Cysteine-Cystine Photoregeneration for Oxygenic Photosynthesis of Acetic Acid from CO_2 by a Tandem Inorganic-Biological Hybrid System

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Supporting Information

Fig. S1-2

Materials and Methods

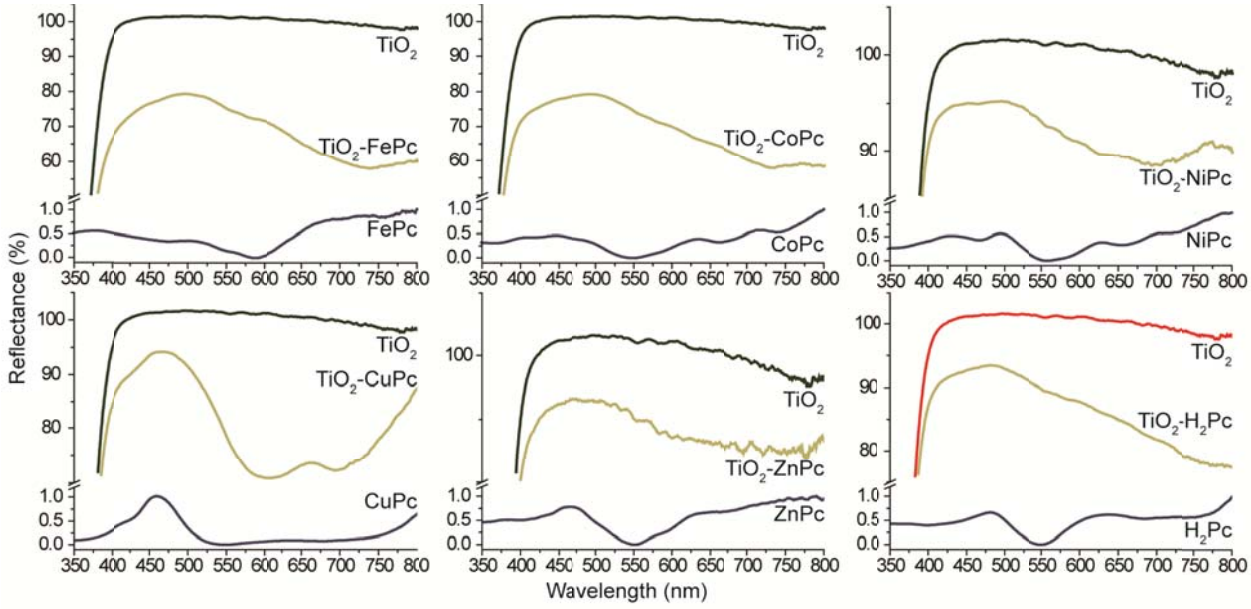

Figure S1. Reflectance Spectra of TMPc and TiO_2-TMPc. Spectra of TiO_2-TMPc show distinct differences from the neat TMPc. Features in the range of 400-500 nm are diminished on TiO_2, while absorption in the range of >600 nm is enhanced.

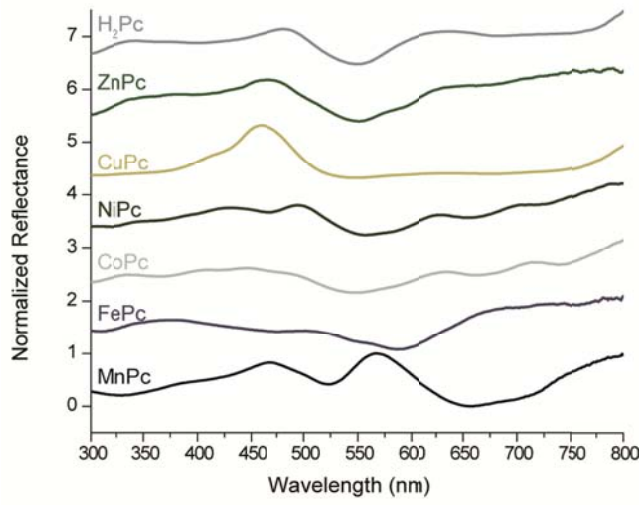

Figure S2. Direct Comparison of TMPc and H_2Pc Reflectance Spectra.

