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 this project allows understanding of catalytic behavior and identification of intermediate species present in the photocatalytic conversion of CO_2. Additionally, new capabilities in novel physical vapor deposition techniques allow SRNL to design uniquely structured nanomaterials for potential uses in photocatalysis.

Project Team

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

Abstract

Recent research in CO_2 photocatalysis has largely focused on exploring new catalysts; however, details of the relationship between charge carrier dynamics and gas dynamics on the surface of nanomaterials often remain unclear. Knowledge of these processes will allow one to rationally design highly efficient catalysts for solar CO_2 conversion. This project aimed to develop state-of-the-art techniques and establish new capabilities in SRNL to enable the study of photocatalysts and other materials in 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 at various wavelengths of excitation. We also established a new in-house capability for catalyst synthesis and product evaluation which enables a deep understanding of how catalyst preparation methodologies impact product generation. In FY22, we gained in-house expertise and knowledge on the newly constructed a physical vapor deposition device, i.e. glancing angle deposition (GLAD) system, and constructed a flow photoreactor system for CO_2 photoconversion and other photocatalytic studies.

Objectives

- Develop expertise in physical vapor deposition, i.e. Glancing Angle Deposition (GLAD), catalyst synthesis capabilities at SRNL
- Design photoreactor system for bulk photocatalyst testing
- Synthesize novel catalysts for flow photoreactor studies
- Establish in situ diffuse reflectance UV-Vis technique at SRNL
- Evaluate photocatalytic behavior of heterojuction semiconductor catalysts

REVIEWS AND APPROVALS

1. Authors:

___A.B. Thompson____9/30/2022_____
Name and Signature   Date

2. Technical Review:

___P. Ward____9/30/2022_____
Name and Signature   Date

3. PI's Manager Signature:

___J. Cortes-Concepcion____9/30/2022_____
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

Carbon dioxide (CO_2) is a primary driver of global climate change and a primary 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 provides the opportunities to drive these reactions 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 drive reactions with species bound or sorbed at the surface. However, the details of this process are unclear and highly dependent on the nature of the catalyst and reaction conditions. Additionally, catalyst activities and selectivities are still too low for commercial viability. Deep knowledge of these processes will help design the next generation of CO_2 conversion photocatalysts.

This project aimed to elucidate the interaction between charge carriers, adsorbed gases, and reaction intermediates in CO_2 photoconversion over semiconductor nanocatalysts. Photocatalytic nanostructured materials were synthesized by physical vapor deposition, i.e. Glancing Angle Deposition (GLAD), solution precipitation (sol-gel techniques), and solid-phase sintering techniques. These materials were characterized by scanning electron microscopy/ energy dispersive x-ray spectroscopy (SEM/EDX) and tested in CO_2 photocatalytic conditions using a custom-constructed flow photoreactor system.

Approach

Diffuse reflectance spectroscopy is a powerful technique for studying materials such as powdered catalysts that scatter light in all directions. In FY21 we developed an *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) system for probing surface bond formation in photocatalytic reactions. This technique is especially sensitive towards CO_2, CO, and other possible reaction intermediates in CO_2 photoreduction which have long lifetime intermediates on the surface of the catalyst. An optical parametric oscillator (OPO) pumped by a Nd:YAG laser was coupled with a DRIFTS *in-situ* cell with variable temperature capability and integrated with a residual gas analyzer (RGA) for probing gas species of interestThis allows for the variable wavelength excitation of the photocatalyst while feeding reactants over the surface and mass spectrometric identification of the products.

In FY22,a variety of semiconductor heterojuction catalysts were produced by sputtering techniques, direction nanoparticle sintering, and sol-gel approaches. 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 unique nanopillar architectures due to a shadowing effect. This technique is especially useful for photocatalyst synthesis as it can be generate with multifunctional semiconductor oxides such as TiO_2, In_2O_3, and CuO.

The SRNL GLAD system contains an RF power supply and a DC power supply with two guns that can be loaded with different sputtering targets, allowing for synthesis of wide array of unique materials of various compositions. The fully configured and operational system is shown in Figure 1. A cross-sectional SEM-EDX image is shown in Figure 2 with TiO_2 deposited onto a glass slide.

