

Supplementary Material

Calculations of faradaic efficiencies

$$\text{Faradaic efficiency} = \frac{\text{Amount of N or C fixed} \times \text{Number of electrons needed}}{\text{Total number of electrons delivered at cathode}} \times 100$$

N₂-, CO₂-fixing bioelectrochemical cell

At OD ~0.9, cell dry weight = 300 mg/L.

Therefore, at an OD of ~ 0.12 (OD at the start of the experiment), cell dry weight = 40 mg/L

At OD ~0.5 (OD at the end of 8 days in 100 mL bioelectrochemical cell), cell dry weight = 170 mg/L

Cell dry weight fixed in 8 days = 130 mg/L

Fixed N:

Assuming 14% of cell dry weight is N, weight of fixed N after 8 days = 1.82 mg/100 mL

Average rate of fixed N production = 0.23 mg/100 mL/day = 16.25 μmol N/100 mL/day

Number of electrons delivered at cathode = 576 μmol/100 mL/day

Number of electrons needed to fix one N atom (Assuming 0% recycling of H₂ produced by nitrogenase) = 4

Faradaic efficiency of N fixation = 11.3%

Number of electrons needed to fix one N atom (assuming 100% recycling of H₂ produced by nitrogenase) = 3

Faradaic efficiency of N fixation = 8.5%

Fixed C

Assuming 50% of cell dry weight is C, weight of C fixed after 8 days = 6.5 mg/100 mL

Average rate of fixed C production = 0.8 mg/100 mL/day = 67.7 μmol C/100 mL/day

Number of electrons delivered at cathode = 576 μmol/100 mL/day

Number of electrons needed to fix one C atom = 4 (2 NADPH, and hence 4 electrons per CO₂ needed for the Calvin cycle only; not considering electrons needed for further reduction to sugars or fatty acids)

Faradaic efficiency of C fixation = 47%

CO₂-fixing bioelectrochemical cell

At OD ~0.9, cell dry weight = 300 mg/L.

Therefore, at OD ~0.095 (OD at the start of the experiment), cell dry weight = 31.7 mg/L

At OD ~0.41 (OD at the end of 8 days in 100 mL bioelectrochemical cell), cell dry weight = ~137 mg/L

Cell dry weight fixed after 8 days = 105 mg/L

Fixed C

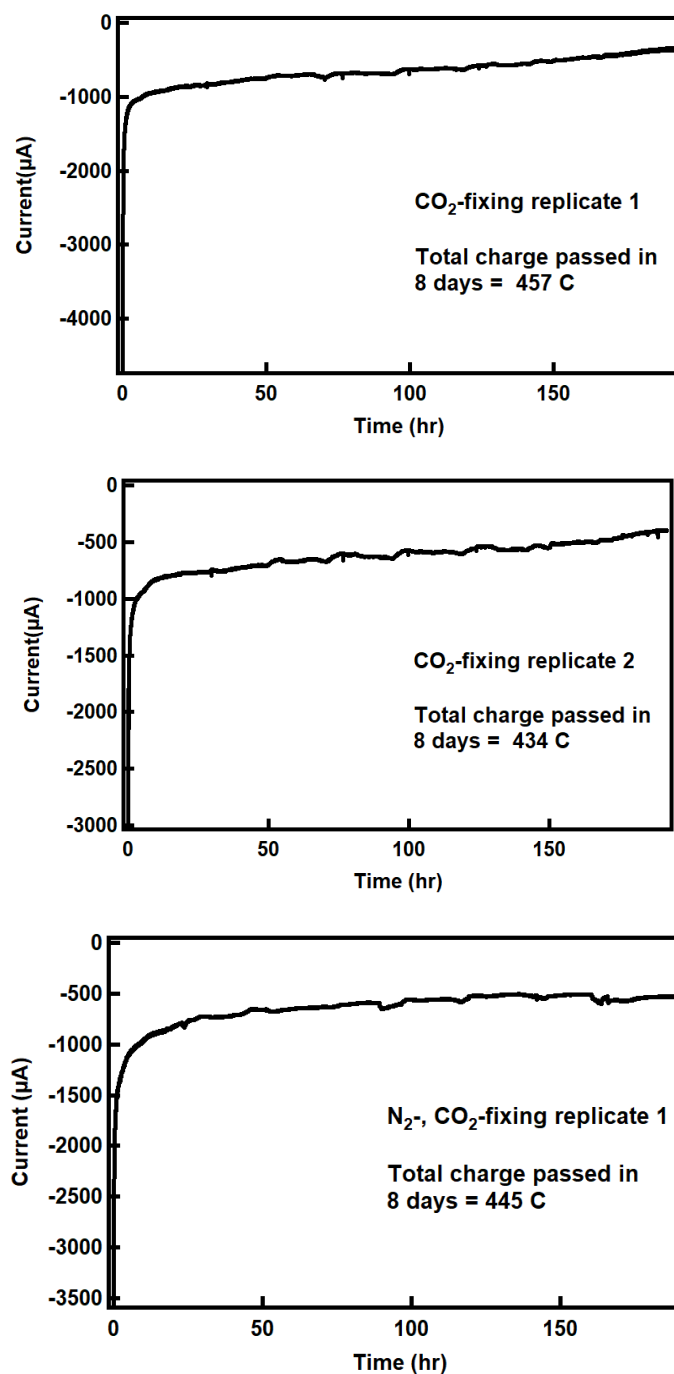
Assuming 50% of cell dry weight is C, weight of C fixed after 8 days = 5.26 mg/100 mL

