, Shatin New Territories, Hong Kong, China*

[c] *Institute for Energy Research, Jiangsu University, Zhenjiang, 212013, China*

[d] *School of Energy and Environment, City University of Hong Kong, Kowloon, Hong Kong, China.*

[e] *Department of Physics, The Chinese University of Hong Kong, Shatin New Territories, Hong Kong, China*

[f] *Institute of Environmental Health and Pollution Control, School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 510006, China.*

‡ *Equal contribution*

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*Corresponding authors.

pkwong@cuhk.edu.hk (Po Keung Wong)

jimyu@cuhk.edu.hk (Jimmy C. Yu)

jfwang@phy.cuhk.edu.hk (Jianfang Wang)

Table of contents

Experimental Section

Strategies for the CdS-*R. palustris* hybrid system construction

■ *Cell maintenance*

The *R. palustris* (ACCC 10649) was daily maintained in 60 mL clear collection vials (Thermo Scientific, USA) fully filled with 60 mL MN medium[1] (Table S1) for anaerobic culture (Fig. S1). The collection vials were incubated on an orbital shaker (MX-RD-Pro, Scilogex, USA) at 10 revolutions per minute (RPM) and illuminated by fluorescent tubes (FT, 80 W/m^2) with a 2 cm distance. The temperature was controlled at 30 ± 1 °C.[2] The cells were transferred to fresh MN medium every five days.

■ *Rapid biomass accumulation and growth curve determination*

To collect high density of synchronized *R. palustris* cells for further study in a short time, 20 mL of the maintained cells in MN mediums were centrifuged and transferred to 60 mL freshly prepared supplemented MN medium (SMN, Table S1) in 60 mL clear collection vials for anaerobic incubation (Fig. S1). The vials were incubated by the rotating incubator under 80 W/m^2 FT illumination and 30 ± 1 °C. The standard curve of cell density against optical density at 680 nm (OD_{680})[3] was plotted (Fig. S2a) by preparing a sequence of dilutions of a concentrated *R. palustris* cell suspension (1.0×10^{10} cell/mL) and counting the cell number a via hemocytometer (Cambridge Instruments, USA) under a light microscopy (E220, Nikon, Japan). Then the corresponding OD_{680} values were measured by a UV/VIS spectrometer (BlueStar A Split Beam, LabTech, USA). The cell density-OD_{680} standard curve was fitted by non-linear regression. The standard curve of dry cell mas against optical density at 660 nm

$(OD_{660})^4$ was plotted (Fig. S2b) by preparing a series of 50 mL dilutions of a concentrated *R. palustris* cell suspension (1.0×10^{10} cell/mL) in triplicate and centrifuged at 13,000 × g for 10 min and discarded the supernatants. The pellets were heated at 80 °C for 72 h. The dry mass of each dilutions was measured by subtracting the mass of pre-weighted centrifuge tube from the total mass. The corresponding OD_{660} values was measured by the UV/VIS spectrometer. The dry mass-OD_{660} standard curve was fitted by non-linear regression. The growth curve (Fig. S2c) of *R. palustris* in SMN was measured by recording the OD_{680} at fixed time intervals and normalized by the cell density-OD_{680} standard curve.

■ *CdS coating*

The *R. palustris* cells at (1) mid-exponential growth phase ($OD_{680} \approx 1.5$, cell density $\approx 1.4 \times 10^9$ cell/mL) and (2) early-stationary growth phase ($OD_{680} \approx 2.1$ cell density $\approx 2.9 \times 10^9$ cell/mL) were collected and centrifuged at 13,000 × g for 10 minutes, respectively. The cell pellets were diluted by modified MN medium (MMN, Table S1) to an initial OD_{680} around 0.6 and cell density around 5×10^8 cell/mL. Parallel of the *R. palustris*-MMN medium (50 mL) were aliquoted into 60 mL clear collection vials with headspace filled with pure CO_2 gas at atmospheric pressure. The behavior of *R. palustris* collected from different growth phase was first studied by adding 0.1 mM $Cd(NO_3)_2$ and 1mM cysteine to the MMN medium. All the clear collection vials were anaerobically incubated on the orbital shaker at 10 RPM and illuminated by fluorescent tubes (80 W/m^2) and the culture temperature was controlled at 30 ± 1 °C. After 48 hours culturing time, aliquots of 1 mL sample from the *R. palustris* cultures were collected for characterization of the CdS-*R. palustris* hybrid system. Since the CdS NPs

is observed to uniformly distributed on the surface of the swarmer cells[5] and successfully developed to mature hybrid system (Fig. S3). However, the CdS NPs only clustered at one end of the mother cells[6] (Fig. S4), which was not beneficial for the material-cell interaction and effective electron transduction. Therefore, the *R. palustris* cells in the swarmer dominating growth phase were collected for the effective hybrid system construction.

The CdS coating efficiency of the *R. palustris* cells collected from mid-exponential growth phase was evaluated. Different volumes of 100 mM stock solution of $Cd(NO_3)_2$ were added in the MMN medium with *R. palustris* cells to the final concentrations of 0.05-0.5 mM, and 1 mM cysteine was supplemented to serve as the sulfur source. The 48h cultured samples from CdS coating groups were collected and centrifuged at 13,000 × g for 10 min. The supernatants were collected for measuring the remained Cd^{2+} in the MMN medium by an atomic absorption spectroscopy (AAS, Hitachi Z2300 flame, Japan). Finally, the CdS coating efficiency (*CE*) was calculated by the equation (1):

$$CE = \left(1 - \frac{Cd^{2+}\ remained\ in\ the\ MMN\ medium}{Cd^{2+}\ added\ into\ the\ MMN\ medium}\right) \times\ 100\% \qquad (1)$$

