Contract No:

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Disclaimer:

Title of Project
Understanding Photocarrier and Gas Dynamics to Rationally Design Heterostructured Nanocatalysts for Efficient Solar CO_2 Conversion

Project Start and End Dates
Project Start Date: 10/1/2020
Project End Date: 9/30/2022

Project Highlight
This project has established several new and unique capabilities that enable SRNL to synthesize unique nanomaterials and evaluate their performance as catalysts in chemical processes relevant to clean energy technologies, such as CO_2 photoconversion. The instrumentation developed in FY21 of this project allows understanding of electron transfer processes on extremely short timescales, which is relevant to photovoltaic cells and other applications in addition to photocatalysis.

Project Team
Principal Investigator: A.B. Thompson
Team Members: P. Ward, L. Hannah, Z. Duca, S. Murph
External Collaborators: Y. Zhao, S. Ullrich, H. Meyer, M. Asadinamin (University of Georgia)

Abstract
Recent research in CO_2 photocatalysis has largely focused on exploring new catalysts; however, details of how these materials work often remain unclear. Knowledge of these processes will allow one to rationally design highly efficient catalysts for solar CO_2 conversion. This project aims to develop new techniques and establish new capabilities in SRNL to enable the study of photocatalysts and other materials in extreme detail. In FY21, we developed two new *in situ* techniques that are unique to SRNL, allowing the study of reaction intermediates and adsorbed gases during photocatalysis. We also established new in-house capabilities for catalyst synthesis and transient absorption (TA) spectroscopy, which enables the study of very short-lived excited states on photocatalysts. These capabilities will be used extensively for this project and in other current projects relevant to clean energy technologies such as photovoltaic cells, providing a good return on investment in the coming years.

Objectives
- Synthesize new heterostructured nanomaterials for CO_2 photoconversion
- Establish Glancing Angle Deposition (GLAD) catalyst synthesis capabilities at SRNL
- Establish Transient Absorption (TA) capability at SRNL
- Develop novel *in situ* EPR technique for study of radical reaction intermediates and paramagnetic metal ions
- Develop novel *in situ* variable-temperature DRIFTS technique for study of adsorbed gases and intermediates

REVIEWS AND APPROVALS

1. Authors:

A.B. Thompson 10/15/2021

Name and Signature Date

2. Technical Review:

P. Ward 10/15/2021

Name and Signature Date

3. PI's Manager Signature:

J. Bobbitt 10/15/2021

Name and Signature Date

4. Intellectual Property Review:

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

SRNL Legal Signature

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Name and Signature

Introduction

CO_2 is a primary driver of global climate change and the ultimate product of fossil fuel combustion. As such, the development of commercially viable fuels from atmospheric CO_2 would help combat the climate issue both by actively removing CO_2 from the atmosphere and reducing its production from fossil fuel use. Although CO_2 conversion reactions such as the water-gas shift reaction and CO_2 methanation typically require high energy input in the form of heat, solar CO_2 conversion can occur at ambient temperature using primarily ultraviolet and visible light from the sun. Metal oxide semiconductor materials can catalyze solar CO_2 conversion by photon absorption, which excites an electron from the valence band to the conduction band, forming an electron-hole pair (charge carriers). Charge carriers can diffuse to the surface of the material to form excited states that increase reaction rate by attacking adsorbed CO_2 or reaction intermediates. However, the details of this process are unclear and highly dependent on catalyst and reaction conditions, and catalyst activities are still typically too low for commercial viability. Deep knowledge of these processes will help design the next generation of CO_2 conversion photocatalysts.

This project aims to elucidate the interaction between charge carriers and adsorbed gases and reaction intermediates in CO_2 photoconversion over semiconductor nanocatalysts. Novel materials and nanostructures are synthesized by Glancing Angle Deposition (GLAD) and tested in CO_2 photocatalysis using novel *in situ* techniques developed by SRNL including EPR and DRIFTS with tunable laser excitation. The ability to excite with high-intensity laser light of any desired wavelength allows for experiments to be run over a range of excitation wavelengths, unlike traditional in situ techniques using white light or broad UV light for excitation. This allows collection of data as a function of excitation wavelength for a single system, potentially giving better insight into charge transfer processes.

Approach

Two new techniques unique to SRNL were developed for this project. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is a vibrational technique used to probe bonds on diffuse light-scattering surfaces such as powdered catalysts. This technique is especially sensitive towards CO_2, CO, and other possible reaction intermediates in CO_2 photoreduction. A tunable laser has been coupled with a DRIFTS *in situ* cell with variable temperature capability and online product detection to study adsorbed gases and metal sites during CO_2 photocatalysis (Figure 1 and Figure 2). Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) is a technique that measures unpaired electrons in a system. CO_2 photocatalysis reactions are generally accepted to begin with the formation of a CO_2 radical anion and potentially go through other radical intermediates in the reaction pathway. Although these radical species are short-lived, they can be trapped by forming an adduct with a secondary molecule called a spin trap (typically a nitrone compound), which forms a more stable radical that can be directly observed by EPR (Figure 3). An EPR flow cell was designed and constructed, and similar to the DRIFTS cell, has been coupled with a tunable laser and online product detection, allowing detailed study of radicals and other paramagnetic species such as metal sites during photocatalyst reactions (Figure 1).

