Simple Photoreduction of Carbon Dioxide to Formic Acid and True Quantum Yield

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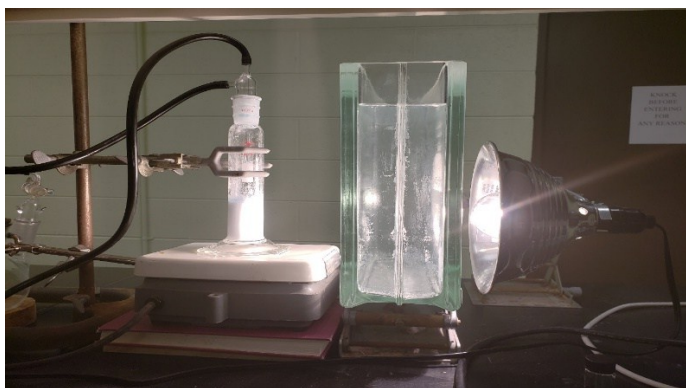
Supplemental Figure S1.

Figure S1. Photoreduction experimental setup (Photographed by Ovuokenye Omadoko).

S2: Stoichiometric Yield Based on the Amount of Carbon Dioxide.

$$P_{CO_2} = k_H \, [CO_2]_{aq} \tag{S1}$$

Equation S1 was used to find the theoretical yield by determining the amount of formate possible. In this equation, P_{CO_2} represents pressure of atmospheric CO_2 in atm, and 'k_H' is Henry's constant for CO_2 in atm/M at room temperature (29 atm/M).[23] At 1.00 atm the concentration of aqueous CO_2 can be calculated using equation S1 and is 0.034 M. Equation S2 shows the conversion of this concentration to ppm.

$$\left(\frac{0.034 \text{ mol } CO_2}{L}\right)\left(\frac{1 \text{ mol HCOOH}}{1 \text{ mol } CO_2}\right)\left(\frac{45.00 \text{ g}}{1 \text{ mol HCOOH}}\right)\left(\frac{1,000 \text{ mg}}{1 \text{ g}}\right) = 1,530 \text{ ppm formate}$$

(S2)

Using the experimental yield of formate after 96 hours of illumination of the TiO_2/InPC system

(23.5 ppm), and the theoretical yield of 1,530 ppm results in a stoichiometric yield of 1.54%.

S3: Calculating the True Quantum Yield.

A Hamamatsu S2387 33R photodiode was calibrated using the potassium iron oxalate

actinometry method using Equation S3.[63]

$$N_q = \frac{\Delta A \; V_1 \; V_3}{\Phi(\lambda) \; \mathcal{E}(514 \text{ nm}) \; V_2 \; l \; t}$$

(S3)

N_q is moles of incident photons in einsteins per second. The quantity ΔA is the change in

absorbance of the iron 1,10-phenanthroline complex before and after illumination. The term

$\Phi(\lambda)$ is the quantum yield for reduction of Fe^{3+} to Fe^{2+} ion, which is 0.93 for a 0.2 M potassium

iron oxalate solution using 514 nm radiation. The quantity V_1 is volume of $K_3Fe(C_2O_4)_3$ solution

irradiated, V_2 is volume of solution analyzed after irradiation, V_3 is total volume of the solution

after adding 0.1% 1,10-phenanthroline buffer solution and water, $\mathcal{E}$ (514 nm) is the molar

absorption coefficient of the iron 1,10-phenanthroline complex (11,100 L·mol-1·cm⁻¹), l is

optical pathlength and t is irradiation time in seconds. For trial 1 using equation S3, the number

of moles of photons per second absorbed is calculated in Equation S4.

Table S1. Three actinometry trials calibrating the photodiode.

