

Carbon Capture and Recycling by Photocatalysts Supported on Silica Nanosprings

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ABSTRACT

GoNano Technologies Inc. is currently developing Carbon Capture and Recycling (CCR) technology as an alternative and/or a complement to the Carbon capture and sequestration technology (CCS). CCR involves the conversion of captured or emitted CO₂ into useful products such as formic acid and formaldehyde using anatase TiO₂ nanoparticles immobilized on silica Nanosprings catalyzed by incident solar light or UV LEDs. The CCR system utilizes a solar panel like reactor that has an embedded photocatalyst mat and a quartz window. The assessment of the CO₂ conversion is done by two types of reactions: A) CO₂ conversion into methanol from aqueous solutions and B) CO₂ reduction into formaldehyde and formic acid in the presence of 1% methanol. The results indicate that the CCR technology is capable of selectively reducing CO₂. Enhancing the conversion efficiencies with interface engineering of the photocatalyst is now being pursued.

Keywords: Carbon utilization, photocatalysis, Nanosprings.

1 INTRODUCTION

Fossil fuels are our primary source of energy. Unfortunately, CO₂ emissions generated in using these fuels has drastically increased in recent years [1]. Increased concentrations of CO₂ in the atmosphere are certain unless energy systems reduce their carbon emissions [2]. In the United States it is estimated that one third of all CO₂ emissions come from large single sources, such as power or industrial plants [3]. The United States and the international community have agreed that a reduction of greenhouse gas (GHG) concentrations must occur to avoid future health and environmental damage. Several approaches to stabilize and reduce GHG concentrations have been tested. CCS is the most common method by which CO₂ is isolated from the emissions stream, compressed, and transported to an injection site where it is stored underground permanently [3]. However, safety concerns have arisen due to possible underwater contamination and sudden CO₂ escape back into the atmosphere, which could have fatal consequences [3-6]. Staving off increasing CO₂ emissions due to higher power consumption and larger restrictions to GHG emissions by world governments [7], require an alternative to CO₂ sequestration. This alternative must be capable of adapting to actual industry and power plant

stacks without major modification, so that energy costs do not suffer a large increase.

The idea of converting captured CO₂ into usable chemical feedstocks is very promising. The sale of these products not only offsets the energy penalties incurred in the capture and conversion but also provides a more efficient and environmentally friendly way of manufacturing the products. It is envisioned by GoNano Technologies that the cost to install a capture system in an industrial plant would be similar to the cost of installing a CCR system. To help reduce costs and energy consumption due to H₂ usage in the hydrogenation system, GoNano Technologies is developing, in parallel, a photo-hydrolysis system, which could be placed within the same industrial complex. For synthesis of formaldehyde and formic acid, methanol produced in the initial stages of the cycle can be reinjected. The combination of these two systems in offsetting the CO₂ sequestration cost will be beneficial for power and industrial companies and to the final users. The most desirable products of CO₂ hydrogenation are methanol and formaldehyde, both used extensively in chemical, textile, resin, and paint industries. Moreover, methanol is a cleaner burning fuel, which could be used by the same power plant. Methanol, is a key chemical intermediary that finds extensive use in the production of formaldehyde, acetic acid, and other chemicals, with formaldehyde production accounting for more than one-third of all methanol demand [8]. Changing demand patterns have witnessed stagnant growth of methanol consumption in the fuel market. Currently, about 90 percent of the worldwide production of methanol is derived from methane, the main component of natural gas [8]. Today's methods of producing methanol have two stages: converting methane into syngas, a mixture of primarily carbon monoxide and hydrogen, and then into methanol [8]. Although these steps have become more efficient over time, the elimination of the syngas step could save money, since it currently accounts for up to 70 percent of the cost [8]. Furthermore, the production of methanol from CO₂ and CO instead of methane would decrease demand for natural gas. Likewise, formaldehyde is mainly produced from methanol and accounts for up to 40 percent of the worldwide consumption of methanol. By producing separately methanol and formaldehyde, the demand for methanol could therefore be reduced by 40 percent and the methanol resulting from the increase in supply could be used as an alternative clean burning fuel or for other applications in the chemical industry.

2 TECHNICAL DESCRIPTION

The method used to grow silica Nanosprings has been previously reported by Wang *et al.*[9] and McIlroy *et al.* [10]. For this specific application the Nanosprings are synthesized on glass fiber mats as substrates in a furnace operated at atmospheric pressure. The growth of Nanosprings uses a thin gold layer as a catalyst, which is then exposed to a proprietary silicon precursor. A constant O₂ flow rate is maintained concomitant with the silicon precursor.

2.1. The Photocatalyst

Anatase TiO₂ has been used as a photocatalytic material capable of converting CO₂ emissions into more useful feedstock chemicals such as methanol since its discovery in 1979 by Honda [11-14]. TiO₂ nanocrystals were coated on the Nanosprings by atomic layer deposition (ALD) at approximately 0.8 Å per cycle. Figure 1 shows a FESEM image at two different resolutions. Figure 2 shows the bright-field TEM image of TiO₂ coated Nanosprings. The surface chemistry of the Nanosprings and the temperature of the ALD process limits the formation of TiO₂ nanocrystallites to the anatase phase.