Characterization of CdS-*R. palustris* hybrid

To avoid the potential toxicity to the *R. palustris*, 0.2 mM $Cd(NO_3)_2$ was added for constructing the CdS-*R. palustris* hybrid system since 91.93% of the toxic Cd^{2+} could be efficiently precipitated (Table S2) with the existence of cysteine (1 mM) as the S^{2-} source.[7] The 48h cultured CdS-*R. palustris* was prepared for characterization, including observation by high-

angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), high-resolution transmission electronic microscopy (HRTEM), Energy-dispersive X-ray spectroscopy (EDS) mapping and X-ray photoelectron spectroscopy (XPS) analysis. To prepare the sample for HAADF-STEM observation, aliquots the CdS-*R. palustris* culture (1 mL) were centrifuged at 13,000 × g for 10 min and the pellets were washed by phosphate buffered saline (PBS, pH at 6.8) for three times. The samples were fixed by 4% glutaraldehyde at 4 °C for 2 h, followed by two times PBS washing. The fixed samples were then sequentially dehydrated by 50%, 70%, 85%, 95% and 100% of ethanol and deposited on 200-mesh copper grids (Electron Microscopy Sciences, USA). The sample were observed via the HAADF-STEM model of a Tecnai F20 TEM (FEI, USA) and the EDS mapping of C, Cd and S elements from the HAADF-STEM images was conducted. To prepare the thin-sectioned sample for HRTEM observation, aliquots of the CdS-*R. palustris* culture (1 mL) were washed by PBS and then pre-fixed by 4% glutaraldehyde at 4 °C for 2 h. The fixed samples were washed by PBS for two times and then stained by fresh prepared 1% OsO4 in PBS for 1 h. After PBS washing for three times, the samples were sequentially dehydrated in 50%, 70%, 85%, 95%, and 100% of acetone, then sequentially embedded and infiltrated by 1:2, 1:1, 3:1 of resin: acetone, each time lasting for 8 h. Next, the samples were embedded by pure resin (Spurr's, Electron Microscopy Sciences, USA) and baked at 80 °C overnight. The embedded samples were sectioned to 70 nm by diamond knife (Diatome Ultra 45°, MF277, Switzerland) and deposited on 100-mesh copper grids (Electron Microscopy Sciences, USA). Finally, the sample were observed via the HRTEM model of the Tecnai F20 TEM. For XPS analysis, the samples were

freeze-dried and grinded into powers and then measured on an ESCALAB MK X-ray photoelectron spectrometer.

Isolation and characterization of the CdS NPs

To isolate the surface CdS for further electrochemical characterization, 10 L of the CdS-*R. palustris* hybrid system culture was prepared and centrifuged at 13,000 × g for 20 min to collect the cell pellet. Then the pellet was lysed by 1 L QIAGEN Buffer P2[8] and ultrasonicated by Branson 2510E ultrasonicator overnight. The lysed sample was centrifuged at 13,000 × g for 30 min, and the pellet in yellowish layer was carefully scratched and collected in a new centrifuge tube. Next, the obtained pellet was washed by ethanol and ultra-pure water, each for 3 times. Finally, the sample was freeze-dried and grinded into power and stored at 25 °C. The isolated CdS (1.5 mg) and 1.5 mg commercial CdS (MKAA3516V, Sigma-Aldrich, USA) were fixed onto fluorine-doped tin oxide (FTO) glass as photocathode to further testing the photocurrent density under fixed and variable potentials by an electrochemical workstation (CHI650E, CH Instruments, USA). A xenon lamp (PLS-SXE300C, PerfectLight, China) with 420 nm filter was used to provide visible light irradiation.

CO_2 fixation performance study

The volume of cell culture collected from mid-exponential growth phase was 50 mL and the initial cell density was adjusted to 5×10^8 cell/mL (OD680 ≈ 0.6). For the CdS-*R. palustris*

groups, 120 μL of 100 mM stock solution of $Cd(NO_3)_2$ and 1 mM cysteine were added in the MMN medium with *R. palustris* cells. A parallel group without addition of $Cd(NO_3)_2$ was set for control experiment. All the vials were filled with pure CO_2 gas at atmospheric pressure at the headspace and anaerobically incubated on the orbital shaker at 10 RPM and illuminated by fluorescent tubes (80 W/m^2). Parallel groups in dark condition (light off) were also added for reference. The culture temperature was controlled at 30 ± 1 °C. The CO_2 fixation study last for 180 h. At fixed time intervals, 1 mL aliquots of samples from CdS-*R. palustris* group and control group were collected in triplicate for measuring the cellular NADPH level, glyceraldehyde 3-phosphate (GAP) concentration, cell density, dry mass, carotenoids content and Poly-β-hydroxybutyrate (PHB) content.

■ *NADPH assay*

The NADP/NADPH Assay Kit (ab65349, abcam, UK) was used to quantify the NADPH level in *R. palustris* cell. 300 μL aliquot of sample was centrifuged at 13,000 × g for 5 min and washed with cold PBS, then homogenized with 300 μL Extraction Buffer and freeze/thawed (20 min/10 min) for 3 times. The sample was then vortexed for 10 seconds and centrifuged at 13,000 × g for 5 min. Then, 200 μL supernatant was transferred to a new tube and heated at 60 °C by water bath for 30 min. Finally, 50 μL aliquot of the sample was mixed with 100 μL Reaction Mix in a clear 96 well flat-bottom plate (Costar, USA). After the addition of 10 μL of NADPH Developer into each well, the variation of OD_{450} in 1-4 h was monitored by the spectrophotometric multi-well plate reader until the value became stable. Finally, the NADPH concentration was normalized by the standard curve plotted by NADPH standards (0 - 100

pmol). The assay was conducted in triplicate and the standard deviation was calculated accordingly.

