

SAND23XX-XXXXR**LDRD PROJECT NUMBER:** 229495**LDRD PROJECT TITLE:** Science Driven Discovery of Nanoparticle Photocatalysts**PROJECT TEAM MEMBERS:** A. Talin (PI), J. Stoffel, D. Robinson, R. Horton, A. Bhandarkar

ABSTRACT: Photocatalytic water splitting using suspensions of nanoparticle photocatalysts is a promising route to economically sustainable production of green hydrogen. The principal challenge is to develop photocatalysts with overall solar-to-hydrogen conversion efficiency that exceeds 10 percent. In this project we have developed a new platform for investigating candidate materials for photocatalytic water splitting. Our platform consists of patterned Au electrodes and a Ag/AgCl reference electrode on an insulating substrate onto which we disperse nanoparticle photocatalysts. We then cover the substrate with a thin layer of ionogel containing a protic ionic liquid that dissolves water from the ambient. Using this platform we have demonstrated photoelectrochemical activity mapping for single and small clusters of BiVO₄ nanoparticle photocatalysts and correlated these results to their Raman and photoluminescence spectra. The preliminary results suggest a strong correlation for low efficiency nanoparticles, followed by saturation for those with higher activities, indicating that interface reaction or electrolyte transport become the limiting factor. We anticipate that further application of this platform to investigation of candidate photocatalyst materials will provide useful insights into the mechanisms that limit their performance.

INTRODUCTION AND EXECUTIVE SUMMARY OF RESULTS: Solar-driven water splitting (WS) is an attractive route to generate green hydrogen, an easily storable and clean fuel, and approaches based on nanoparticle photocatalyst suspensions are projected to be among the most cost-effective.[1, 2] However, these projections are based on a 10% STH efficiency, while state-of-the-art efficiencies are ~1% [2]. We propose to dramatically improve efficiency by developing the ability to rapidly characterize photocatalytic activity and correlate it to spectral and transport properties of photocatalysts. Photocatalytic water splitting comprises three basic steps: 1) light absorption, 2) transport of photocarriers to the surface of the nanoparticle, and 3) H₂ and/or O₂ evolution, often aided with a co-catalyst. Whether using a single type of nPC or separated H₂ and O₂ reactions (z-scheme), optimizing all three steps within a single material system is a considerable challenge. Traditional semiconductors are unstable in the aqueous media. Various transition metal oxides are low cost, stable, and have appropriately positioned conduction band minima and valence band maxima to drive H₂ and O₂ evolution, respectively. However, these compounds absorb only a small fraction of the solar radiation due to their large bandgaps (>3eV)[3]. To increase visible absorption, dopants like N, C, S and various transition metals are introduced to alter the electronic structure to form an impurity band[4]. This approach has yet to work mainly due to formation of deep traps that severely reduce photocarrier lifetime[5]. Addressing this challenge is difficult because many oxides form complicated bulk and surface defects, including oxygen and cationic vacancies, interstitials, line and planar defects; and while certain defects like oxygen vacancies may degrade photocarrier transport in the bulk, their presence at the surface may accelerate catalytic charge transfer reactions[6]. Furthermore, nPCs

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are typically synthesized using methods like solvothermal, sol-gel, or spray pyrolysis, where control over defects, impurities, dimensions and surface chemistry can be difficult to establish. The complexity of the photocatalytic materials make it difficult to establish which aspects are rate limiting and what modifications are needed to improve efficiency. To address this challenge, we have in this project developed a platform for correlative microscopy of individual nPCs. This platform, based on ultrathin ionogel electrolytes, enables correlation of photocatalytic activity with Raman spectroscopy, photoluminescence spectroscopy, and scanning electron microscopy. Using this approach, we have demonstrated the first correlative maps for BiVO₄ photocatalysts, a promising candidate material for oxygen evolution reaction.

DETAILED DESCRIPTION OF RESEARCH AND DEVELOPMENT AND

METHODOLOGY: The lack of detailed knowledge regarding how photocatalyst nanoparticle properties relate their ability to split water can be linked to the difficulty associated with measuring water splitting on single nanoparticle photocatalysts. Since direct measurement of H₂ and/or O₂ evolved is nearly impossible for one or few photocatalysts, photoelectrochemical measurements are used instead. Here, a laser focused to ~1 mm diameter spot is used to illuminate nanoparticle photocatalysts dispersed onto a metal (Au) electrode covered with a liquid electrolyte (dilute H₂SO₄), with a counter and reference electrodes. The difficulties associated with use of liquid cells include particle movement, vibration, bubbles, and frequent leaks. Most importantly, the liquid cell approach makes it almost impossible to use other tools, such as scanning and or transmission electron microscopy, to analyze the same particles. Our methodology to address this issue is to construct photoelectrochemical cells utilizing ultra thin solid state ionogel electrolytes. These electrolytes consist of a porous silica matrix filled with an ionic liquid. Macroscopically, the ionogel electrolyte behaves like a solid. However, at the nano/molecular scale, the behavior is dominated by the ionic liquid within the pores. By choosing a protic ionic liquid that is transparent for wavelengths > 300 nm, we perform photoelectrochemical measurements without needing a liquid cell. Furthermore, the ionogel ‘fixes’ the nanoparticle photocatalysts to the substrate, making it easy to find them in subsequent measurements, including scanning electron microscopy.

