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1. Executive Summary

The project was centered on developing new ceramic materials to improve efficiency of solar energy capture for photovoltaic cells and for catalysts to split water to make hydrogen. The work has led to one possible breakthrough material, a nanoscale photocatalyst that can be used to assemble nanocomposite catalysts. Another important result of the work is the development of synthesis methods to create nanostructured and mesoporous oxides for use in solar energy harvesting. Specifically, we have developed two new methods potentially useful for preparing high performance electrodes for PV cells.

2. Comparison of the actual accomplishments with the goals and objectives

The principal objective of the project was to develop and test new meso- and nano-structured titanate oxide ceramics for use in solar energy harvesting, specifically in photovoltaic (PV) cells and photocatalytic reactors. The materials of interest for both applications, namely wide bandgap semiconductors, are critical in both applications, and we aimed to build an improved understanding of their function to reach higher device efficiencies.

The project focused on two nanostructured oxide materials, which can be modified to yield mesostructured devices by exfoliation, scrolling, pillaring and particle size control. The materials of interest are Aurivillius phases and beta-gallia rutile (BGR) intergrowth phases.

The accomplishments of the project include great success in making nanostructured layered Aurivillius oxides and testing their photoactivity and optical absorption behaviors, and successful synthesis of the BGR materials as nanopowders with nanostructures and TiO_2 as a mesoporous solid. While we were unable to perform efficiency testing of these materials in actual devices, the project has clearly defined the layered materials as potential candidates for next-generation photocatalysts and PV cell electrodes.

3. Summary of Project Activities:

The major activities, significant results, and major findings are summarized by task below.

Task 1.0 Materials synthesis by chemical and solid state approaches

Combustion synthesis

The beta gallia-rutile intergrowth materials (BGR intergrowths, $\text{Ga}_4\text{Ti}_{n-4}\text{O}_{2n-2}$) for solar cell applications were studied, with many attempts to synthesize the complex intergrowths using combustion synthesis. When we first began we used carbohydrazide and di-hydroxybis(ammonium lactate) titanium(IV) as our fuel sources, and gallium nitrate as the gallium source. Ammonium nitrate was used to vary the fuel-to-oxidizer ratio to keep the titanium and gallium stoichiometry the same. The as-synthesized powders were amorphous in nature, so we decided to implement a calcining step, in which we heat treat the powders at 1400°C for two hours. We decided on this temperature after trying heat treatments at 1200°C , 1300°C , and 1400°C , and finding that we were able to successfully stabilize the phase at the higher temperature. This information can be found in **Figure 1**. In the beginning we were able to synthesize pure beta-gallia rutile (BGR). After changing batches in carbohydrazide we ran into some oddities that did not allow us to repeat the procedure. We were not able to produce the same phase pure samples as we were before. On top of this, we concluded that we were successfully stabilizing a lower n value, 11, than what we had expected through the calculation of d -spacing.

We decided to attempt to combust stoichiometric amounts of titanium and gallium with carbohydrazide to produce the $n=11$ intergrowth. After synthesizing the $n=11$ phase using various fuel-to-oxidizer ratios, 1.29, 1.25, 1.22, and 1.13, and using the original carbohydrazide, we saw positive results for a BGR intergrowth with some other impurities. We also saw similar results when using carbohydrazide from a different supplier, also using the same fuel-to-oxidizer ratios. Understanding that the carbohydrazide fuel was probably reacting with the precursors prior to combustion or precipitating out due to pH variations, we decided to remove it from the equation.

Figure 1. The X-ray diffraction patterns for the $n=25$ BGR intergrowth structures combusted in the presence of carbonylhydrazide, and then heat treated at varied temperatures for 2 hours.