We have also established two new capabilities for catalyst synthesis and study of photoactive materials in-house. Glancing Angle Deposition (GLAD) is a physical vapor deposition technique in which materials are sputtered at an oblique angle to a rotating sample stage. The rotational speed and direction and the angle of sputtering are variable, which allows synthesis of unique heterostructured catalyst

architectures. The oblique angle of the incoming vapor usually results in nanopillar architectures due to a shadowing effect. This technique is especially useful for photocatalyst synthesis as it can be performed with semiconductor oxides such as TiO_2, In_2O_3, and CuO. This system will be used extensively in the following years to develop unique materials for solar CO_2 conversion as well as other applications. Figure 4 shows the GLAD deposition chamber during the first deposition with the new system as well as an SEM image of the resulting material. Transient Absorption (TA) spectroscopy is a pump-probe technique capable of characterizing electron transfer processes on extremely small timescales. A pump laser pulse is sent through a sample to create excited states, followed by a probe pulse of white light to measure the sample's absorption spectrum. The time elapsed between the two pulses is adjustable from zero to 8 ns using a moving mirror delay line, which allows the collection of an entire UV-Vis spectrum of the sample at any given delay time. The ground-state spectrum is typically subtracted from the excited-state to give a transient absorption spectrum. An optical parametric amplifier (OPA) allows the pump wavelength to be adjusted over the UV-Vis-NIR spectrum. The ability to vary pump wavelength and delay time allow for a very large amount of data to be collected for a single sample, giving important insight into excited states and electron transfer processes in the sample.

Accomplishments

- Developed novel techniques for *in situ* photocatalyst characterization using IR and EPR spectroscopy with tunable laser excitation and online product detection (Figure 1)
    - Demonstrated proof-of-concept $CO_2^{\bullet-}$ radical anion detection by EPR (Figure 3)
- Synthesized and tested mixed-valent cobalt (II, III) oxide photocatalysts by solution method
- Synthesized and characterized TiO_2, In_2O_3, and CuO heterostructured catalysts by Glancing Angle Deposition (GLAD) through collaboration with University of Georgia
- Established in-house Glancing Angle Deposition (GLAD) capability for synthesizing unique catalyst architectures
- Established femtosecond pump-probe spectroscopy capability for characterizing photocatalysts and other photoactive materials

Future Directions

- Optimize parameters for GLAD system to make unique heterostructured photocatalysts
- Continue catalyst screening and testing in newly developed IR and EPR setup
- Construct larger-scale flow photoreactor for measuring catalytic activity on bulk materials
- Build *in situ* capability for pump-probe experiments

FY 2021 Peer-reviewed/Non-peer reviewed Publications
N/A

Intellectual Property
N/A

Total Number of Post-Doctoral Researchers
2 – Lauren Hanna (SRNL), Zach Duca (SRNL)

Total Number of Student Researchers
1 – Mona Asadinamin (University of Georgia graduate student)

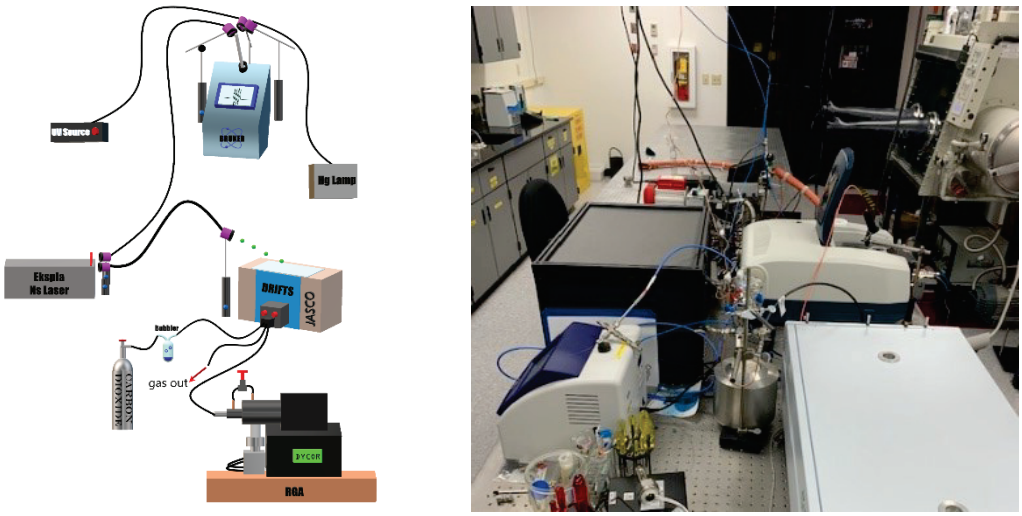

Figure 1: Diagram and photo of tunable laser DRIFTS/EPR setup with RGA product detection