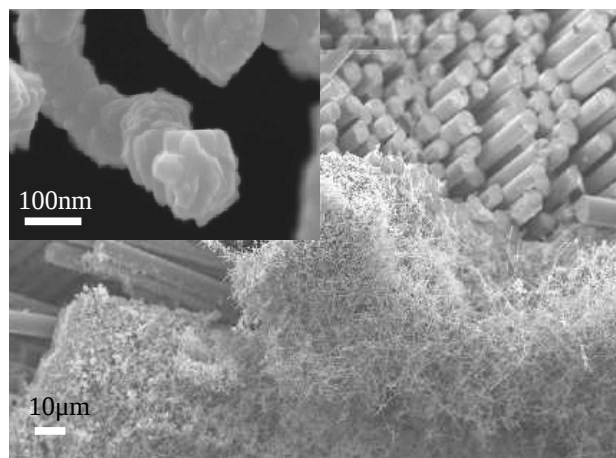


Figure 1. FESEM images of Nanosprings mat grown on a glass fiber mat. Inset shows the TiO₂ particle coated Nanosprings.

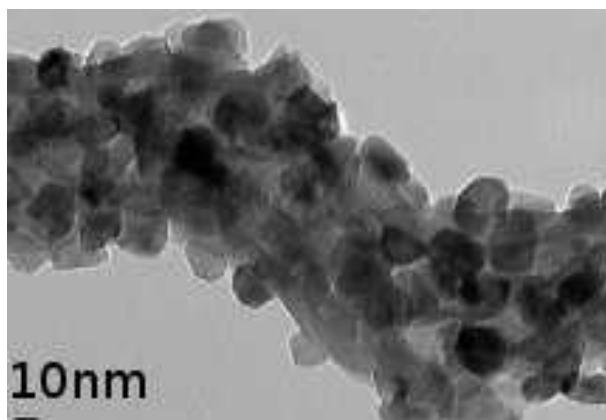


Figure 2. TEM image of the anatase TiO₂ particles

Brunauer Emmett Teller (BET) surface area measurements were carried out on samples that had various ALD cycles and it was found that the most photoactive sample had about 4 times the surface area of the commercially available P25 particles from Degussa. Fig 3 shows the surface area comparison.

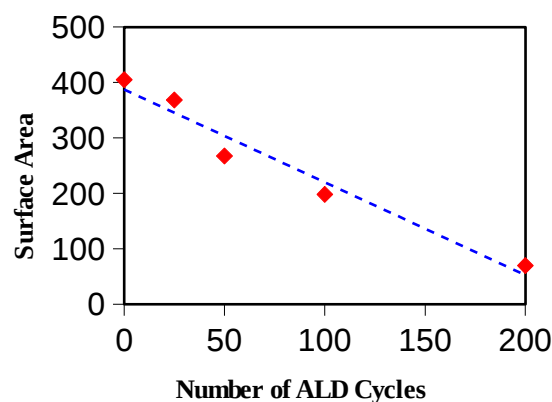


Figure 3. BET surface area(m²/g) comparisons of TiO₂ on Nanosprings

2.2. Photodegradation of Alizarin Red

The assessment of the photoactivity of silica Nanosprings supported TiO₂ samples was carried out by measuring the rates of photodegradation of alizarin red (AR), which is considered a model environmental contaminant. A sample was placed on the side wall of a spectrophotometer (Ocean Optics USB4000) cuvette, which was then filled with a solution of alizarin red (1mL, 1 mM). The spectrophotometer lamp was used as light source and the progress of the photodegradation process was monitored by measuring the absorbance (420 nm) of the solution every 10 minutes. Figure 4 shows the performance of the the most

photoactive sample and the same was used to test the reduction of CO_2 .

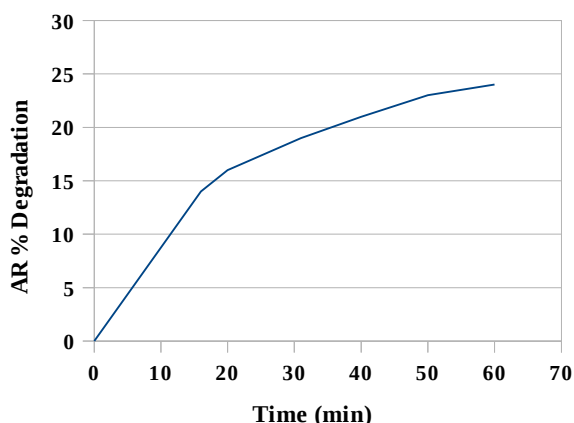


Figure 4. The Photodegradation curve of alizarin red

2.3. Carbon Recycling by Photoreduction

An efficient solar panel like reactor was designed for quantifying the conversion efficiencies of the various photocatalysts produced at GoNano. The reactor has lower losses, a more uniform flow rate across the catalyst mat and ensures maximum UV light utilization for electron-hole generation. The top half has a UV transparent quartz window and an inlet port that is designed for liquid phase and gaseous phase reactant mixtures.

