Nanostructured Photocatalytic Approach to CO_2 Conversion

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ABSTRACT

Several approaches to stabilize and reduce atmospheric CO_2 concentrations have been tested. While carbon capture and storage (CCS) has been hailed as the most promising approach for sequestering CO_2 safely away from the atmosphere, the technology remains unproven, costly, and will likely not be commercially available for decades. An alternative to CCS is to consider CO_2 as a commodity that can be converted or more specifically recycled into useful and valuable chemicals and/or clean burning fuels. This approach not only reduces or eliminates the amount of CO_2 entering the atmosphere, but it creates a revenue stream to offset the cost of implementation. GoNano Technologies, Inc. has demonstrated a nanostructured titanium dioxide (TiO_2) photocatalyst that can be used to selectively convert CO_2 into methane, methanol, formic acid, and/or formaldehyde.

Keywords: Silica Nanosprings, carbon recycling, CO_2, greenhouse gases

1 INTRODUCTION

In their Grand Challenges for the 21st Century the National Academy of Engineering stated: The growth in emissions of carbon dioxide (CO_2), implicated as a prime contributor to global warming, is a problem that can no longer be swept under the rug [1]. Currently, twenty seven billion tons of CO_2 is emitted yearly from the burning of fossil fuels and this number is projected to reach 43 billion metric tons by 2030 [2]. Fossil fuels are the world's primary source of energy and increased concentrations of CO_2 in the atmosphere are certain unless energy producers reduce their carbon emissions. The United States and the international community have agreed that a reduction of CO_2 concentrations must occur to avoid future dire environmental consequences. Several approaches to stabilize and reduce CO_2 concentrations have been tested. While carbon capture and storage (CCS) has been hailed as the most promising approach for sequestering CO_2 safely away from the atmosphere, the technology remains unproven, costly, and will likely not be commercially available for decades [3]–[5]. There is no full-scale CCS project that captures and sequesters CO_2 from a coal-fired plant and estimates suggest that it may be more than 20 years before CCS technology is readily available. An alternative to CCS is to consider CO_2 as a commodity that can be converted "or more specifically recycled" into useful and valuable chemicals and/or clean burning fuels. This approach not only reduces or eliminates the amount of CO_2 entering the atmosphere, but it creates a revenue stream to offset the cost of implementation. The innovative approach of the present work is Carbon Capture and Recycle (CCR) where a highly active nanocrystalline titanium dioxide (TiO_2) photocatalyst can be used to selectively convert CO_2 into methanol, formic acid, and/or formaldehyde. These chemicals are important raw materials for a number of industries including the manufacture of plastics and rubber and in the case of methanol and formic acid there are potential applications in fuel cells.

The anatase phase of TiO_2 is a well known photocatalyst and has been shown to be capable of converting CO_2 emissions into useful feedstock chemicals such as methanol since its discovery in 1979 by Inoue *et al.* [6]. A common approach has been the photocatalytic conversion in liquid by dissolving CO_2 in water [7]–[10]. So far this type of catalytic reaction has been successfully tested with conversion efficiencies in the range of $10 - 15\%$. However most of the CO_2 converted, approximately $60 - 80\%$, ended up producing methane due to the batch conversion process that was used [7]–[12]. Several approaches to converting CO_2 directly to methanol, such as doping TiO_2 with SiO_2 or the addition of Pt and Cu nanoparticles, have proven technically viable, but not scalable [10], [11]. A particularly exciting aspect of the gas-to-gas continuous process for CO_2 conversion is that it opens up the possibility of tailoring the output product. Formic acid, formaldehyde, methanol, and eventually methane that can be obtained from the catalytic reaction of CO_2 using TiO_2.

2 FABRICATION

Nanosprings can be grown on a variety of substrates, including polymers such as polyimide. The only requirement is that the substrate can withstand the process temperature. In this present study, the Nanosprings were grown on 250μm glass frits and fiberglass cloth. A scanning electron microscope (SEM) image of an as-grown silica Nanospring mat is shown in Figure 1. McIlroy *et al.* [13] and Wang *et al.* [14] have described the Nanospring process in some detail. Due to the pending application for a US patent [15] on Nanospring technology, only a condensed description of the process will be presented. The Nanospring synthesis was performed at atmospheric pressure for 15 minutes. The general principles of this furnace were discussed in detail by McIlroy *et al.* [13]. A thin catalyst layer was sputtered on the fiberglass prior the Nanospring synthesis.

The TiO_2 is formed as a nanostructured anatase coating on the silica Nanospring mats using atomic layer deposition (ALD). The reactive metal precursor, titanium tetrachloride ($TiCl_4$) is oxidized with H_2O forming a uniform nanocrystalline coating. This nanocrystalline structure is formed due to the open template and unique surface chemistry of the silica Nanospring mats. Figure 2b is a SEM image of a uniform nanocrystalline anatase-phase TiO_2 grown on silica Nanosprings mats. The transmission electron microscope (TEM) image in Figure 2a shows a detailed structure of the deposited nanocrystalline anatase TiO_2.