■ *Glyceraldehyde 3-Phosphate measurement*

The intracellular GAP concentration was quantified by measuring the optical density of colorimetric (450 nm) product when converting the G3P to 1,3-bisphosphate glycerate (BPG) by the glyceraldehyde 3-phosphate dehydrogenase (GAPDH). A 200 μL aliquot of sample was centrifuged at 13,000 × g for 5 min and homogenized with 200 μL ice-cold assay buffer (MAK277A, Sigma-Aldrich, USA) for 10 min. Then the sample was centrifuged at 10,000 × g for 5 min and 96 μL of the supernatant was mixed with 2 μL GAPDH Developer (MAK277C, Sigma-Aldrich, USA) and 2 μL GAPDH (MAK277E, Sigma-Aldrich, USA) in a clear 96 well flat-bottom plate (Costar, USA). After incubation at 37 °C for 60 min in dark, the absorbance at 450 nm (OD_{450}) was measured by a spectrophotometric multi-well plate reader (Tecan Safire, USA). The standard GAP solution (G5251, Sigma-Aldrich, USA) was sequentially diluted and treated by the same procedures, then used for plotting a standard curve. Finally, the cellular GAP concentration was then normalized by the standard curve and the assay was conducted in triplicates.

■ *Cell density & dry mass measurement*

At fixed time intervals, 1 mL aliquots of the samples from experimental and control groups were collected by a sterile syringe. The cell density and dry mass were measured by recording the OD_{680} and OD_{660} using the UV/VIS spectrometer, then normalized by the cell density-

OD_{680} and dry mass-OD_{660} standard curves (Fig. 2a-b), respectively. Triplicate measurement was conducted for calculating the standard deviation.

■ *Carotenoids and Poly-β-hydroxybutyrate (PHB) assay*

The carotenoids content (mg/g dry mass) of the cells at the early stationary growth phase from *R. palustris* group and CdS-*R. palustris* group was quantified by using the Carotenoids ELISA kit (Cat. # JL46073, JianglaiBio, China). For the PHB assay, 50 mL aliquots of cells at early stationary phase were collected from *R. palustris* group and CdS-*R. palustris* group. The samples were centrifuged at 13,000 × g for 10 min, and the pellets were freeze-dried and weighted. As described by Zilliges *et al*.,[9] the PHB in the pellet was hydrolytic degraded to its monomer (R)-3-hydroxybutyric acid (R-3-HB) by adding NaOH and incubating at 90 °C. The samples were vigorously vortexed for completely hydrolyzing. After 60 min incubation and cooling, the samples were neutralized by adding equal concentration of HCl. Then the samples were centrifuged at 5,000 × g for 5 min to collect the R-3-HB containing supernatant. Finally, the collected R-3-HB in the sample was spectrophotometrically quantified by the β-Hydroxybutyrate Assay Kit (MAK041, Sigma, USA). The calculated R-3-HB content was used to stand for the obtained PHB content (% of dry mass).

■ *Isotopic labelling study*

The C13-CO_2 isotopic labeling experiments were conducted by substituting the $^{12}CO_2$ to the $^{13}CO_2$ gas in the headspace, then conducting the CO_2 reduction experiments. The collected solid samples of the CdS-*R. palustris* hybrid system were treated by high temperature (1000

°C), then the converted CO_2 in the gaseous phase was measured by a GC-IRMS (Thermo Scientific DELTA V, USA).

Photosynthetic efficiency determination

The photosynthetic efficiency (PE) was defined as the ratio of the light energy transferred to the biomass to the total received light energy.[10] PE was calculated using the equation (2):

$$PE = \frac{Energy\ output\ rate\ (produced\ photosynthetic\ biomass)}{Energy\ input\ rate\ (light\ input + consumed\ organic\ substrate)} \quad (2)$$

$$= \frac{P \times (-\Delta H)}{TLEI + (-\Delta H') \times MCE}$$

Where P = biomass productivity (g h^{-1}),

$P_{R.\ palustris}$ = (2.25 g L^{-1} – 0.228 g L^{-1}) × 0.06 L ÷ 80 h = 1.5165 × 10^{-3} g h^{-1},

$P_{CdS\text{-}R.\ palustris}$ = (3.344 g L^{-1} – 0.228 g L^{-1}) × 0.06 L ÷ 90 h = 2.0773 × 10^{-3} g h^{-1};

-ΔH = heat of combustion of the ash-free biomass, which was calculated by the equation (3)[3]:

$$-\Delta H = \frac{(\%C \times 2.664 + \%H \times 7.936 - \%O) \times 100}{398.9} \times 13.2586\ (Kcal\ g^{-1}) \quad (3)$$

Where 398.9 is the degree of reduction of CH_4, and 13.2586 is the heat of combustion of CH_4.[11]

The biomass composition (% of C, H, O, N) of *R. palustris* and CdS-*R. palustris* cultured in MMN medium was analyzed by an elemental analyzer, according to the result (Table S3):

-$\Delta H_{R.\ palustris}$ = 6.2568 Kcal g^{-1}, -$\Delta H_{CdS\text{-}R.\ palustris}$ = 6.3767 Kcal g^{-1};

The TLEI is the total light energy input, which is estimated by the following equation:

$$TLEI = TSR \times 2.75 \times 10^{-3} \times 0.64 \times 0.89 \quad (4)$$

$$= 80 \times 0.85986 \times 2.75 \times 10^{-3} \times 0.64 \times 0.89$$

$$= 0.10775\ (Kcal\ h^{-1})$$

Where TSR is the total solar radiation impinging on horizontal surface per m^2 (Kcal h^{-1} m^{-2}); 80 is the light intensity of the fluorescent tubes (W m^{-2}); 0.85986 is the conversion factor from W m^{-2} to Kcal h^{-1} m^{-2}; 2.75×10^{-3} is the horizontal surface area of the 60 mL clear collection vials; 0.64 is the coefficient factor of the photosynthetic available radiation of *R. palustris* from 400 to 900 nm; 0.89 is the glass transmittivity.

