

Supplementary Information

Self-assembled photosystem-I biophotovoltaics on nanostructured TiO₂ and ZnO

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Part of the motivation behind the use of high surface area photoanodes in the form of TiO₂ nanocrystals and ZnO nanowires in this study was making obsolete the need for incident-photon conversion efficiency (IPCE) curves obtained by laser illumination. Self Assembled Monolayers (SAMs) of photosynthetic proteins have very low optical densities (ODs) which is the reason nature employs highly convoluted folded membrane structures (such as those found in chloroplasts) for photosynthetic light harvesting. In order to achieve a practical framework for characterization-optimization feedback loops aimed at increasing efficiencies for PS-I and other low-yield biophotovoltaics devices, it is advantageous to move away from low-OD systems. This is not only because blasting photosystems with coherent light containing 100x the power of AM1.5 sunlight, concentrated into the absorption peaks is a dramatically unrealistic emulation of the natural illumination the complex evolved and generally operates in, but also because study under these conditions requires complex, expensive equipment. The need for this unrealistic and esoteric arrangement makes the study of biophotovoltaics a niche field addressable only by the higher-end equipped laboratories. We have strived to “engineer the difficulty out” of biophotovoltaics research in order to democratize access hoping to start an efficiency and lifetime race by laboratories around the world.

Our controls were rigorously designed to show how it is possible to be certain the photovoltaic action comes from the active ingredient, without necessitating the use of laser IPCEs. Specifically: the shapes of the IV curves shown in Figure 4 of the main text, which were obtained upon exposing our devices to AM1.5 sunlight for both PS-I complexes on TiO₂ and bioengineered PS-I on ZnO nanowires, show striking similarity to conventional DSCs. After accounting for the UV-excited photocurrent (shown in main text Fig 2 B). the following four types of control devices, containing all buffer components and electrolyte, did not yield any additional photovoltaic action:

- i) Devices made with denatured PS-I (boiled for 10min)
- ii) Blanks without PS-I or A₆K
- iii) Blanks without PS-I but with A₆K
- iv) Devices with PS-I but no A₆K.

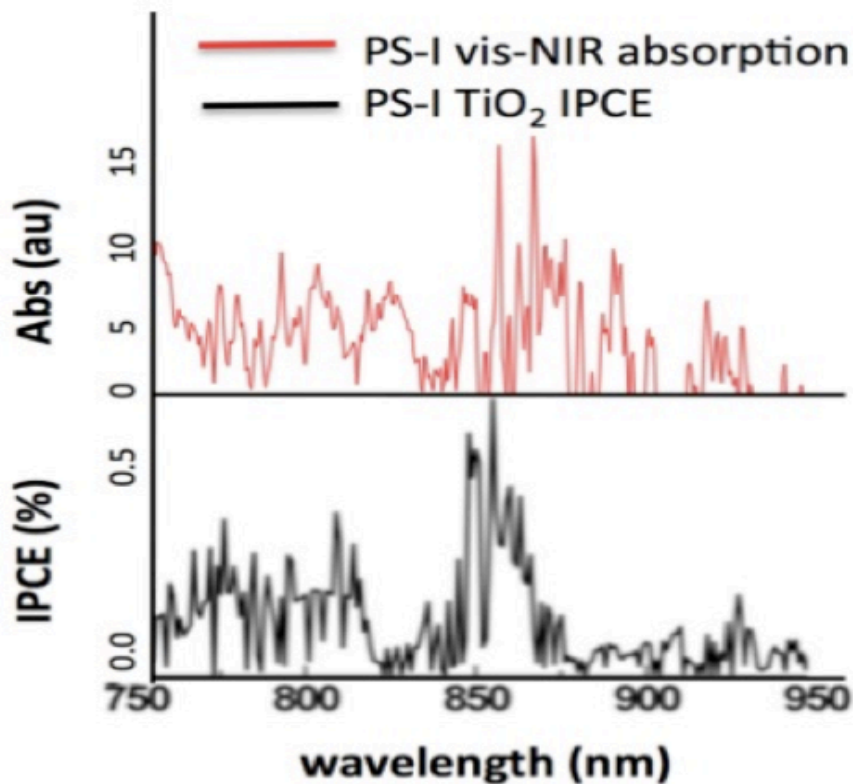
These four controls leave stabilized, non-denatured PS-I as the only possible agent behind 80% of the maximum measured photocurrent (the remaining 20% being due to UV excitation of TiO₂ and ZnO).