We switched back to synthesizing higher n values of 23, 25, and 27, with the di-hydroxybis(ammonium lactate) titanium(IV), gallium nitrate, and ammonium nitrate. Utilizing the di-hydroxybis(ammonium lactate) titanium (IV) as the lone fuel, we were able to synthesize pure phase gallium titanate again, with good repeatability. We have successfully synthesized a variety of gallium titanate samples with three different n values, 23, 25, and 27, each varying the fuel-to-oxidizer ratio. The X-ray diffraction patterns for the three samples with fuel-to-oxidizer ratios of ~ 1 is presented in **Figure 2**. The $n=25$, and 27 samples exhibited phase purity, while the $n=23$ sample showed some rutile phase, and gallium oxide.

Figure 2. X-ray diffraction patterns for the $n=23$, 25, and 27 samples with fuel-to-oxidizer ratios of ~ 1 . The circle and the triangle markers indicate rutile and gallia, respectively.

Upon closer inspection of the XRD data, we observed that we were actually stabilizing much lower n values between 9 and 15. The $n=23$, 25, and 27 were actually $n=9$, 11, and 15, respectively.

Additional synthesis experiments were carried out to produce the $n=11$ and $n=25$ intergrowths. Two sources of the fuel and two sources of oxidizer were tested for multiple batches of the two compositions. For the $n=11$ phase, several fuel-to-oxidizer ratios were employed, resulting in some samples containing the phase of interest.

In summary, the work focused on combustion synthesis has provided samples of the intergrowths for testing and has additionally built a framework of knowledge about the experimental details for synthesis of these phases.

Sol-gel synthesis

A series of porous titanium dioxide, niobium oxide, and titanium-niobium oxide nanocomposite powders were prepared via modified sol-gel processes. Titania sols were prepared using titanium isopropoxide, ethanol, and acetic acid while niobium oxide sols were prepared using niobium chloride, butanol, and acetic acid. In order to produce the mixed oxide nanocomposite the two sols were mixed with a molar ratio of Ti:Nb of 1. After sol preparation, the solvent was evaporated and the resultant solid was initially heated to 150 °C for 24 hours, producing xerogels. These xerogels were then heat treated to 500, 550, and 600 °C in air to produce porous powders. Thermal properties of these powders were measured using differential thermal analysis (DTA). The crystallinity as a function of temperature of all powders was determined with x-ray diffraction (XRD). Approximately 50 synthesis attempts were required to reach the goal of a mesoporous solid.

Results indicate that the phases of interest (anatase, niobium pentoxide, and mixed titanium-niobium oxide) were synthesized when heating the respective xerogels to 500 °C for 24 hours. Further characterization of these powders via scanning electron microscopy (SEM) and gas adsorption/desorption were completed. Pore analysis for titanium dioxide and niobium pentoxide (Figure 3) powders was performed via nitrogen adsorption/desorption confirmed a porous structure.

Figure 3: Nitrogen adsorption/desorption isotherm of porous titanium dioxide powders prepared via sol-gel synthesis, demonstrating the presence of mesopores in the solid.

Task 2.0 Hydrothermal synthesis of candidate materials

There is no literature that documents the synthesis of this ternary material through hydrothermal methods, however, literature shows that the most stable form of the BGR intergrowths (as synthesized via solid state reactions) occurs when $n = 25, 27$, or 29 . In these syntheses, a variety of titanium and gallium precursors were used with the expectation of producing phase pure $\text{Ga}_4\text{Ti}_{21}\text{O}_{48}$. The modified titanium isopropoxide was prepared using titanium isopropoxide in a 1:1 ratio with 2,4 pentanedione. All other precursors were used in their original state and reactions were carried out using stoichiometric ratios of Ti:Ga unless otherwise indicated. Careful phase characterization using X-ray diffraction (XRD) was utilized to observe the phases present for the as-synthesized and heat treated powders

In general, the resulting powders from these experiments were largely amorphous and required heat treatments of 1000°C for 1 hour to obtain crystalline phases. Increasing the pH of the initial solutions appeared to increase the amount of rutile phase present once the structure was entirely crystalline. The highlights of these experiments are compiled in Table 1.

Table 1: Summary of the hydrothermal reaction experiments and results.

