Supplementary Information to:

Artificial Foliage with Remarkable Quantum Conversion Efficiency in Bicarbonate to Formate

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Experimental procedures

Materials

 TiO_2 and Cu_2O , glycerol, zinc and cobalt phthalocyanines were purchased from Sigma-Aldrich and used without further purification. Quartz plates with 3.5" diameter was purchased from Technical Glass Products (TGP).

Device fabrication. Quartz plates were cleaned with soap water, ethanol, and acetone. Zinc and cobalt phthalocyanine were each deposited at 100 nm thickness. Cu₂O was also thermally deposited at 10^{-5} mbarr with a deposition rate setting at 2A/s while TiO₂ was spin coated. Control experiment 1 was conducted by adding 0.1 mg/mL of Cu₂O into the buffer, testing its photocatalytic efficiency alone, and suspending a quartz plate of zinc or cobalt phthalocyanine (denoted Cu₂O, Cu₂O ZnPc, and Cu₂O CoPc). Control experiment 2 was conducted by adding 0.1 mg/mL of TiO₂ into the buffer, testing its photocatalytic efficiency alone, and suspending a quartz plate of zinc or cobalt phthalocyanine (denoted TiO₂, TiO₂ ZnPc, and TiO₂ CoPc). Device 1 consisted of a bilayer of Cu₂O and zinc/cobalt phthalocyanine (each 100 nm thick) (denoted Cu₂O/Pc) and device 2 consisted of a bilayer of TiO₂ thin films were tested with the phthalocyanine layer (denoted Cu₂O/ and TiO₂/). Mass amounts for each MPc/Sc thin film are listed in Table S1.



Figure S1. a) Schematic of reactor, b) 100 nm zinc phthalocyanine on quartz plate as indicated by MBraun layer-depth indicator, and c) photograph of photo-experiments using the reactor.

Characterization for ZnPc/Cu₂O Device

The as-prepared sample was coated with 20 nm thick Al by e- beam evaporation to increase the conductivity in SEM/FIB and to protect the sample surface as well. The 80 nm thick cross-sectional TEM thin section was prepared in a FEI Q3D dual beam system. Prior to the sectioning, the sample surface was coated by 150 nm e-beam Platinum deposition (Pt-dep), and additional 4 um Pt-dep was made by ion-beam assisted deposition on top of the e- beam Pt-dep, to further protect the surface, preventing the surface from being damaged by ion beam. TEM analysis was carried out on JEOL 2010F TEM/Scanning TEM.





Figure S2. In scanning TEM mode, EDS spectra were collected while the beam was scanning across the sample surface vicinity (see the yellow line), demonstrating the existence of Cu_2O layer and ZnPc layer.



Figure S3. (a) Regular TEM image, the contrast is a bright-field contrast, wherein heavy features look dark. (b) Scanning TEM image, using Annular dark-field detector. The contrast is a dark-field contrast, wherein heavy features look bright



Figure S4. XRD shows peaks for the Zn component (corresponding peaks for [100,200] at 6.8° and [-101,-202] at 9.4°); however Cu₂O is seems to be missing. This may be due to the Cu₂O on quartz slide is amorphous or in too small concentration for the detection.

<u>FTIR</u>

No peaks were observed. The concentrations of ZnPc and CuO could be below the detection limits.

UV-VIS spectra



Figure S5. Optical absorption spectrum of thin film ZnPc and Cu₂O on quartz disk.

Luminescence Spectrum of the thin film



Figure S6. Normalized solid state fluorescence spectra of thin film with excitation at 450 nm.

Photo-experiments. Irradiation experiments were carried out in a self-built reactor. A petri dish was filled with the bicarbonate buffer and placed under the solar simulator. Fishing wires were used to suspend the quartz plate containing the thin films so that the semiconductor layer is in contact with the buffer.

Reaction matrix: a buffer made of 20 mL, 0.3 M NaHCO₃, 2 M glycerol as a sacrificial hole scavenger, and Milli-Q water. For experiments in the aqueous phase, Cu₂O and TiO2 catalysts were added at a concentration of 0.1 mg/mL. The matrix was transferred to a petri dish, and placed under an ABET Technologies SunLiteTM solar simulator with AM 1.5 filter for 8 hours. The light source was a 1000 W xenon arc lamp with an output of 1000 W/m², the equivalent of 1 sun.¹ Aliquots were collected at two hour increments, and formate concentration was quantified by ion chromatography.

UV-Vis spectroscopy. UV-Vis spectra of the particles were obtained using a Varian Cary 50 Scan UV-Vis spectrophotometer, with wavelength ranging from 800 to 200 nm. Cu_2O samples were dispersed in ethanol, while the TiO₂ samples were dispersed in milli-Q water.

Diffuse reflectance spectroscopy (DRS). TiO₂, Cu₂O, and phthalocyanine powders were analyzed by a Thermo Scientific Evolution 260 Bio UV-Vis spectrophotometer with an integrated sphere in order to obtain its band gap. To prepare the sample, 5% of semiconductor or phthalocyanine and 95% KBr pellets were mixed and ground using a mortar and pestle. Wavelengths were scanned from 800 to 200 nm. The resulting absorbance spectra were treated to a Kubelka-Munk function plotted against the energy of the incident light to obtain band gap information.