$-\Delta H'$ = heat combustion of malate = 2.387 (Kcal/g);

MCE is the malate consuming efficiency (g/h), which is calculated by the malate assay:

The remained malate concentration in the MMN culture medium was quantified by the Malate Assay Kit (ab83391, abcam, UK). 200 μL aliquot of sample was centrifuged at 13,000 × g for 5 min and 100 μL supernatant was 100× diluted by 10 mL ultra-pure water. Then 50 μL of the diluted sample was aliquoted and mixed with 50 μL Reaction Mix in a clear 96 well flat-bottom plate (Costar, USA). The plate was incubated at 37 °C for 30 min in dark. The OD_{450} was measured by the spectrophotometric multiwell plate reader. Finally, the malate concentration was normalized by the standard curve plotted by Malate Standard (0 – 10 nmol). The assay was conducted in triplicate.

According to the result (Fig. S7), $MCE_{R.\ palustris}$ = 0.0471 g h^{-1}, $MCE_{CdS\text{-}R.\ palustris}$ = 0.0477 g h^{-1}. After calculation, the $PE_{R.\ palustris}$ = 4.31 %, and $PE_{CdS\text{-}R.\ palustris}$ = 5.98 %

Mechanism studies

■ *Light/dark cycle (12h:12h) experiment*

The cell culture collected from mid-exponential growth phase in SMN medium was centrifuged and adjusted to 6×10^8 cell/mL (OD680 ≈ 0.6) in the MMN medium. Aliquots of 50 mL the prepared culture medium was used to prepare the CdS-*R. palustris* hybrid system and control group as previously described. All the 60 mL vials were filled with pure CO_2 gas at atmospheric pressure at the headspace and anaerobically incubated on the orbital shaker at 10 RPM and illuminated by fluorescent tubes (80 W/m^2) using a 12h:12h light on/light off cycle. The culture temperature was controlled at 30 ± 1 °C. The CO_2 fixation study last for 8 d. At fixed time intervals, 1 mL aliquots of samples from the CdS-*R. palustris* group and control group were collected in triplicate for measuring the cell density.

■ *CdS loading experiment*

To investigate the relationship between increased cell density and the loaded CdS NPs on the cell surface, *R. palustris* loaded with different amount of CdS NPs was prepared by adding 0, 30, 60, 90 and 120 μL of 100 mM stock solution of $Cd(NO_3)_2$ and 1 mM cysteine in the MMN medium with *R. palustris* cells collected from the mid-exponential growth phase. The practical loaded concentration of CdS was calculated by the initial Cd^{2+} concentration and the CdS coating efficiency (Table S2). The experimental vials were incubated on the orbital shaker at 10 RPM and illuminated by fluorescent tubes (80 W/m^2) or in dark. The culture temperature was controlled at 30 ± 1 °C. Both the final cell density of the CdS-*R. palustris* group and control group under light irradiation and in dark were measured.

■ *CdS separation study*

To investigate the function of the close connection between CdS and cell, the isolated CdS NPs and chemically synthesized CdS from $Cd(NO_3)_2$ and cysteine was mixed with the natural *R. palustris* cells to simulate the situation of no connection. The mixed sample was denoted as separation study group. To make the intergroup result comparable, 0.2 mM and 1.0 mM chemically synthetic CdS from $Cd(NO_3)_2$ and cysteine was added into the prepared *R. palustris* culture for study. The CdS-*R. palustris* hybrid constructed from 0.2 mM Cd^{2+} were used for comparison. The obtained final cell density in all groups were measured.

■ *Electron scavenger study*

The Cr(VI) was used as electron scavenger to quench the photo-generated electrons from surface CdS for study. Before study, a biologically safe dosage range was surveyed by adding 0.05 - 0.5 mM Cr(VI) into the untreated *R. palustris* cell culture. The concentration that not resulted in significant loss of cell was defined as the safe range. According to the result (Fig. S8), 0.05 - 0.2 mM Cr(VI) was further used for scavenger study. Different volumes of stock solution of Cr(VI) was added into the 48 hours cultured CdS-*R. palustris* CO_2 fixation experimental groups, and the obtained cell density was monitored.

■ *Reduced organic carbon supplying study*

To investigate the enhanced inorganic carbon usage ability, the MMN medium with reduced malate was prepared for study (Table S1). After 48 h culture in MMN medium (44.7 mM malate), the formed CdS-*R. palustris* hybrid was transferred to MMN medium with reduced malate (original, 15 mM and 0 mM) for further CO_2 fixation study. Corresponding groups of

natural *R. palustris* were manipulated by the same procedures and set as control groups. The cell density in all groups were monitored.

■ *Initial cysteine concentration study*

To investigate the potential nutritional function and hole sacrificing function of the remained Cys in the medium to the CdS-*R. palustris* hybrid system, different initial concentration of Cys (0.25, 0.5, 0.75 and 1.0 mM) were added as the S^{2+} source for the CdS coating process. In addition, parallel control groups without adding 0.2 mM Cd^{2+} were added for comparison. The *R. palustris* with and without 0.2 mM Cd^{2+} prepared by different initial Cys concentration were anaerobically incubated on the orbital shaker at 10 rpm and illuminated by fluorescent tubes (80 W/m^2). The culture temperature was controlled at 30 ± 1 °C. 1 mL aliquots of samples from different groups were collected in triplicate for measuring the final cell density.

CO_2 fixation study under practical condition

The cell culture collected from mid-exponential growth phase in SMN medium was centrifuged and adjusted to 6 × 10^8 cell/mL (OD680 ≈ 0.6) in the MMN medium. Aliquots of 50 mL prepared culture medium were used to prepare the CdS-*R. palustris* hybrid system and control group in the 60 mL vials filled with pure CO_2 gas at atmospheric pressure at the headspace. All the vials were anaerobically incubated on the orbital shaker at 10 RPM and illuminated by a 300W xenon lamp with solar simulator accessories (Air Mass 1.5 filters, 100 W m^{-2}). The 12h:12h solar/dark cycle was applied. The culture temperature was controlled at 30 ± 1 °C. The CO_2 fixation study last for 8 d. At fixed time intervals, 1 mL aliquots of samples from the

CdS-*R. palustris* group and control group were collected in triplicate for measuring the cell density. The final dry weight of the obtained solid biomass and the carotenoid and PHB content in both groups were measured.