3 EXPERIMENTAL

Several approaches were analyzed to test and measure the reaction efficiency of the CCR system. First a chamber to precisely control the flow of gases

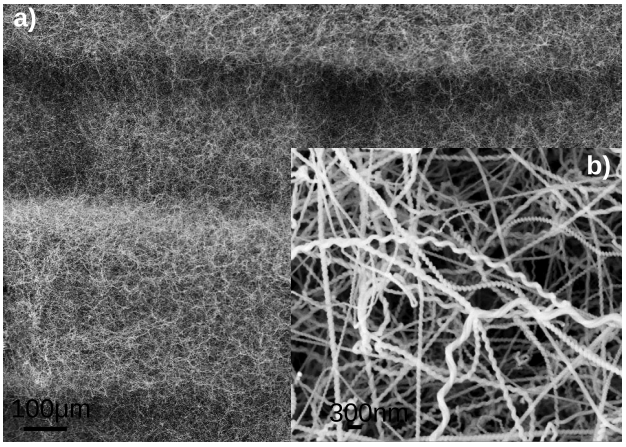

Figure 1: a) SEM image of a Nanospring coated fiberglass cloth b) SEM image of silica Nanosprings.

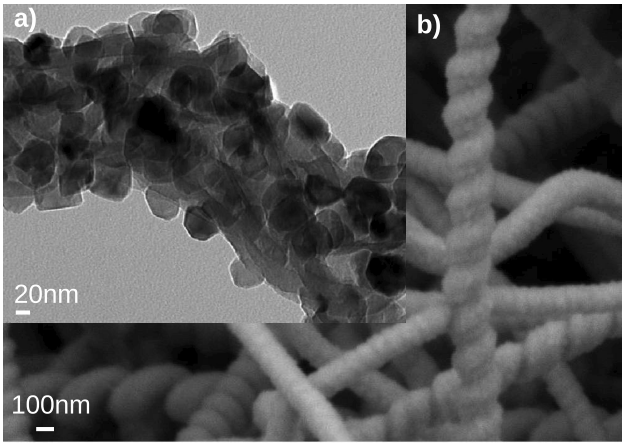

Figure 2: a) TEM image of a Nanospring with TiO_2 nanocrystals b) SEM of a TiO_2 coated Nanosprings

over the catalyst was built, shown in Figure 3. A Nanospring mat was grown on a glass frit from Adams & Chittenden, Berkeley, CA. The Nanosprings were then coated with anatase TiO_2 by the ALD process. A stainless steel reactor with inlets for CO_2 and H_2 with a quartz window on the top was used. The photocatalyst was exposed to ultraviolet light (UVA, $\lambda = 395$nm), industrial grade CO_2(99.9%) and water vapor were flown in at rates of 3 sccm and 1 sccm respectively. The gases from the outlet were sampled with a two chambered vacuum system with the higher vacuum chamber having a residual gas analyzer (mass spectrometer).

The second set of experiments used the same frit from the first experiment. Approximately 100μl of 18MΩcm water was pipetted out onto the surface of the frit. This was then placed inside an airtight 500ml airtight flask facing a quartz tube enclosed USHIO

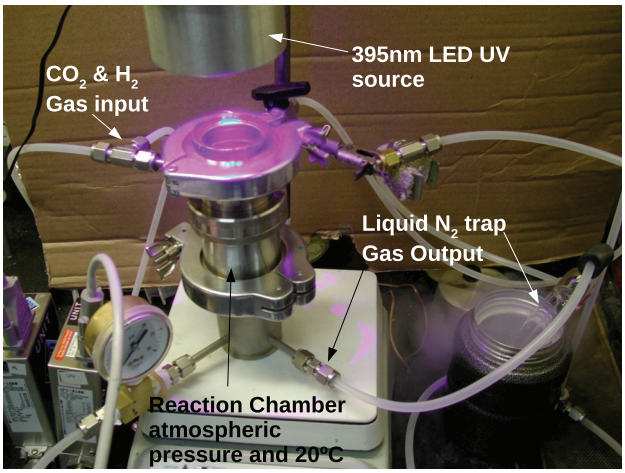

Figure 3: Laboratory scale CCR reactor

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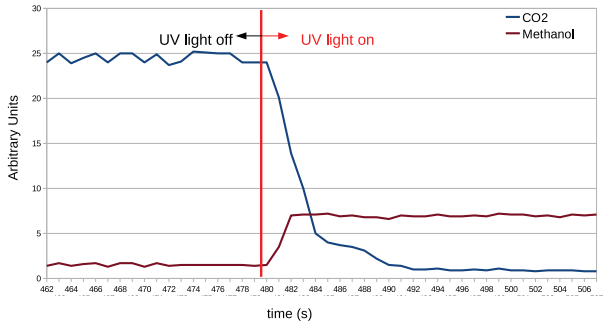

Figure 4: Plot of concentration (arbitrary units) versus time (s) showing photocatalytic conversion of CO_2 to methanol.