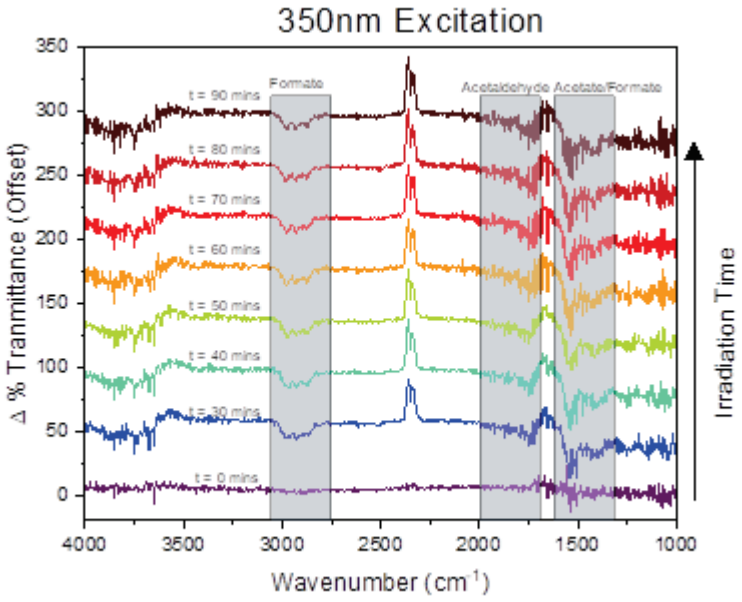

Figure 2: *In situ* DRIFTS difference spectra of TiO_2 nanocatalyst showing product formation in EtOH oxidation

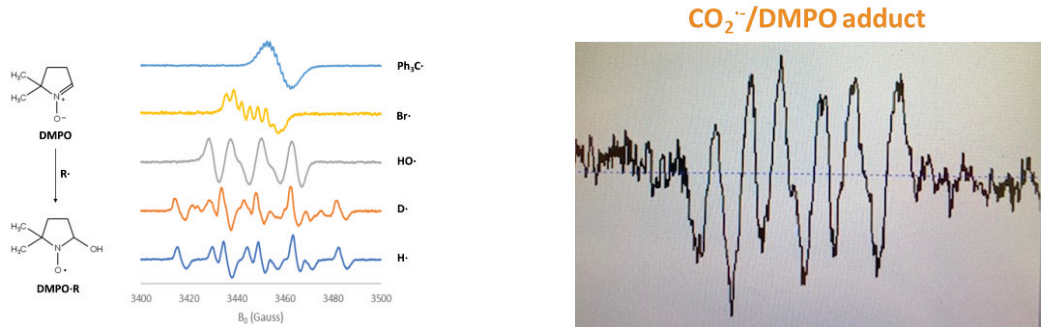

Figure 3: *In situ* EPR spectra showing spin trapping capabilities and proof-of-concept detection of various radicals, including the $CO_2^{\bullet -}$ radical anion relevant to CO_2 photoreduction

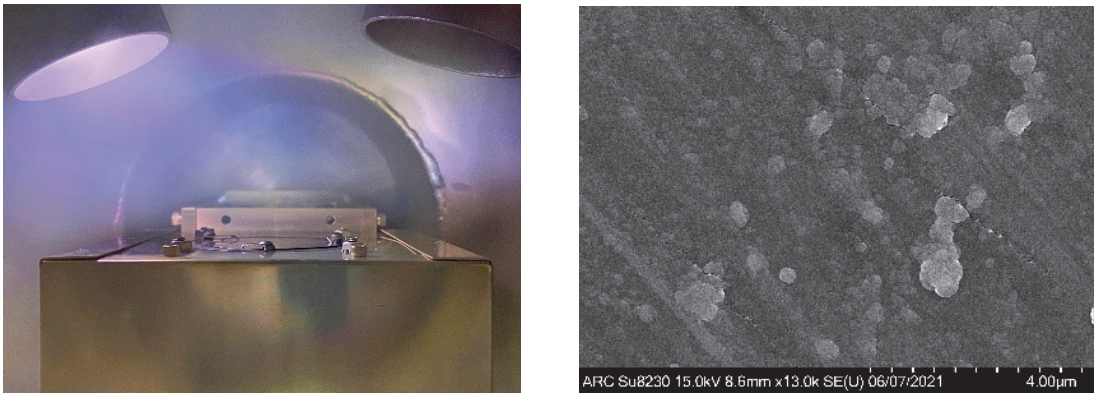

Figure 4: Deposition chamber of newly-developed GLAD system during first deposition; SEM image from first deposition of TiO_2