**Photocatalytic Conversion of CO$_2$ into CH$_4$**

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**Nanowire Synthesis**

**Tungsten Oxide Nanowires**

DI water and Sodium tungstate dehydrate were mixed together and then acidified to pH 1.0-1.2 using HCl. EDTA and Sodium sulfate were then added to the solution. Put reaction mixture in acid digestion bomb and performed a hydrothermal reaction for 8 hours at 140-180°C. Nanowires were purified using ethanol and a sonicator followed by being air dried.

(Left Picture) Synthesized Tungsten oxide nanowires in test tubes. Bulk WO$_3$ has a white appearance. WO$_x$ nanowires are reported to have an emission at 479nm which accounts for the blue appearance. (Middle Picture) Scanning Electron Microscope (SEM) image of the synthesized WO$_x$ nanowires. The estimated length and diameter of the nanowire bundles are 0.5µm and 54nm, respectively. The reported, respective values are 1.5-2.5µm and 100-150nm. (Right Picture) Raman spectroscopy analysis of the synthesized WO$_x$ nanowires. The peaks are at 244nm, 328nm, 750nm, and 807nm which correspond to the reported peaks of 242nm, 325nm, 745nm, 807nm. Also, the relative intensities of the peaks match those that have been reported.

**Titanium Oxide Nanowires**

(Intended Procedure) P-25 titanium oxide (commercial mix of crystalline rutile and anatase phases) and 15M NaOH to be mixed together. Mixture placed in acid digestion bomb and a hydrothermal reaction performed for 3 days at 170°C. To purify, HCl used to neutralize base followed by a sonicator and water to wash. Dried using hot plate. Nanowires then placed in an oven for 4 hours at 400°C, completing procedure.

Synthesis of TiO$_2$ nanowires not fully completed. Pictures of expected results and were obtained by analyzing TiO$_2$ nanowires prepared by another lab. (Left Picture) Titanium oxide nanowires. (Middle Picture) SEM image of TiO$_2$ nanowires showing estimated lengths and diameters of 0.5µm and 34nm, respectively. The reported, respective values are 2-450µm and 20-40nm. (Right Picture) Raman spectroscopy analysis of TiO$_2$ nanowires. The peaks are at 200nm, 244nm, 296nm, 378nm, 644nm and 869nm which correspond to the reported peaks of 200nm, 290nm, 298nm, 475nm 640nm and 860nm. Also, the relative intensities of the peaks match those that have been reported.

**Introduction**

As fossil fuels become increasingly depleted, the development of clean energy sources becomes increasingly important. Both Titanium(VI) oxide and Tungsten(VI) oxide nanowires have been used to harness the electromagnetic waves given off by the sun to turn water into hydrogen and oxygen gas; using the UV and visible spectrum, respectively. Investing in this principle, we will design a novel device that converts carbon dioxide and water vapor into methane in a cost effective manner. The device will use a composite of the two complementary nanowires in order to obtain broader solar absorption.

To reach our goal, the needed TiO$_2$ and WO$_x$ nanowires first need to be synthesized. The synthesis for WO$_x$ nanowires has already been accomplished via a hydrothermal reaction in which the nanowires form by self-assembly. The synthesis of TiO$_2$ nanowires is ongoing and also proceeds via a self-assembly, hydrothermal reaction. Other ongoing work includes applying the nanowires to a glass substrate using an LB trough and then running photoelectrical tests to determine the efficiency of the composite nanowires. Eventually, a thin layer will be applied to silk worm silk, or any alternate substrate that gases can pass through, which will be incorporated into the final design.

**Thin Film Processing**

A Langmuir-Blodgett (LB) trough will be used to apply a layer of ordered nanowires to at least, two substrates. The pictures below represent the principles of LB processes. The nanowires (green) are suspended in a solvent (purple) that evaporates quickly at room temperature and is, preferably, immiscible with water (we will be using a mixture of Chloroform, Hexane, and Isopropanol alcohol). (Left-Most Picture) The mixture is then poured onto water (blue) between two barriers (black) one drop at a time using a syringe until the surface is moderately covered. (Left-Center Picture) When the solvent evaporates, a monolayer of nanowires is formed on top of the water. (Right-Center Picture) The barriers are then used to compress the monolayer into an ordered layer, (Right-Most Picture) The substrate (white) is then dipped into the liquid so that the nanowire layer can be deposited on it.

Substrates

Below are pictures of the substrates we will be using and the final reactor. (Left Picture) The left-most glass slide has been treated with Octadecyltrimethoxysilane to make it hydrophobic. This substrate, coated with nanowires, will be used to run initial photoelectrical tests to determine efficiency. (Center Picture) For the final substrate, the nanowires will be applied to a substrate that gases can pass though; pictured is silk worm silk. (Right Picture) The device that the final, nanowire-coated substrate will be incorporated into.

**Conclusion**

The procedure for the synthesis of Tungsten oxide nanowires was successful. While it is true that the synthesized nanowires are shorter and thinner than the reported values, the color and Raman spectra suggest that WO$_x$ nanowires were indeed synthesized. Bulk WO$_3$ is white in color and it has been reported that, upon forming nanowires, WO$_3$ turns blue as our nanowires did. In addition to the color change, the Raman spectra matches the reported spectra in peak location and relative intensities. The possible reason for nanowires that are smaller than they should be is due to the reaction vessel. The only difference between our procedure and the model procedure is that we used an acid digestion bomb while the other research group used a autoclave.

Our Titanium oxide nanowire analyses successfully compared with previously reported analyses for TiO$_2$ nanowires. The model procedure we will be following, for TiO$_2$ nanowire synthesis also uses an autoclave. It will be interesting to see if the use of an acid digestion bomb causes the TiO$_2$ nanowires we will synthesize to show, in contrast to reported values, size differences similar to WO$_x$.

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**References**