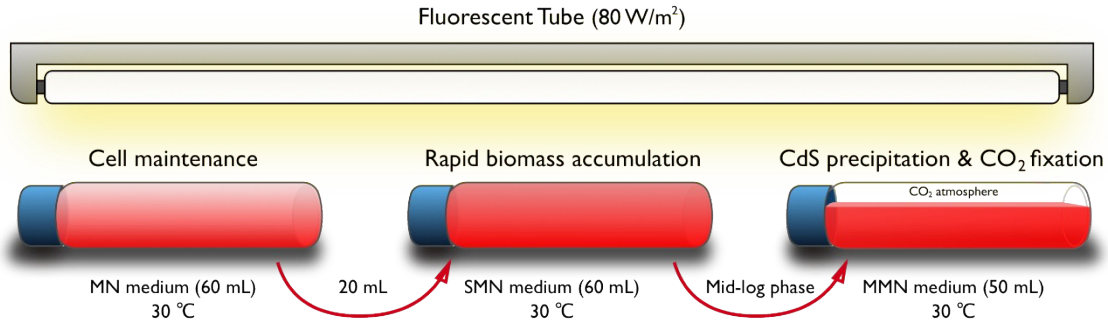

Fig. S1 Strategies of cell maintenance, rapid biomass accumulation and CdS precipitation & CO_2 fixation study

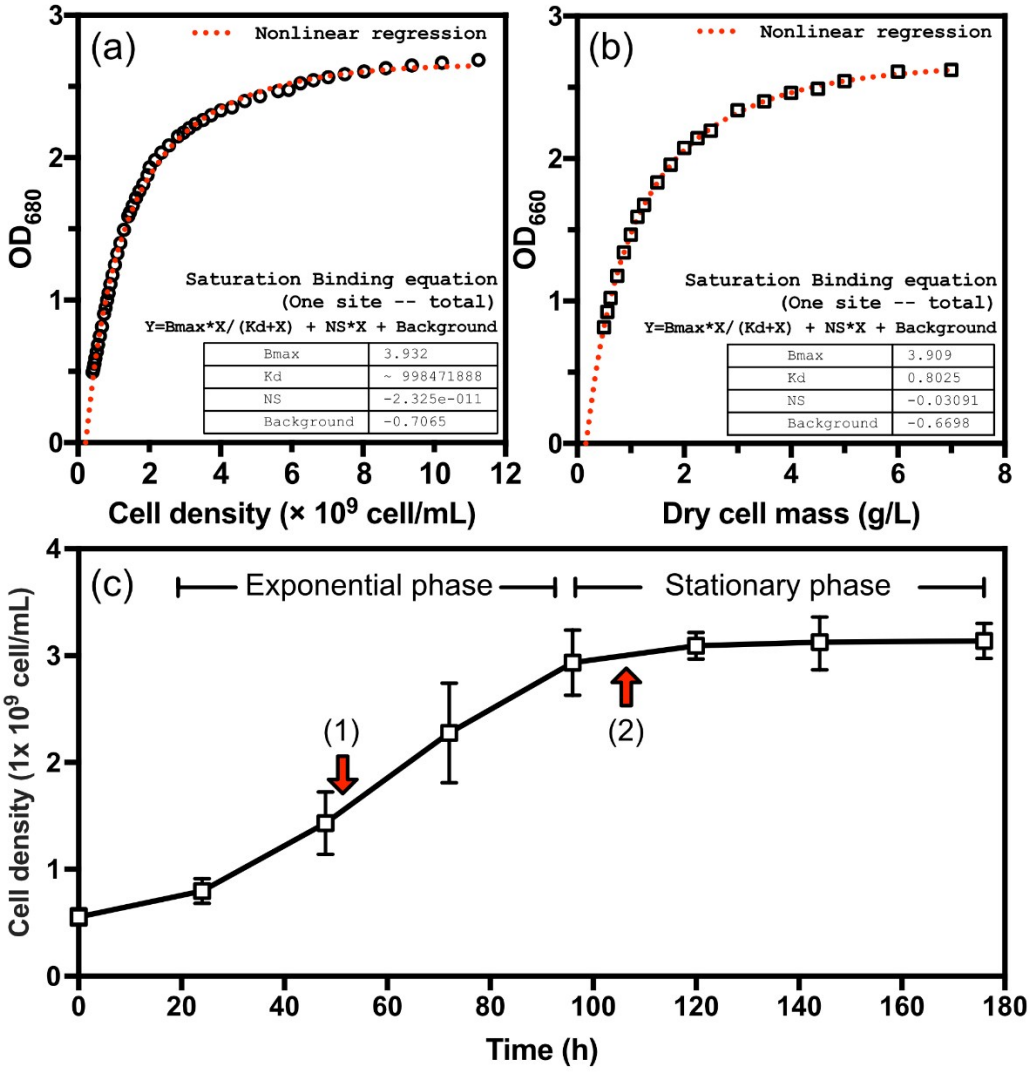

Fig. S2 (a) Standard curve of cell density (cell/mL) against optical density at 680 nm (OD_{680}), (b) Standard curve of dry mass (g/L) against optical density at 660 nm (OD_{660}) and (c) Growth curve of *R. palustris* in SMN culture medium. (1): mid-exponential growth phase, (2): early-stationary growth phase.

