Electrical Power and Hydrogen Production from a Photo-Fuel Cell Using Formic Acid and Other Single Carbon Organics

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Photocurrent Optimizations on Carbon Paper

A 5mg/mL TiO_2 solution in methanol was prepared and stirred for at least 30 minutes before using. Carbon paper electrodes were cut into 5cm by 1cm strips for optimization testing of loading amount and annealing temperature. The TiO_2 was then deposited on $2cm^2$ of the electrodes via a drop-cast method as well as a spray method. Varying amount of TiO_2 from $0.5mg/cm^2$ to $5mg/cm^2$ was deposited on an electrode. The electrodes were then heated to 400°C. Once the electrodes were prepared, they were then put in a 1M methanol solution with 0.1M sulfuric acid as an electrolyte. Nitrogen gas was bubbled for 15 minutes to purge oxygen from the system. Photocurrent measurements were taken to determine the optimum TiO_2 loading and optimum method of deposition (drop-cast vs. spraying). The results are shown below in Figure S1.

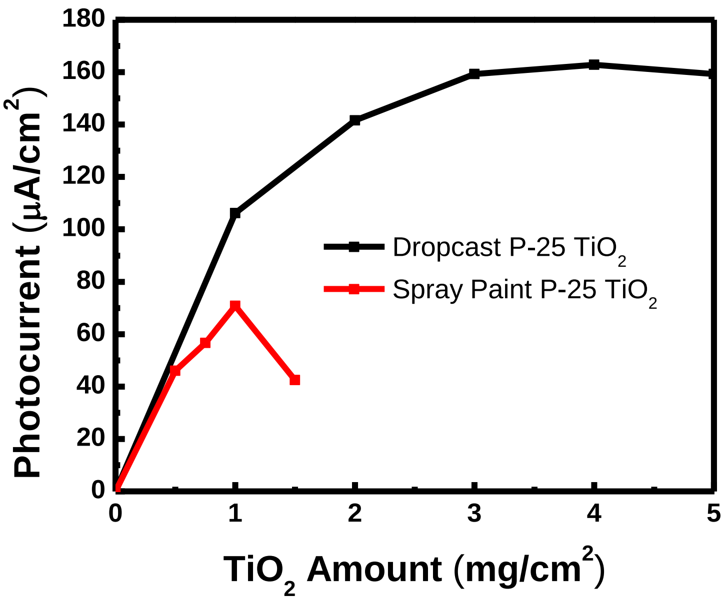

Figure S1: Optimization of concentration and deposition method of TiO_2 on carbon paper

Photo-efficiency Estimations

We determined the photo-efficiency via the following equation:

$$\%\,efficiency = 100\% * \frac{P_{out}}{P_{in}}$$

Where P_{out} is the amount of photons used for hydrogen production and P_{in} is the amount of photons with an energy high enough to photo-excite the TiO_2 semiconductor. To determine P_{out} , the amount of hydrogen gas was converted to moles electrons using the ideal gas law. The calculations are shown below.

$$n = \frac{PV}{RT}$$

$$n(e^-) = \frac{\frac{60\mu L\ H_2}{hr * cm^2} \times 1atm}{82{,}057\frac{\mu L\ H_2 * atm}{mol\ H_2\ * K} \times 298K} \times \frac{2\ mol\ e^-}{1\ mol\ H_2} = 4.9 \times 10^{-6}\,\frac{mol\ e^-}{cm^2 \times hr}$$

The catalyst used was P-25 TiO_2, which consists of 70% anatase TiO_2 and 30% rutile. Since rutile has a lower bandgap, it will be conservatively assumed that TiO_2 can potentially absorb all photons with an energy equal to or higher than the rutile bandgap. In terms of wavelengths, this corresponds to any photon with a wavelength greater than 413nm. Using an AM1.5 solar simulator we can approximate the solar flux to match that of the sun (e.g. ASTM G173-03 Reference Spectra). By integrating the solar flux from 0 to 413nm the number of incoming photons (P_{in}) can be determined.

$$P_{in} = \int_0^{413} \text{of ASTM G17303 Reference Spectra} = 7.07 \times 10^{-5}\,\frac{mol\ photons}{cm^2 \times hr} = 7.07 \times 10^{-5}\,\frac{mol\ e^-}{cm^2 \times hr}$$

Thus by dividing the electrons used to produce hydrogen by the total electron-hole pairs produced, a photon to electron efficiency can be found as followed:

$$\%\,efficiency = 100\% * \frac{4.9 \times 10^{-6}\frac{mol\ e^-}{cm^2 \times hr}}{7.07 \times 10^{-5}\frac{e^-}{cm^2 \times hr}} = 7\%$$

However if it is assumed that current doubling occurs for the formic acid oxidation (1 electron-hole pair produces 2 electrons), the efficiency of the cell would then be 3.5%.