A photoreactor system was constructed in FY22 which allows photocatalyst testing and product evaluation. The system contains a gas mixer and variable temperature humidifier integrated into a photocatalytic testing chamber with a transparent viewport. The gas humidifier system feeds a custom photoreactor and the photoreactor exhaust is sampled by RGA, allowing for online gas product detection. The photoreactor could be used with the newly obtained solar simulator in SRNL but can be used with any visible or ultraviolet light source, including laser sources. The reactor itself contains a modified ConFlat fitting with a UV-grade fused silica window (Figure 3). A custom filter gasket containing a sintered metal filter was fabricated with a small tube fed through the gasket as a gas inlet. In this way, gas flows into the reactor through the tube near the top and is forced down through the catalyst and through the filter gasket. The customized gasket was sized so that a thin layer of catalyst could be loaded on top and secured in place by the UV window. This ensures that the catalyst remains in place and is fully illuminated during testing. Although most experiments were done in a flow configuration at atmospheric pressure, this system allows for high-pressure, high-temperature, and/or batch catalyst testing as well.

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)
- Established in-house Glancing Angle Deposition (GLAD) capability for synthesizing unique catalyst architectures
- Developed photocatalytic testing station for product generation and evaluation
- Established a collaboration with the University of Georgia

Future Directions

- Optimize parameters for GLAD system to make unique heterostructured photocatalysts
- Continue catalyst screening and testing in newly developed IR and EPR setup
- Integrate pump-probe spectroscopic techniques to evaluate electron transfer processes