To standardize the testing procedure for all the catalyst samples, two types of reactions have been identified keeping in mind that ultimately the product yield should be economical. It was observed that use of a liquid phase reaction mixture yields more consistent results compared to gaseous phase reaction mixtures. Hence all the tests were done in liquid phase where CO_2 is dissolved in 18.2 MΩ water.

2.3.1 CO_2 Reduction into Methanol

A typical experiment consists of flowing CO_2 dissolved in water at room temperature and pressure (solution flow rate into the reactor ~ 0.5 ml/hr) and have the UV light, a 50 W solar simulator Hg lamp, AM 1.5, shine on the reactor through a quartz window. Aliquots of 0.1 ml, sampled by a syringe attached to the reactor, are analyzed by a flame ionization detector (150°C with He Carrier gas at 30 ml/min) on a HP5890 Series II Gas Chromatograph. Figure 5 shows a chromatogram that indicates a conversion efficiency of 3.17% of dissolved CO_2 being converted into methanol, after 3 hours of irradiation on the photo catalyst. The space time yield is 4.21 mmol/(g cat.h) compared to $\mu\text{mol}/(\text{g cat.h})$ ranges from commercially available Degussa P25 TiO_2 catalyst.

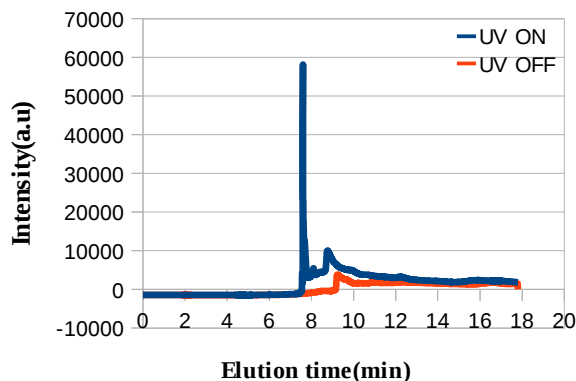


Figure 5 Chromatogram showing elution of methanol after 3 hrs of UV radiation.

2.3.2 CO_2 Reduction into Formaldehyde and Formic Acid in the Presence of Methanol

A typical experiment consists of flowing CO_2 dissolved in water. Solution flow rate into the reactor of ~ 0.5 ml/hr was maintained. Methanol is added to the CO_2 solution to make a 1% v/v solution. The UV light is allowed to shine on the reactor through the quartz window. Aliquots of 0.1 ml, sampled by a syringe attached to the reactor, are analyzed by the flame ionization detector (150°C with He Carrier gas at 30 ml/min) on the HP5890 Series II Gas Chromatograph. The chromatogram shown in figure 6 indicates a conversion efficiency of 12% of dissolved CO_2 into formaldehyde(72.3%) and formic acid(27.7%) with all the methanol being consumed, after 3 hours of irradiation. The conversion of CO_2 can be enhanced by using excess methanol. Methanol produced in the first stages of the CCR process can be completely consumed to produce formaldehyde and formic acid depending on the needs of the customer and the existing prices of the products.

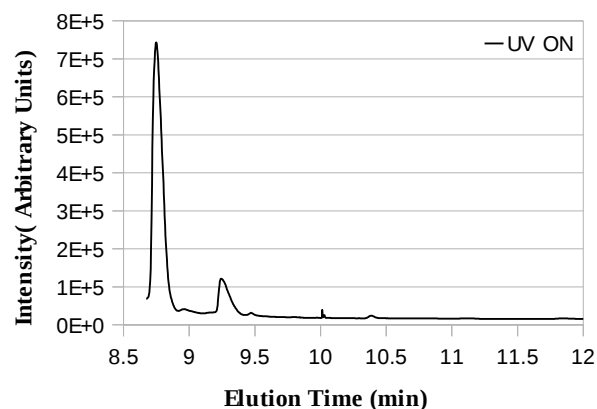


Figure 6. Elution of formaldehyde and formic acid.

3. CONCLUSIONS

The conversions efficiencies by the photocatalysts supported on SiO₂ Nanosprings have been proven to be more efficient than the other TiO₂ based photocatalysts reported. GoNano Technologies is now pursuing other catalysts that can provide better efficiencies in a continuous flow regime. Meanwhile interface engineering of the already working TiO₂ photocatalyst is also being studied.

Modeling of a scaled up CCR system based on the present conversion efficiencies indicate that with an energy penalty of approximately 1 MWh/T of CO₂ converted, sale of the chemical feedstock would provide a profit of \$76/Ton of CO₂ converted. Thus the CCR system not only mitigates the CO₂ but also provides for access to profits from the chemical feedstock market.

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