Average rate of fixed C production = 0.66 mg/100 mL/day = 54.8 μ mol C/100 mL/day

Number of electrons delivered at cathode = 577 μ mol/100 mL/day

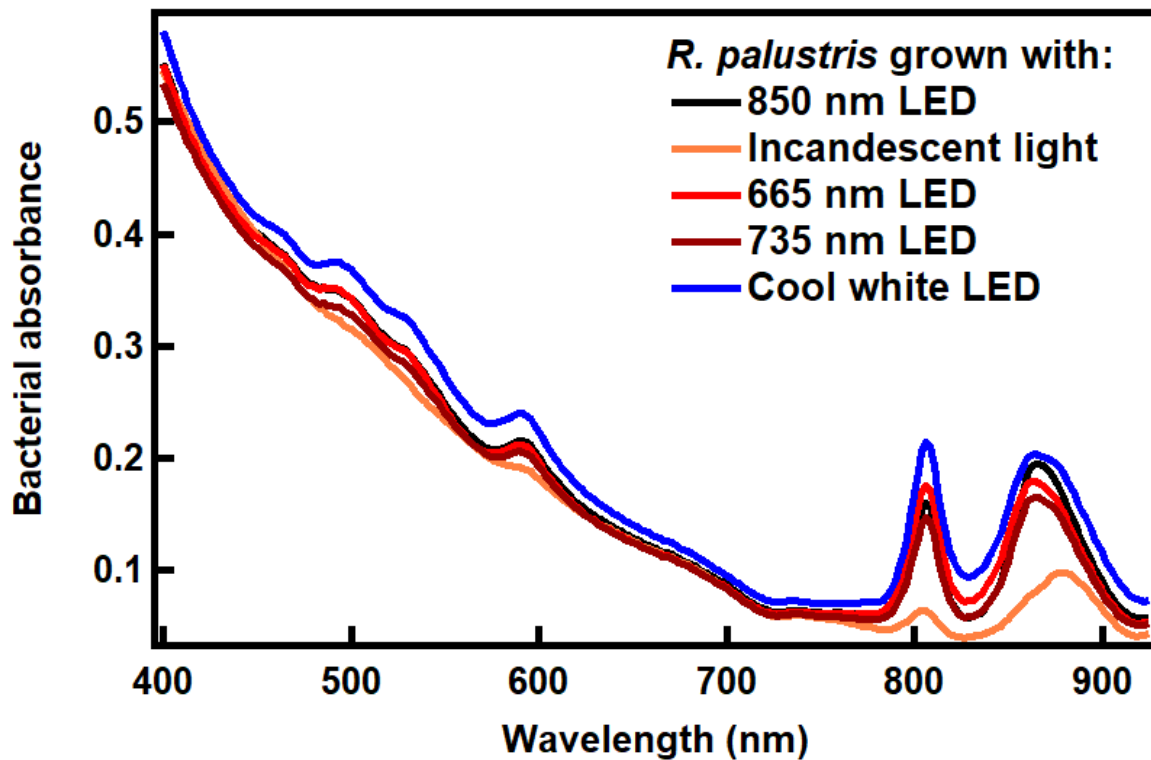
Number of electrons needed to fix one C atom = 4 (2 NADPH, and hence 4 electrons per CO₂ needed for the Calvin cycle only; not considering electrons needed for further reduction to sugars or fatty acids)