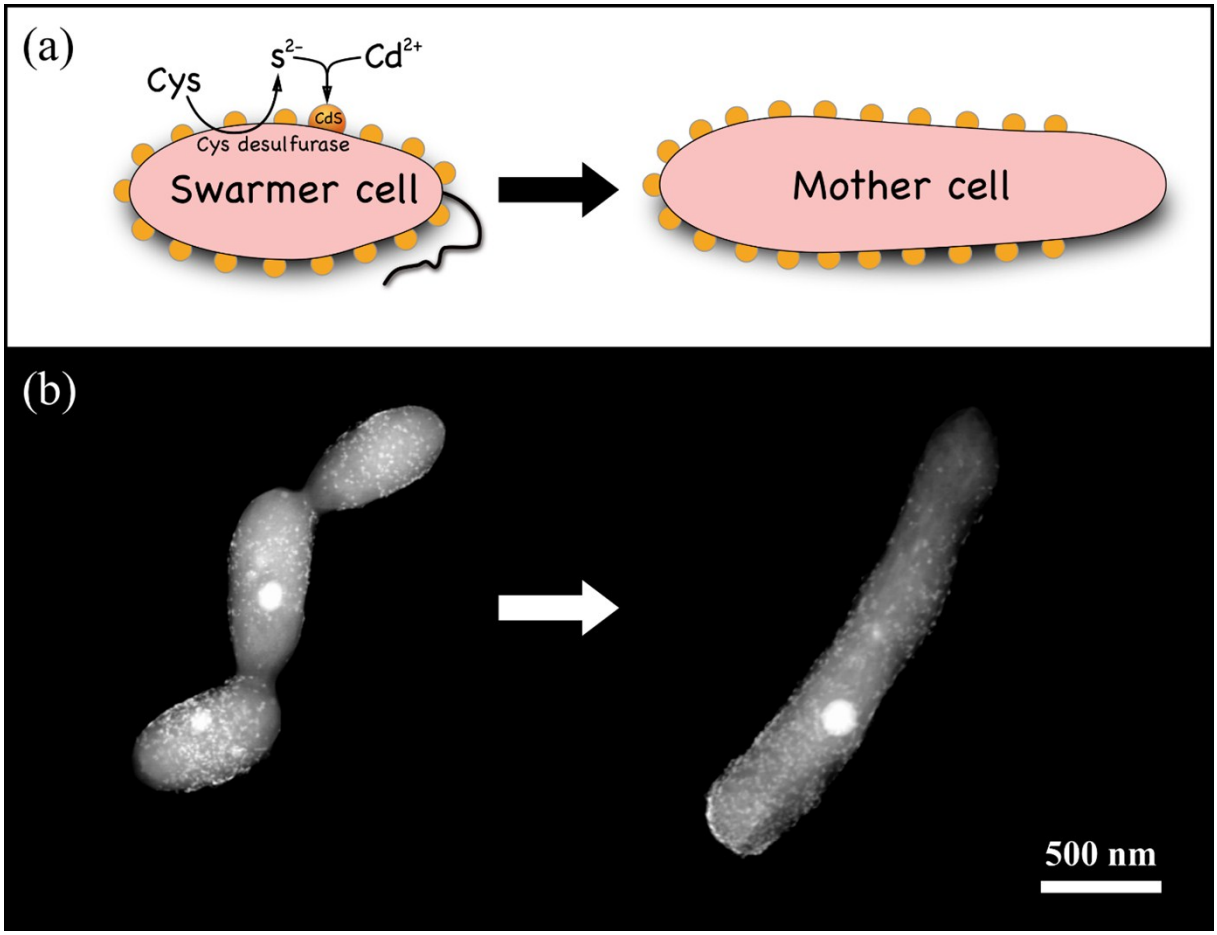

Fig. S3 (a) Schematic illustration of CdS formation on the swarmer cells from mid-exponential growth phase and development to mother cells, (b) HAADF image of the swarmer cell and developed mother cell.

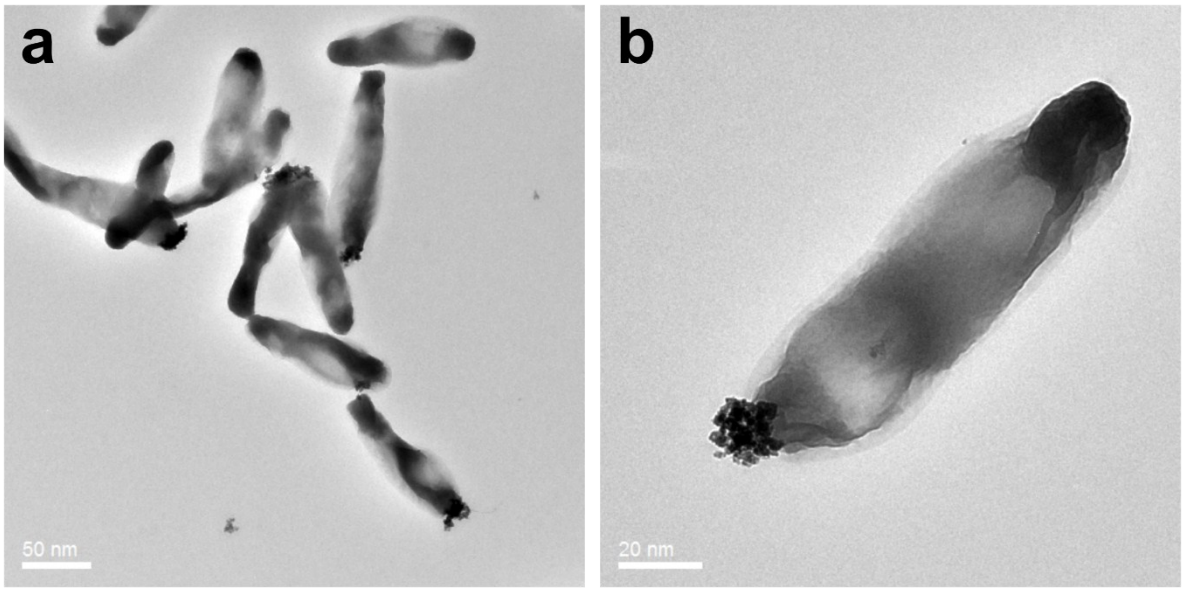

Fig. S4 TEM images of the CdS aggregated on one end of the mother cells from early-stationary growth phase.

