**Supplementary Material**

**Bicarbonate Reduction with Semiconductor Photocatalysts: Study of Effect of Positive Hole scavenger**

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**Experimental procedures**

Materials

Nano-particulate TiO2 and Cu2O, 2-propanol, glycerol, and sodium sulfite were purchased from Sigma-Aldrich. Ethylene glycol, EDTA, and TEA were purchased from Fisher. All chemicals were used without further purification.

**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. Cu2O and TiO2 samples were dispersed in milli-Q water.

**Size, crystal structure, and surface area determination**. Dynamic Light Scattering (DLS) was performed using a Microtrac Zetatrac Particle Size Analyzer to obtain the hydrodynamic radius of the particles. Crystal structure information was obtained using a X’Pert Pro X-ray diffraction (XRD) instrument. BET surface area measurements were performed on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer, and scanning electron microscopy (SEM) was performed using a Hitachi S-4100 scanning electron microscope.

**Diffuse reflectance spectroscopy (DRS)**. The dry Cu2O and TiO2 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 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*. For powder samples, suspensions were made of 1 mg/mL in ethanol and sonicated for one hour to ensure suspension. After sonication, 60 μL of 5% Nafion solution was added to the suspension, and 4.5 μL 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.

**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.

**Photo-experiments**. Reaction matrix: a buffer made of 0.3 M NaHCO3, 2 M or 0.1 M hole scavenger, and Milli-Q water. Hole scavenger concentrations are as follows: IPA, glycerol, ethylene glycol, and TEA were prepared at 2 M, while EDTA and sodium sulfite were prepared at 0.1 M, which are typical values found in literature. TiO2 and Cu2O catalysts were added at a concentration of 0.1 mg/mL. The matrix was transferred in a quartz tube, sealed, and placed under an ABET Technologies SunLite™ 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. Aliquots were collected at two hour increments, and formate concentration was quantified by ion chromatography.

**Apparent Quantum Efficiency (AQE)**. Using an Ophir Photonics Nova II laser energy meter, the energy output of the solar simulator was measured. This power measurement was converted to moles of photons per second. This photon flux was then used to calculate the apparent quantum efficiency (AQE) of the catalyst using equations (1) and (2).

$$n mol photons ∙ \frac{1 mol e^{-}}{mol photons } ∙ \frac{mol formate}{2 mol e^{-}} =theoretical \left(1\right)$$

$$\frac{actual mol formate}{theoretical mol formate } ∙100 =\%AQE (2) $$



Figure S1. Band gap energies of TiO2 and Cu2O.

  

Figure S2. SEM images of Cu2O and TiO2.



Figure S3. Diffuse reflectance spectra of TiO2 and Cu2O, and Kubelka-Munk treated plots.



Figure S4. Cyclic voltammogram of Cu2O and TiO2.



Figure S5. Formate production in terms of concentration (left) and productivity (right) with TiO2 and Cu2O with no hole scavenger present.

Table S1. Semiconductor characterization.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Particle population | Diameter (nm) | Surface area (m2/g) | VB | CB | Band gap23 (eV) |
| Cu2O | <350 | 6.49 | 1.3 | -0.7 | 2.0 |
| TiO2 | 21 | 56.33 | 3.38 | 0.15 | 3.23 |

Table S2. Productivities for Cu2O and TiO2 in different hole scavengers (in units of mmol formate/g cat-hr)\*.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | IPA | Glycerol | Ethylene glycol | Sodium sulfite | EDTA | TEA |
| Cu2O | 0.22 ± 0.0009 | 2.16 ± 0.1 | 0.56 ± 0.01 | 0.62 ± 0.02 | 0.43 ± 0.008 | 0.51 ± 0.003 |
| TiO2 | 0.06 ± 0.0003 | 2.52 ± 0.2 | 1.22 ± 0.09 | ------ | 0.11 ± 0.003 | 0.43 ± 0.02 |

\*All reported values are from triplicate measurements. Dashed lines signifies no formate was produced.