Trial	Before Illumination	After Illumination

	Absorbance	Absorbance
1	0.103	0.169
2	0.103	0.186
3	0.103	0.181

$$\frac{(0.066)(3.5\ mL \times 10^{-3})(10.4\ mL)}{(0.93)(11,100\ Lmol^{-1}cm^{-1})(1.2\ mL)(1\ cm)(18,000\ s)} = 1.1 \times 10^{-11}\ einsteins/s$$

(S4)

The number of einsteins/s, the photodiode current measured (1.8 µA), given area of the

photodiode (5.7 mm^2) and incident area of heterogeneous solution (3,500 mm^2) enabled

determination of a photodiode constant ($S_{\lambda,A}$) in units of einsteins/(A·s). This calculation is

shown in equation S5.

$$S_{\lambda,A} = \frac{(1.1 \times 10^{-11}\frac{einsteins}{s})(3,500\ mm^2)(0.7)}{(1.8 \times 10^{-6}A)(5.7\ mm^2)} = 2.6 \times 10^{-3}\ einsteins/(A·s)$$

(S5)

The photodiode increases in sensitivity linearly from 0.2 A/W at 400 nm to 0.5 A/W at 800 nm

as given in the data sheet for the photodiode. Assuming an ideal sensitivity of 0.5 A/W across the

visible range, an area ratio (0.7) of the sensitivity of the photodiode from approximately 400 to

800 nm corrects the photodiode constant in equation S5 for counting polychromatic photons.

Three trials calibrating the photodiode resulted in an average value of

3.2 ± 0.4 x 10^{-3} einsteins/(A·s). The calibrated photodiode was illuminated directly by the 150

W incandescent source and the direct current (183 µA) was measured using a multimeter. The

photodiode was also used to measure the reflected light from the heterogeneous solution and photoreactor (165 µA). The difference is 18 µA and using time in seconds (86,400 s) the number of photons incident are calculated in equation S6.

$$(3.2 \pm 0.4 \times 10^{-3}\frac{einsteins}{A.S})(0.18 \pm 0.06 \times 10^{-4}A)(86,400\ s) = 5.0 \pm 1.8 \times 10^{-3}einsteins \tag{S6}$$

To determine the number of photons absorbed, the absorbance from Diffuse UV-Visible experiments using integrated sphere measurements of the MPC/TiO$_2$ solutions was used. The spectra were integrated using Vernier logger-pro software to determine the area. To account for absorption of photons due to the added InPC only, the absorbance area of TiO$_2$ only was subtracted from the area with InPC and divided by the area of TiO$_2$ and InPC. Using 0.5 g TiO$_2$ and 10 mg InPC, the number of absorbed photons is given in Equation S7.

$$(5.0 \pm 1.8 \times 10^{-3}einsteins)(\frac{145.92}{957.19}) = 7.6 \pm 2.7 \times 10^{-4}einsteins \tag{S7}$$

The amount of formate obtained using 0.5 g TiO$_2$ with 5 mg of InPC and irradiation in 50 mL solution was determined to be 3.6(±0.2) ppm. The corresponding number of moles is given in Equation S8.

$$\frac{(7.2 \pm 1.2\ mg)(1\ g)(1\ mol)(0.05\ L)}{(1\ L)(1000\ mg)(45\ g)} = 8.0 \pm 1.3 \times 10^{-6}\ mol\ formate \tag{S8}$$

Considering that one einstein is a mole of photons, the quantum yield for formate obtained within 24 hours of irradiation can be calculated as shown in Equation S9.

$$\Phi_{formate} = \frac{2(8.0 \pm 1.3 \times 10^{-6}mol)}{(7.6 \pm 2.7\ x\ 10^{-4}\ einsteins)} \text{ x } 100\% = 2.1 \pm 0.8\% \tag{S9}$$

The quantum yield of formate for using 0.5 g TiO_2 and 5 mg InPC was found to be $1.9 \pm 0.7\%$, $1.8 \pm 0.7\%$ and $1.7 \pm 0.6\%$ after 48, 72 and 96 hours of irradiation respectively. The results indicate that quantum yield is identical within error from 24 to 96 hours of illumination.