Ti Precursor	Ga Precursor	Time (hrs)	pH Adjustor	pH	Reaction Product
Anatase TiO_2	$\text{Ga}(\text{NO}_3)_3$	24	$\text{NaOH}/\text{NH}_4\text{OH}$	Entire pH range	Rutile
Rutile TiO_2	$\text{Ga}(\text{NO}_3)_3$	24	$\text{NaOH}/\text{NH}_4\text{OH}$	Entire pH range	Rutile
Modified Ti Isopropoxide	$\text{Ga}(\text{NO}_3)_3$	24	---	1.1	Anatase
Modified Ti Isopropoxide	$\text{Ga}(\text{NO}_3)_3$	24	NH_4OH	2.2-4.0	Rutile/Anatase
Modified Ti Isopropoxide	$\text{Ga}(\text{NO}_3)_3$	24	NH_4OH	5.13	Rutile/GTO
Modified Ti Isopropoxide	$\text{Ga}(\text{NO}_3)_3$	24	NH_4OH	8.1	Rutile/GTO
Modified Ti Isopropoxide	5X $\text{Ga}(\text{NO}_3)_3$	24	NH_4OH	Entire pH Range	Rutile/ β -Gallia/Anatase
Modified Ti Isopropoxide	$\text{Ga}(\text{NO}_3)_3$	24	NaOH	9.8-13.0	NTO/Unknown
Modified Ti Isopropoxide	$\text{Ga}(\text{NO}_3)_3$	24	NaOH	14	NTO
DALT	$\text{Ga}(\text{NO}_3)_3$	24	---	5.1	Rutile/Anatase
DALT	$\text{Ga}(\text{NO}_3)_3$	24	NH_4OH	6.0-9.6	Rutile/Gallia
Modified Ti Isopropoxide	$\text{C}_{15}\text{H}_{21}\text{GaO}_6$	24	NH_4OH	5.0-10.0	Rutile/ β -Gallia/Anatase

$\text{Ga}_4\text{Ti}_{21}\text{O}_{48}$ was only synthesized as a minor phase through hydrothermal synthesis, where rutile TiO_2 was the major phase. The powders that contained this minor phase were characterized using UV-VIS spectroscopy and the band gap was determined to be approximately 2.8 eV. Variation of the titanium and gallium precursors did not appear to have a significant effect on the phases formed, with the exception that the purely anatase and rutile precursors only had rutile as their reaction products, despite changes in pH.

β -gallia, as well as anatase and rutile TiO_2 were phases present in experiments where the modified titanium isopropoxide was used with excess gallium nitrate/2,4 gallium pentanedionate. It should be noted that these are completely separate phases and do not relate to the presence of BGR intergrowths.

The use of NaOH as a pH modifier had an interesting consequence. The use of NaOH resulted in Na^+ ions incorporating themselves into the structure, resulting in sodium titanium oxide. Due to this development, additional experiments were performed. Band gap, as determined by UV-VIS spectroscopy, was approximately 2.5 eV for these powders.

Although phase pure BGR was not achieved, interesting morphologies were nonetheless produced through the use of hydrothermal synthesis as seen in figures 4 and 5 below. Platelet structures were produced where DALT was used as the precursor and wires were produced using an anatase precursor modified with NaOH. In general, the majority of synthesized powders were well below $1\mu\text{m}$ and were spherical in morphology.

Figure 4. Nanostructured powders produced using DALT as precursor.

Figure 5. Nanostructured powders produced using anatase titania and NaOH, with substantially different morphology (compare to Fig. 4).

Overall, using a series of 14 experimental conditions, under a designed experiment, allowed us to develop the experimental process for producing nanostructured BGR materials. Although we did not achieve 100% phase purity, the complex shapes and morphologies are of great interest for high surface area photocatalytic and PV cell electrode applications. Of particular interest is the ability to form platelets with thickness $< 20\text{nm}$ and to control the process to produce whiskers or nanoparticles, an exciting new finding that we continue to study with other funding sources.

Task 3.0 Characterization of candidate materials

Physical characterization (including diffraction, surface area, band gap where applicable) has been undertaken for the all powders prepared using the methods described in Tasks 1 and 2, with examples shown in Figs. 1-4.