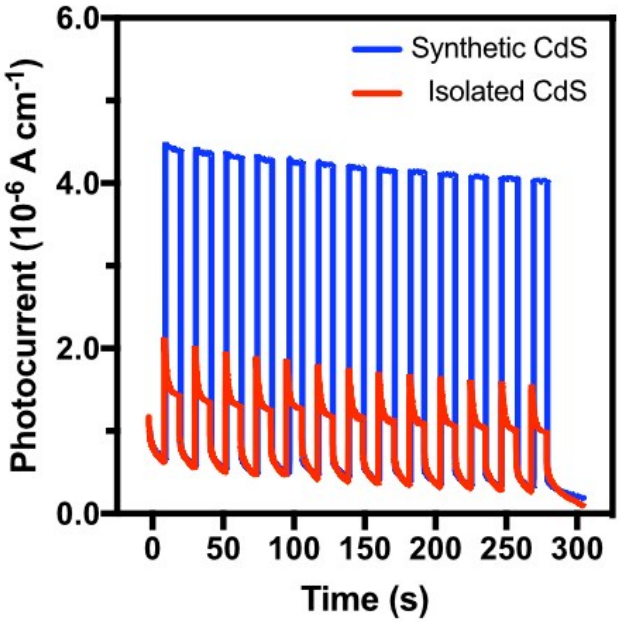

Fig. S5 Transition photocurrent of the isolated and synthetic CdS at 0.6 V versus Ag/AgCl

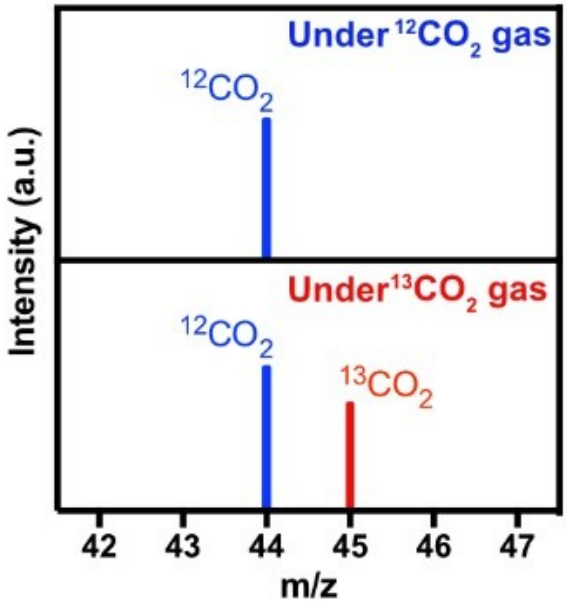

Fig. S6 Detection of the generated $^{12}CO_2$ (m/z=44) and $^{13}CO_2$ (m/z=45) from the solid samples of CdS-*R. palustris* hybrid system cultured under $^{12}CO_2$ and $^{13}CO_2$ gas, respectively.

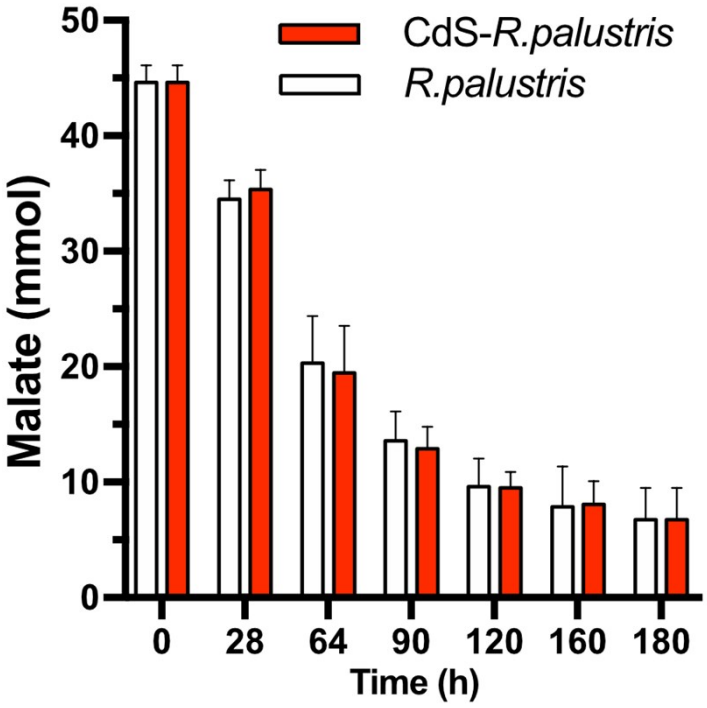

Fig. S7 Malate concentration of the CdS precipitation group and control group during the CO_2 fixation study.

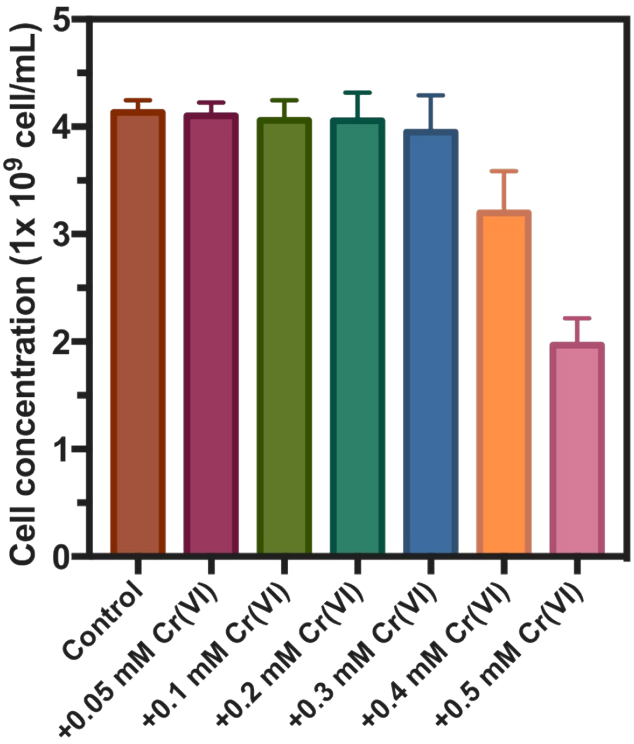

Fig. S8 Cr(VI) toxicity test to the *R. palustris*.