As in the main text, we re-emphasize here that these photocurrents cannot be attributed to sensitization by leached chlorophyll, because unless precisely organized by the PS-I scaffold, chlorophyll alone does not act as a photovoltaic sensitizer¹, the interaction between the chlorophyll ester units with the TiO₂ surface is weak and chlorophyll does not adsorb¹⁷ on TiO₂ or ZnO .

The above results make IPCE curves unnecessary to support any of our conclusions.

However, partly because we had access to the necessary equipment and partly because IPCEs have been (by prior necessity now removed by our findings) accepted as the mainstay of biophotovoltaic studies, we here present the IPCEs obtained upon realistically simulated sunlight illumination of our devices.

Note that it is expected that the photocurrents per wavelength would be at the limit of detection and highly noisy since we are spreading only one sun's AM1.5 power over the entire spectrum instead of 100 suns worth of power, coherently concentrated into individual absorption peaks.



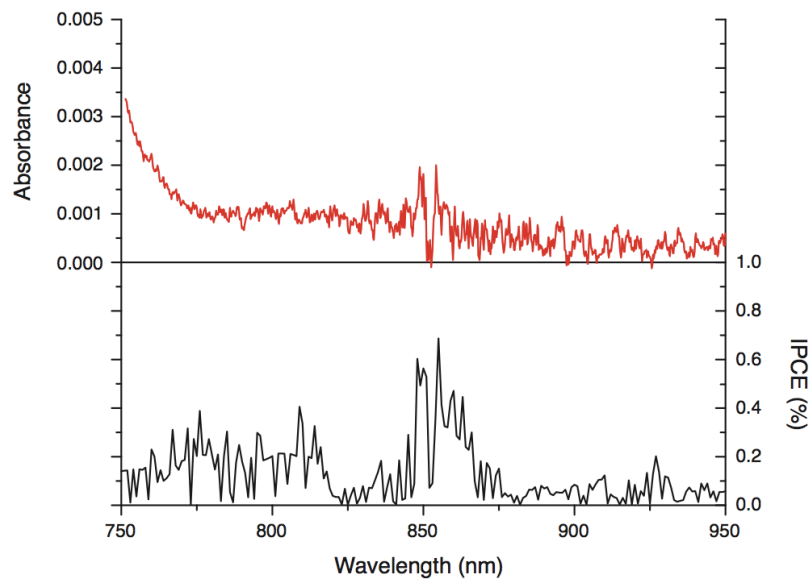
IPCE of PS-I devices on TiO₂ (black) and visible–near-infrared absorption spectrum of PS-I extract (red).

The IPCE shown in the above spectrum was taken as a homage to prior reports⁵⁻⁸. Importantly, the IPCE of a blank TiO₂, identically constructed and illuminated but with no PS-I was undetectable as was the case for controls with denatured PS-I (extract boiled for 10minutes resulted in no changes in color or optical density), further confirming it is indeed the function of PS-I that generates the photovoltaic power.

The visible-near infra-red absorption spectrum of our PS-I was measured as follows.]: PS-I was diluted to 0.2 mg chl a per ml in 20 mM MES pH 6.4, 10mM CaCl₂, 10 mM MgSO₄ and 0.03% BDDM. Absorbance measurements were recorded every 0.5nm between 750 and 950 nm in triplicate using a Shimadzu 3101PC spectrophotometer at room temperature in a 1cm cuvette. Replicates were averaged and smoothed using the Savitzky-Golay method with a window of 11 data points.

Below we also present the unsmoothed data:

Note that the baseline shift is due to the necessary detector monochromator swap between the Vis and NIR portions of the spectrum. The magnitude of this shift was determined and subtracted out of the spectrum. The baseline presented here is corrected and all smoothing removed. The only portions of the spectrum below zero are within the noise level as expected.



Crucially, all control (blank and boiled PS-I) devices on TiO_2 resulted in undetectable IPCE upon exposure to full sunlight giving $P_{\text{out}} 28\mu\text{W}/\text{cm}^2$, with $277\mu\text{A}/\text{cm}^2 I_{\text{sc}}$ and $257\text{mV } V_{\text{oc}}$ with a fill factor of 0.39 consistent with excitation of unsensitized TiO_2