Faradaic efficiency of C fixation = 38%



Supplementary Figure 1: Current passed through the bioelectrochemical system under different growth conditions. All the bioelectrochemical growths were performed at a potential difference of -3 V with respect to the counter electrode (~ -1.4 V vs Ag/AgCl reference) with 16-gauge platinum wires as the cathode and anode. The electrolytes were not stirred under CO₂-fixing conditions, but were stirred under N₂- and CO₂-fixing conditions to allow for higher currents that were necessary to support bacterial growth under N₂-fixing conditions.

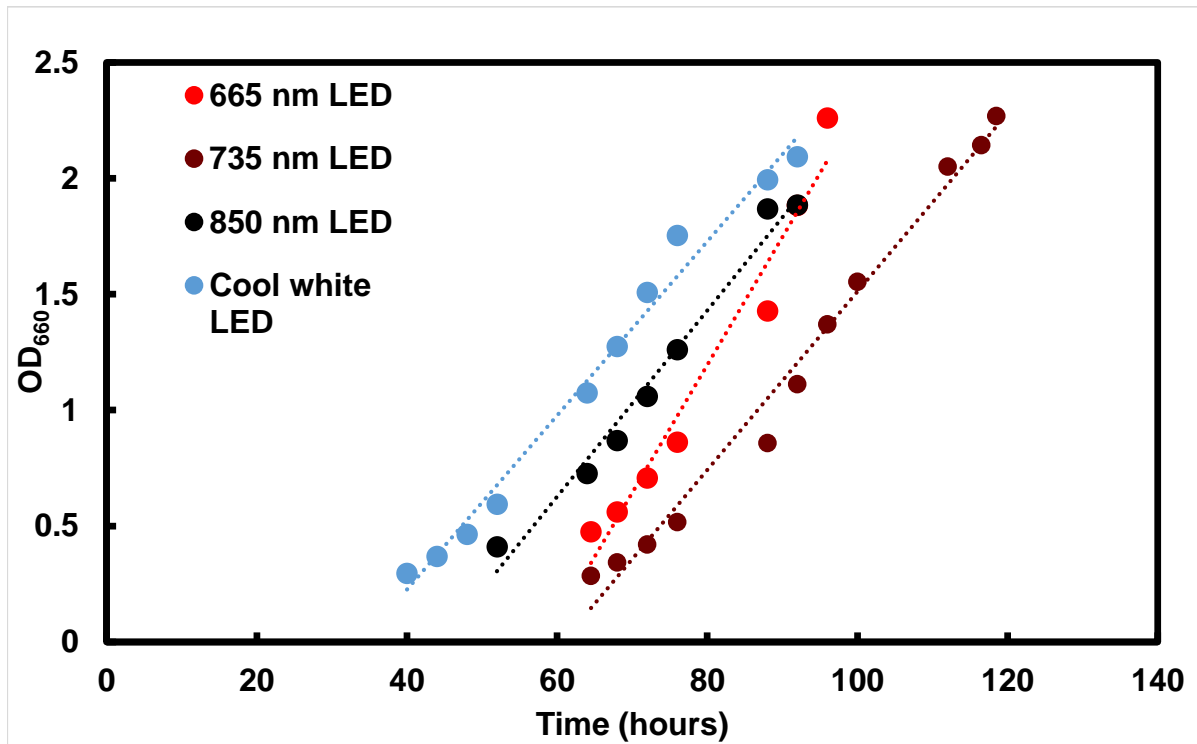
Whole cell absorbance spectra of bacteria grown under different light conditions



Supplementary Figure 2: Whole cell absorbance spectra of *R. palustris* TIE-1 grown under different light conditions. The cell densities were normalised by the OD₆₆₀.

Calculation of doubling time

Doubling times were calculated from the average OD measurements. The data was plotted in Microsoft Excel and the linear region was identified by fitting different time ranges to a linear trendline that would give an R^2 value of 0.95 or greater (**Supplementary figure 3**). Within the identified linear phase, the time taken for one doubling of the bacteria was identified and reported as the doubling time. The doubling times are summarized in **supplementary table 1**.