Task 4.0 Preparation of mesostructured films

Manual screen-printing of thin/thick film electrodes for the PV cells has been undertaken using several powders. A series of ~85 films were deposited and heat treated. Films of the desired thickness (10 to 50 microns) were prepared with porous titanium dioxide, niobium pentoxide, and Degussa P25 powders on glass via a modified screen printing process. The powders were ground to < 10 microns and were ultrasonically cleaned in acetone to remove adsorbed fine particles. Precleaned glass substrates were cut to pieces of 2.5 cm by 2.5 cm via a glass scribe and further cleaned with isopropanol, methanol, and acetone. After a number of iterations, two different screen printing suspensions were developed (1) a suspension of powder, ethylene glycol, and ethanol and (2) powders, polyethylene glycol, ethyl cellulose, terpeniol, and ethanol. Screen printed thick films were then heat treated to various temperatures. It was shown that thick film adhesion and cracking was a function of both solution type and heat treatment temperature.

Figure 6. Thick film deposited via screen printing and heat treated to 300 C using commercially available Degussa P25.

The results show the ability to control film thickness with relative ease, yet further optimization is required to produce crack-free films. Nonetheless, our extensive work in this area has yielded films that could be tested in a PV device.

Task 5.0 Preparation of mesostructured photocatalysts

We have demonstrated for the first time that oxide nanosheets can be ion exchanged and then exfoliated without the use of organic pillaring agents, using a process summarized in Fig. 7. Developing this experimental approach required testing several acids, particle sizes, milling methods, incorporating ultrasonic energy, but yielded success.

An exciting new result is improved photoactivity for composite materials of nanosheets with anatase nanoparticles. The niobate nanosheets shown in Fig. 8 have been successfully combined with anatase particles to produce a composite with improved photoactivity, shown in Fig. 9.

Fig. 7: Schematic of the process of exfoliation and production of the nanocomposite for photocatalyst applications.

Fig. 8: SEM image of exfoliated nanosheets.

Fig. 9: SEM image of nanocomposite material composed of nanosheets coating anatase particles.

Fig. 9: Photoreactivity of the nanosheet-particle composite vs. that for the TiO₂ particles only, demonstrating improved performance from the mesostructured nanocomposite.

Overall Task 6 shows excellent success, although we have not yet clearly determined the mechanisms by which the photocatalytic activity increases.

Task 6.0 Preparation and performance of PV cells

As shown in Task 4, we successfully prepared films of interest, and completed the optimization of the process to prepare PV cells for testing. A thorough literature search was performed to define the processing steps but initial attempts did not produce defect-free films suitable for construction of the remainder of the PV cell. However, we have clearly shown the mesoporous nature our candidate electrodes made via sol-gel synthesis, which are of ideal geometry for PV cells.

Task 7.0 Performance of photocatalysts

The improvement in photoactivity for the nanocomposite (see Task 5) is roughly 15% compared to anatase alone for photodecomposition of methylene blue molecules, when using a remarkably small mass loading of nanoparticles. While we did not attempt in this work to understand the mechanisms for the improved photoactivity we suspect that the nanosheets are useful for separating the electron/hole pair during the photoreaction. Further, we attribute the improved activity to enhanced charge separation to the intimate contact of the nanosheets with the anatase particles, which is possible because our new method does not use organic pillaring agents (which would prevent electrical pathways from forming).

Task 8.0 Project Management and Reporting

Nothing new to report.

4. Products developed under the award and technology transfer activitied

- a. Publications: we are in process of finalizing publications for submission to peer-reviewed journals. We envision 3 papers will result from the project.

- b. Web site or other Internet sites that reflect the results of this project: None
- c. Networks or collaborations fostered: None
- d. Technologies/Techniques: Our new approaches to synthesis – hydrothermal, sol-gel, and exfoliation, are of technological interest and will be the subjects of publications to be shared with the community.
- e. Inventions/Patent Applications, licensing agreements: None
- f. Other products, such as data or databases, physical collections, audio or video, software: None