Materials and Methods

All reagents were used as received without further purification and were purchased from Sigma-Aldrich with the exception of zinc phthalocyanine (Acros Organics), cobalt(II) phthalocyanine (Alfa Aesar), and nickel(II) phthalocyanine (Eastman Kodak). Reagents related to the growth of *M. thermoacetica* (ATCC 39073) and photosynthesis characterization were described previously.[9]

Preparation of TiO_2-TMPc Photocatalyst

Phthalocyanines were loaded onto TiO_2 nanoparticles (Sigma-Aldrich 637254, anatase, <25 nm) by suspending both at the desired ratio in 50 mL of ethanol and 50 μL of 1 M HCl in a 100 mL beaker. The suspension was sonicated with a Microtip Probe Sonicator for 15 min intervals at 21% amplitude and allowed to settle. The solvent was removed by rotary evaporator and stored until further use.

Cystine Photoreduction Assay

Oxygen free 1,4-piperazinediethanesulfonic acid (PIPES, 30 mM) buffered media was made by boiling DI water under a N_2 stream for 5 min. The pH was adjusted to 7 by addition of 10 M NaOH. To the cooled PIPES buffer was added 10mM cystine. Each TiO_2-Pc composite was suspended in the cystine buffer at 0.1 g L^{-1} and sealed in a Balch type anaerobic tube under an N_2 atmosphere. The suspensions were irradiated by a filtered 75 W Xenon lamp (Newport Corp., AM1.5G, 5% sun) for 2 hours with time points taken at 0, 0.25, 0.5, 1 and 2 hrs. Cysteine production was determined photometrically by addition of an equal volume of 5 mM Ellman's reagent in degassed ethanol (freeze-pump-thaw). The mixture was allowed to react and then

centrifuged to remove the photocatalyst and quantified by UV-Vis spectrophotometry (Shimadzu UV3101PC UV-Vis-NIR Spectrophotometer with an integrating sphere). Reflectance spectra were obtained by suspending the photocatalysts or TMPc in ethanol and drop casting onto glass cover slips until an opaque film formed.

Preparation and Photosynthesis Assay of *M. thermoacetica*-CdS+TiO_2-MnPc

M. thermoacetica-CdS was prepared and assayed as previously described with modifications noted below.[9] All techniques were conducted anaerobically under an oxygen-free atmosphere or using standard Hungate technique. Briefly, cryopreserved stocks of *M. thermoacetica* (ATCC 39073) was inoculated at 5 vol.% into undefined precipitation media (UDM) with 25 mM glucose, 0.1 wt.% cysteine·HCl, 250 kPa N_2:CO_2 (80:20) and incubated at 52°C for 3 days until OD_{600}=0.16. The suspension was reinoculated at 5 vol.% into fresh UDM with 50 mM glucose and 0.1 wt.% cysteine·HCl. After 24 hrs of incubation as before, 1mM $Cd(NO_3)_2$ was added. The culture was incubated an additional 2 days with frequent agitation. After 2 days, the yellow suspension was centrifuged under an inert atmosphere and resuspended in half the original volume (5 mL) of defined photosynthesis media (DPM) supplemented with 0.1 wt.% cysteine·HCl and 250 kPa H_2:CO_2 (80:20). The suspension was incubated for 24-36 hrs before the headspace was exchanged for N_2:CO_2 (80:20). Deletional controls (*M.thermoacetica*-CdS, *M.thermoacetica*+TiO_2-MnPc) were prepared in a similar fashion.

The 0.05 wt.% TiO_2-MnPc was suspended in DPM at 1 g L^{-1} and sonicated for 1 hr. To the above *M. thermoacetica*-CdS suspension was added 5mL of the TiO_2-MnPc suspension. The complete 10 mL of *M. thermoacetica*-CdS+TiO_2-MnPc was illuminated by a filtered 75 W Xenon lamp (AM1.5G, 5% sun) with a 12 hrs light/12 hrs dark cycle with heating and stirring

(55 °C, 150 rpm). The suspensions were sampled every 12 hrs. Liquid sample time points were centrifuged to remove cells and nanoparticles and assayed for acetic acid concentration by quantitative ^{1}H-NMR with trimethylsilylpropionate as an internal standard. Oxygen production as monitored by a Neofox in-situ optical oxygen monitoring probe (Ocean Optics, Inc.).