UVC lamp with a predominant emission wavelength of 254 nm. The output gases were analyzed using flame ionization detector (FID) and a thermal conductivity detector (TCD) on an SRI instruments 8610C GC. CO_2 was allowed to flow at 20ml/min into the reactor. The UV lamp was then turned on for 20 min. The last experiment was performed with Nanosprings grown on a glass fiber of 42mm×42mm. This was coated with TiO_2. The sample was placed in 400 ml 18MΩcm water facing the UVC lamp. CO_2 was flown in at 20ml/min. Before the light was turned on the CO_2 was allowed to saturate the water. 1 ml GC samples were then taken from the outlet every 20 min.

4 RESULTS

Mass spectra, from the first experiment, were sampled every 100s and analyzed to identify the peaks of CO_2, H_2, methanol, formaldehyde, formic acid and methane. The concentrations were then plotted against time as shown in Figure 4. The reduction in CO_2 is approximately 30%. The vertical (red) line shows when the UV source was turned on and the corresponding decrease in CO_2 emission and concomitant formation of methanol. The gas composition was measured using MS.

During the second experiment the output flow rate was monitored continuously during the whole process. The initial output flow rate was 20ml/min. There was a significant amount of CH_3OH peak in the GC after the UV light was turned on. The output flow rate reduced to 15ml/min indicating a conversion of 25% of CO_2 into CH_3OH. It was observed that most of the methanol was in the liquid phase and only the gas phase species were detected by the GC. Figure 5 shows the chromatograms from 1 ml samples before and after the UV was turned on experiment 2.

Figure 6 shows two chromatograms before and after the UV light was turned on. There is a significant amount of methanol after the UV was turned on.

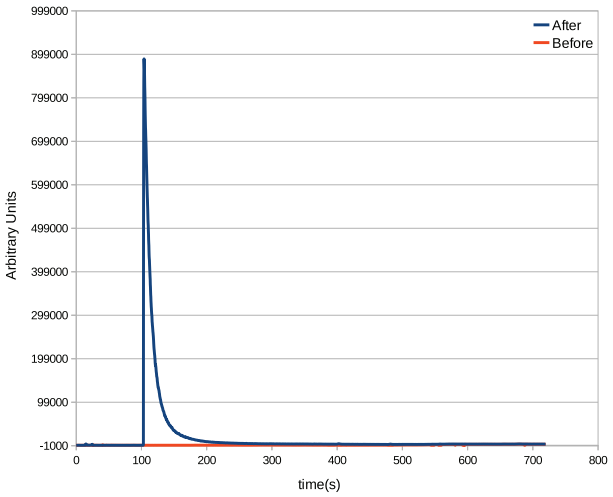

Figure 5: The high peak at 100s is the methanol peak. The conversion efficiency for CO_2 is 25%.

The output flow rate was 17.2 ml/min indicating a conversion of approximately 14%.

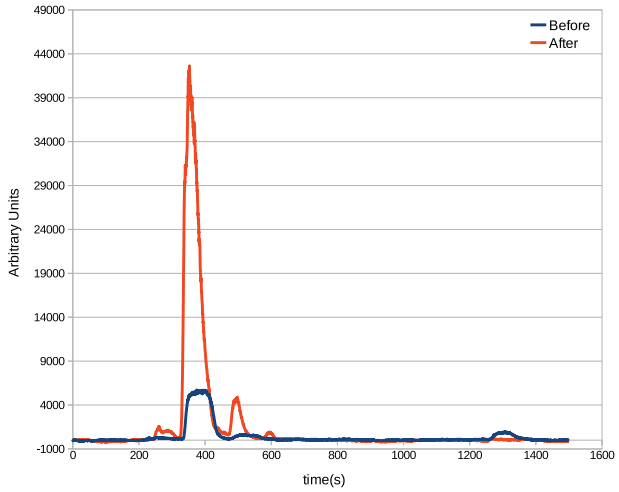

Figure 6: The peak at 400s corresponds to methanol. A very small amount of formaldehyde peak is also seen. Conversion efficiency is approximately 14%.

5 CONCLUSIONS

Effective conversion of CO_2 into formic acid, formaldehyde, methanol and methane was achieved in several experiments. The gas to gas CO_2 recycling experiments were the most successful with an overall efficiency of 30% of CO_2 converted into useful byproducts. The last two experiments where water was in liquid phase also showed large conversion efficiency in the range of 15 to 25%. The variation in these results was

attributed to the particle size of the anatase TiO_2 nanocrystalites and their separation. The frit which has higher conversion efficiencies has a particle separation on the Nanospring surface of the order of a single particle diameter. Once the particles get closer the conversion efficiency is reduce. Currently GoNano Technologies is working on controlling the particle separation and doping the catalyst to move the activity towards the visible light spectrum.

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