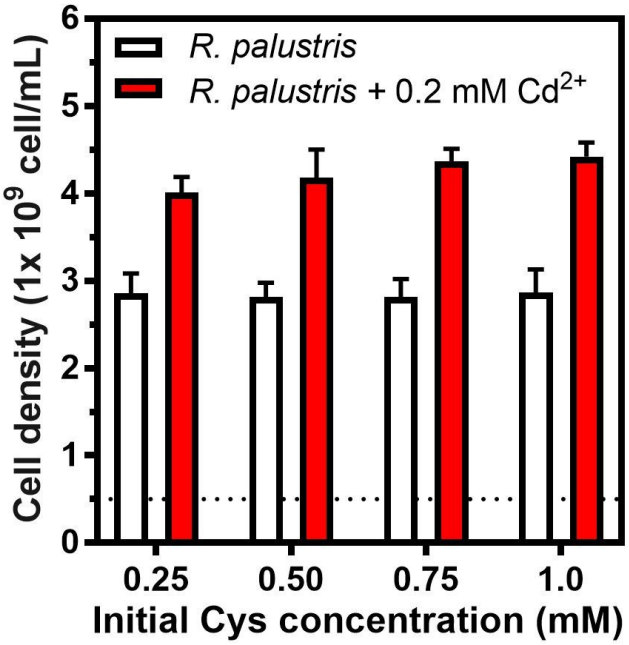

Fig. S9 Initial Cys concentration study. Dash line: starting cell density

Table S1. Mediums for cell culture, fast biomass accumulation, CdS precipitation, CO_2 fixation and mechanism studies.

MN medium	1000 mL
KH_2PO_4	600 mg
K_2HPO_4	900 mg
$MgSO_4 \cdot 7H_2O$	200 mg
$CaCl_2 \cdot 2H_2O$	75 mg
$FeSO_4 \cdot 7H_2O$	11.8 mg
Trace element solution	1 mL
EDTA (2% w/v)	1 mL
4-Aminobenzoic acid (30 mM)	0.1 mL
DL-malic acid	6 g (44.7 mM)
$(NH_4)_2SO_4$	1.25 g
NaOH	Adjust pH to 6.8
Ultrapure H_2O	to 1000 mL

Supplemented MN medium (SMN)	1000 mL
MN medium	1000 mL
Casein hydrolysate	3 g
Yeast extract	3 g

Modified MN medium (MMN)	1000 mL
10× Basic medium	100 mL
Trace element solution	1 mL
EDTA (2% w/v)	1 mL
4-Aminobenzoic acid (30 mM)	0.1 mL
DL-malic acid	6 g (44.7 mM)
$(NH_4)_2SO_4$	1.25 g
Cysteine	0.25, 0.5, 0.75 and 1.0 mM
KOH	Adjust pH to 6.8
Ultrapure H_2O	to 1000 mL

Trace element solution	100 mL
H_3BO_3	280 mg
$MnSO_4 \cdot 4H_2O$	210 mg
$Na_2MoO_4 \cdot 2H_2O$	75 mg
$ZnSO_4 \cdot 7H_2O$	24 mg
$Cu(NO_3)_2 \cdot 3H_2O$	4 mg

MMN (reduced organic carbon)	1000 mL
10× Basic medium	100 mL
Trace element solution	1 mL
EDTA (2% w/v)	1 mL
4-Aminobenzoic acid (30 mM)	0.1 mL
DL-malic acid	2.01/0 g (15/0 mM)
$(NH_4)_2SO_4$	1.25 g
Cysteine	1.0 mM
KOH	Adjust pH to 6.8
Ultrapure H_2O	to 1000 mL

10× Basic medium	1000 mL
MOPS	83.7 g
Tricine	7.2 g
β-glycerophosphate·2Na	3.44 g
$MgSO_4 \cdot 7H_2O$	2 g
$CaCl_2 \cdot 2H_2O$	750 mg
$FeSO_4 \cdot 7H_2O$	118 mg
K_2SO_4	481 mg

All the chemicals were obtained from BD Bacto and Sigma-Aldrich.

All mediums were filter sterilized before use.

Table S2. CdS coating efficiency of the cells collected at mid-exponential growth phase.

$Cd(NO_3)_2$ concentration	Remained Cd^{2+} in medium	Coating efficiency (CE)
0.05 mM	NA	100 %
0.10 mM	0.32 mg/L	97.15 %
0.15 mM	1.32 mg/L	92.19 %
0.20 mM	1.81 mg/L	91.93 %
0.30 mM	9.72 mg/L	71.23 %

NA: under detection limit

Table S3. Elemental composition and heat energy of combustion of *R. palustris* and CdS- *R. palustris* cultured in the MMN medium.

Biomass composition	***R. palustris***	**CdS-*R. palustris* hybrid**
C (%)	54.56	55.41
H (%)	8.67	8.95
O (%)	25.91	26.79
N (%)	10.86	8.85
Molecular formula	$CH_{1.91}N_{0.17}O_{0.36}$	$CH_{1.94}N_{0.14}O_{0.36}$
Heat energy of combustion (Kcal g^{-1})	6.2568	6.3767

Table S4. Photosynthetic efficiency of the natural cell and the CdS-*R. palustris* hybrid system.

Parameters	***R. palustris***	**CdS-*R. palustris***
Biomass productivity (g h^{-1})	1.5165×10^{-3}	2.0773×10^{-3}
Heat of combustion of the biomass (Kcal g^{-1})	6.2568	6.3767
Total light energy input (Kcal h^{-1})	0.10775	0.10775
Heat combustion of malate (Kcal g^{-1})	2.387	2.387
Malate consuming efficiency (g h^{-1})	0.0471	0.0477
Photosynthetic Efficiency (%)	4.31	5.98

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