Cyclic voltammetry. In order to place the band gaps obtained via DRS on an absolute energy scale, cyclic voltammetry was performed using a EDAQ ET014 Echem Electrode kit with an Ag/AgCl reference electrode, platinum wire counter electrode, and a glassy carbon working electrode. The voltage was swept from -1000 to 1000 mV at a rate of 100 mV/s. The electrolyte used was 0.1 M tetraethylammonium tetrafluoroborate (TBABF₄) solution in dry acetonitrile. The procedure for CV was adapted from Fang *et al.*² For powder samples, suspensions were made of 1 mg/mL in ethanol and sonicated for one hour to ensure suspension. After sonication, 60 μ L of 5% Nafion solution was added to the suspension, and 4.5 μ L of the resulting solution was pipette onto a glassy carbon electrode (GCE) and allowed to dry. Several applications of the solution were required to ensure full coverage of the GCE surface.³ Since a Ag/AgCl reference electrode was used, the equation (1) is used to convert onset redox potentials to normal hydrogen electrode (NHE) values.^{3,4}

$$E(NHE) = E (Ag/AgCl) + 0.197 V$$
⁽¹⁾

Ion chromatography. Ion chromatography was performed on a Dionex AS50 IC with a Dionex IonPac ICE-AS6 ion exclusion column and a Thermo Scientific Dionex AMMS-ICE 300 suppressor. The IC instrument is equipped with a Dionex CD25 conductivity detector. Reagents used were 0.4 mM heptafluorobutyric acid as the eluent at a flow rate of 1.2 mL/min and 5 mM tetrabutylammonium hydroxide as the regenerant.

Apparent Quantum Efficiency (AQE). Using an Ophir Photonics Nova II laser energy meter, the energy output of the solar simulator was measured and set it up to 100 mW/cm² (1000 W/m²) The apparent quantum efficiency (AQE) of the catalyst were calculated using equations (2) and (3).

n mol photons
$$\cdot \frac{1 \text{ mol } e^-}{\text{mol photons}} \cdot \frac{\text{mol formate}}{2 \text{ mol } e^-} = \text{theoretical}$$
 (2)

$$\frac{\text{actual mol formate}}{\text{theoretical mol formate}} \cdot 100 = \% \text{AQE}$$
(3)

Number of moles of photons were calculated using equations (4), (5) and (6). Calculations were adapted from *Zubair et al.*⁵

total number of photons absorbed
$$=$$
 $\frac{\text{light absorbed by the photocatalyst}}{\text{light absorbed by the photocatalyst}} \times \text{time}$ (4)

light absorbed by the photocatalyst = intensity of the light \times surface area (5)

energy of the photon (E)
$$=$$
 $\frac{hc}{\lambda}$ (6)

Where h is the plank constant, c is the speed of light and, λ is the average wavelength of broad band light. For an example; for TiO₂; band gap is 3.2 eV and corresponding wavelength is 388 nm. Only the Wavelengths below 388 nm have the energy to excite electrons from VB to CB. Considering the light spectra of ABET Technologies SunLiteTM solar simulator with AM 1.5, the highest energy photons are belongs to 300 nm. Therefore average wavelength of 300 – 388 nm was selected (344 nm).



Figure S7. UV-Vis spectra of thermally deposited Cu_2O and TiO_2 (top), zinc phthalocyanine vs. zinc phthalocyanine and Cu_2O (or TiO_2) (middle), and cobalt phthalocyanine vs. cobalt phthalocyanine and Cu_2O (or TiO_2) (bottom).



Figure S8. Diffuse reflectance spectra of Cu₂O and TiO₂ (top), zinc and cobalt phthalocyanine (middle), and bilayer semiconductor/phthalocyanine (bottom).



Figure S9. Kubelka-Munk treated plots of Cu_2O , TiO_2 (top) zinc and cobalt phthalocyanine (middle), and bilayer semiconductor/phthalocyanine (bottom).



Figure S10. Cyclic voltammograms of zinc and cobalt phthalocyanine, TiO₂, and Cu₂O.



Figure S11. Normalized fluorescence spectra with excitation at 450 nm and 50 μ M (toluene solvent) of zinc phthalocyanine vs zinc phthalocyanine + TiO₂ (left). Normalized fluorescence spectra with excitation at 450 nm and 50 μ M (toluene solvent) of zinc phthalocyanine vs zinc phthalocyanine + Cu₂O (right).



Figure S12. UV-Vis of zinc phthalocyanine (left) and cobalt phthalocyanine (right) before and after photo-experiments.



Figure S13. Recyclability of the device over three catalytic cycles. (Reaction conditions; Aerobic condition, room temperature, pH = 8.5, irradiation condition = AM 1.5 solar simulation condition, 100 mW/cm² and, glycerol as the sacrificial agent)

Catalytic TON with respect to pththalocyanines.

Table S1.

Calculated masses of pththalocyanines on the quartz thin film.

Pththalocyanine	Calculated mass on the thin film	
ZnPc	0.0009314 g	
СоРс	0.0009688 g	

Table S2. Catalytic TON with respect to MPc were calculated using the equation (7);

$$TON = \frac{moles of products}{moles of catalyst}$$
(7)

The productivities were calculated using the following equation (8);

Productivity (MPc) =	(Productivit	y with MPc) –	(Productivit	y without MPc	(8))
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Control/ Device	MPc	Productivity (µmol)	TON
Control 1 (Cu ₂ O)	ZnPc	39.1	11.3
	CoPc	47.1	13.5
Control 2 (TiO ₂)	ZnPc	38.2	11.0
	CoPc	85.7	24.5
Device 1 (Cu ₂ O)	ZnPc	28.9	18.0
	CoPc	41.4	24.4
Device 2 (TiO ₂)	ZnPc	171.1	106.3
	CoPc	247.1	145

Energy Diagram for ZnPc and TiO₂



Figure 14. Energy level diagram illustrating favorable electron transfer interactions between MPc and SC conduction bands.

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