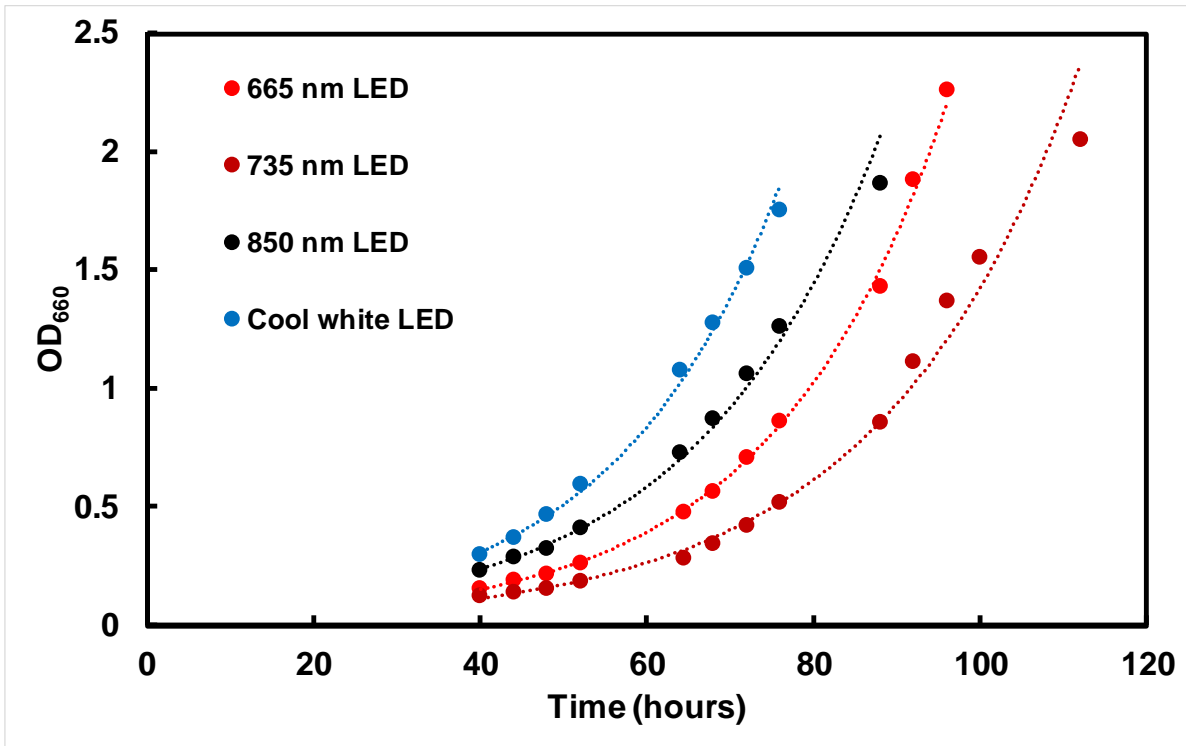
Supplementary Figure 3: Regions of linear growth identified for the four different light conditions identified by fitting the data to a linear trendline on Microsoft Excel 2016 and selecting the range that had the highest R^2 value. All R^2 values for the given range were above 0.95.

Calculation of specific growth rate

$$\text{Specific growth rate} = \frac{\ln \frac{A_1}{A_0}}{t_1 - t_0}$$

Where A_0 , A_1 are absorbances at times t_0 and t_1 respectively.

The region of exponential growth was identified by fitting the data to an exponential curve on Microsoft Excel 2016 and identifying the data range that provided the highest R^2 value. (**Supplementary figure 4**). The first 40 hours was ignored for all wavelength conditions as this most likely represented the lag phase of bacterial growth. The specific growth rate identified was the average of the growth rates during the identified intervals for each growth curve. The identified growth rates are summarized in **supplementary table 1**.



Supplementary Figure 4: Regions of exponential growth identified for the four different light conditions identified by fitting the data to an exponential curve on Microsoft Excel 2016 and selecting the range that had the highest R^2 value. All R^2 values for the given range were above 0.99.

Supplementary table 1: Summary of growth rates calculated for growth with different wavelengths of light

<u>Wavelength condition</u>	Cool white LED	850 nm LED	665 nm LED	735 nm LED
<u>Doubling time (h)</u>	16	20	16	16
<u>Specific growth rate (h⁻¹)</u>	0.05	0.05	0.05	0.04