FY 2022 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
0

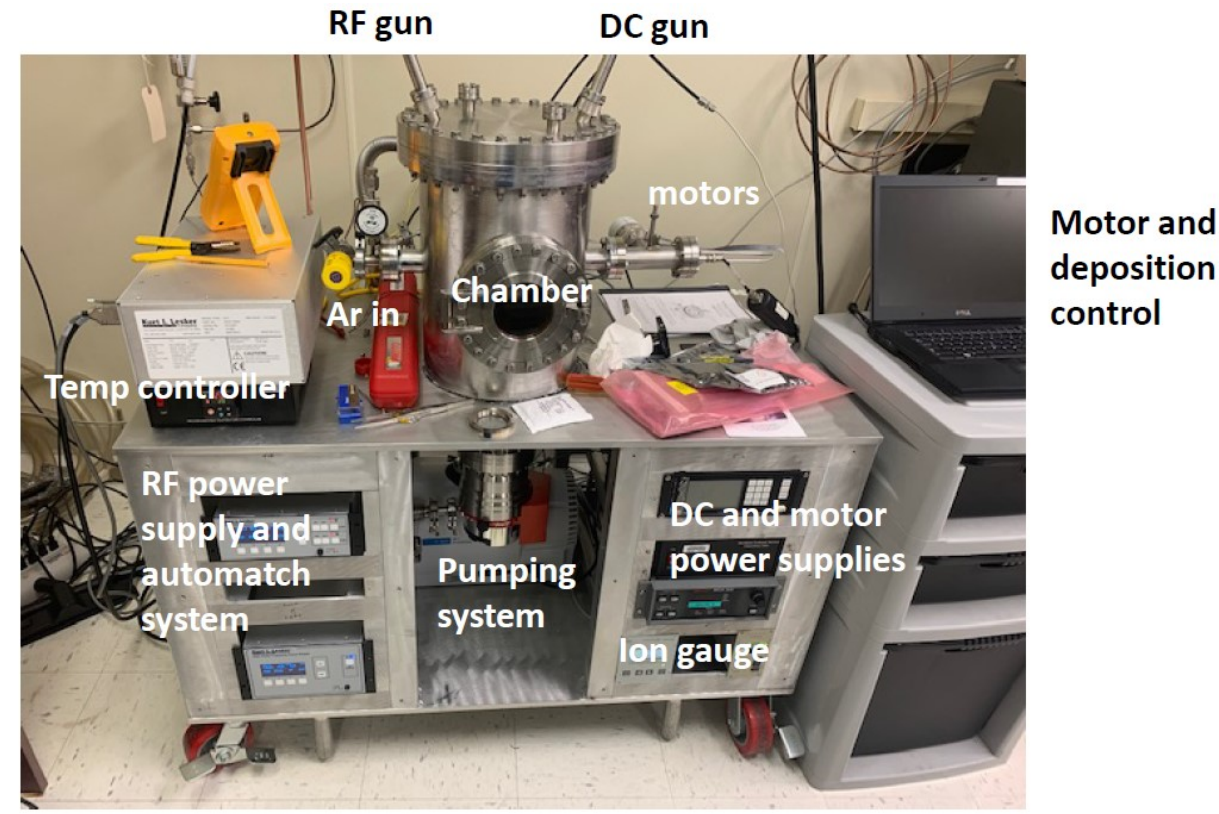

Figure 1: Glancing Angle Deposition (GLAD) system

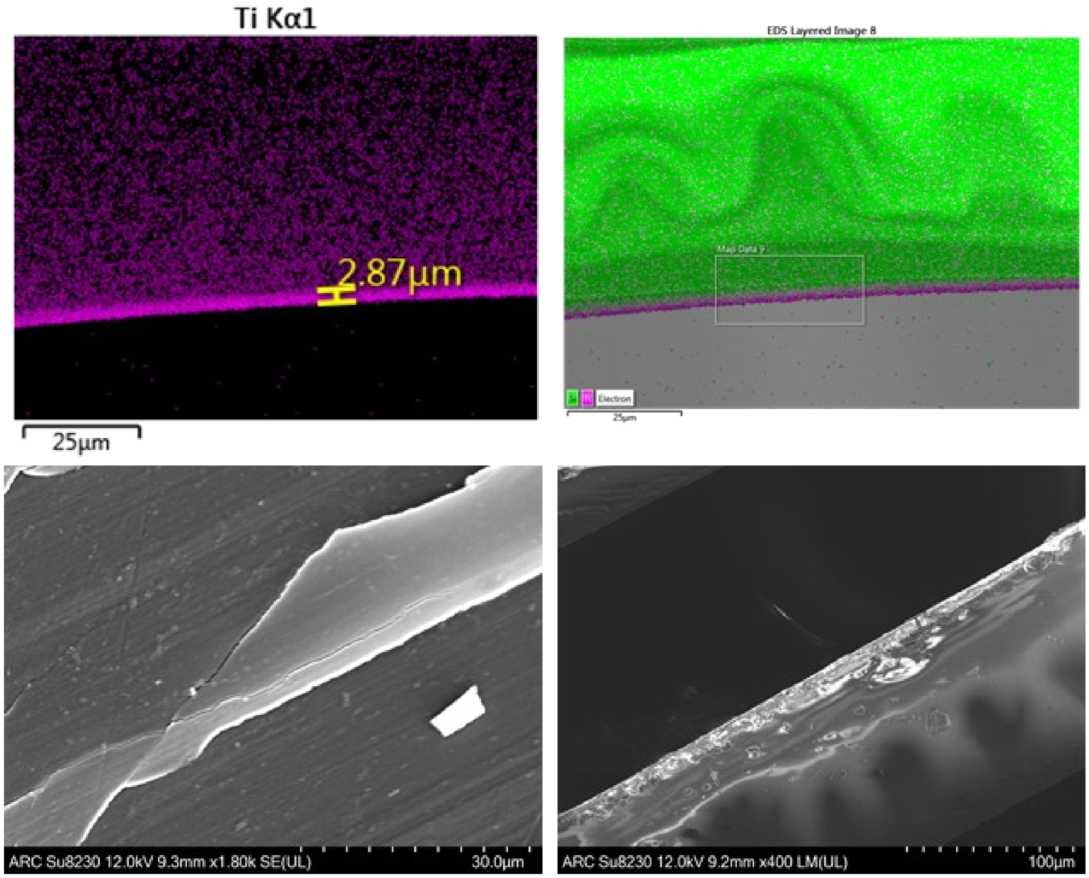

Figure 2: Cross-sectional SEM-EDX of GLAD TiO_2 sputtered on a glass substrate

Figure 3: Custom photoreactor system for CO_2 photocatalyst testing