RESULTS AND DISCUSSION: To be a useful approach for correlative microscopy of nanoscale photocatalysts, the platform must enable 1) photoelectrochemical measurements with a reference electrode 2) must be transmissive to illumination 3) must be stable over prolonged periods in the ambient. To demonstrate our first platform we prepared a silica ionogel film consisting of the ionic liquid methyl diethyl ammonium triflate in a silica matrix. The general procedure for preparing this ionogel is described in ref. [7]. To characterize its ionic conductivity we used interdigitated electrodes and impedance spectroscopy which yielded a value of 0.07 S/cm, very close to the value of the ionic liquid published by the vendor of 0.083 S/cm (see <https://iolitec.de/en/node/440>). This result implies that the silica matrix has a minor effect on the transport of protons. Next, we prepared multiple specimens consisting of BiVO₄ photocatalysts dispersed on Si/SiO₂ substrates and coated with the ionogel, with a thickness of only 350 nm. We then performed photoelectrochemical measurements on single and small clusters of photocatalyst

nanoparticles, revealing an onset of photocurrent at ~ 0.2 V (vs. Ag/AgCl). Subsequently, we mapped the photoelectrochemical current and demonstrated that it can be correlated to the micro-Raman and micro-photoluminescence spectra. We used a 532 nm laser with a power of 300 mW and a spot size of 0.7 mm, corresponding to areal power density of $\sim 8 \times 10^4$ W/cm². This value greatly exceeds the 0.1 W/cm² value corresponding to atmospheric mass 1.5 that is used to simulate solar illumination. Preliminary experiments using Raman line shift do not show a significant increase in the nanoparticle temperature during the illumination however more measurements are needed.

ANTICIPATED OUTCOMES AND IMPACTS: The rapid change in climate driven by fossil fuels possess a substantial threat to US national security. Unlivable conditions due to sea level rise or extreme draught lead to mass migration and international conflict that affect the US. This situation will intensify unless alternative energy sources are developed. Sandia has decades-long international leadership in hydrogen, recently exemplified by its role as the lead labs in the DOE consortia. This work addresses Sandia's energy storage roadmap by providing a practical, safe, carbon-neutral technology for photocatalytic hydrogen generation – a concrete system concept that builds upon our unique combination of expertise and will allow distinguishing growth for Sandia in this field. It addresses the recently announced DOE Hydrogen Earth Shot to reduce the cost of clean hydrogen by 80% to \$1 per 1 kilogram in 1 decade (111 goal). Successful execution of this project helps integrate experimental data collection using different techniques that previously could not be carried out on the same photocatalyst nanoparticle and therefore provided insufficient insight into mechanisms limiting efficiency.

CONCLUSION:

We have demonstrated that ionogel electrolytes containing protic ionic liquids can be deposited using ink jet printing as thin films with thickness approaching 100 nm. We further demonstrated that BiVO₄ photocatalyst nanoparticles deposited onto patterned Au electrode and covered with the ultra thin ionogel films exhibit photoelectrochemical activity when illuminated using 532 nm light. Finally, we demonstrated that the photoelectrochemical activity can be mapped and correlated with Raman and photoluminescence spectroscopy.

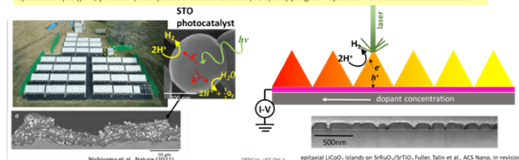
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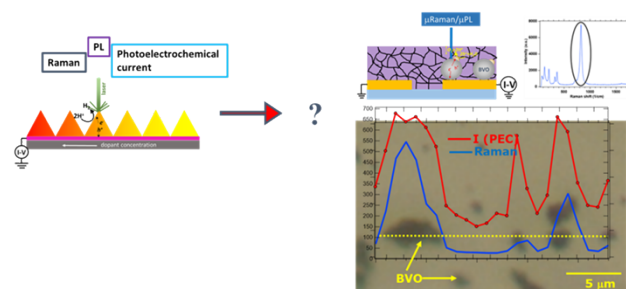
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ADDENDUM:

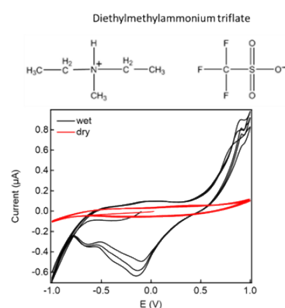
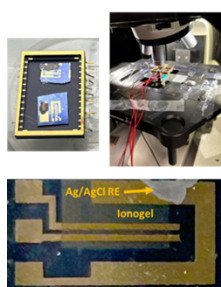
Science-guided Discovery of Nanostructured Photocatalysts (nPCs) for Solar H₂
Photocatalytic (PC) water splitting (summary slide)
• Predicted to be most cost efficient H₂ production; need to improve photocatalyst efficiency from ~1% to >5%.
Knowledge gap:
• How to extend visible absorption in doped SrTiO₃ (STO) photocatalysts (PC) without severely compromising efficiency
Hypothesis project will test:
• Epitaxial STO nPCs with graded dopant concentration will reveal optimum doping, fundamental performance limits.
R&D approach:
• Reduce defects via PLD single crystal growth; spatially vary dopant concentration; use spatially resolved electrical, spectroscopic (μ PL, μ Raman) and photoelectrochemical (PEC) mapping for rapid turn-around characterization.



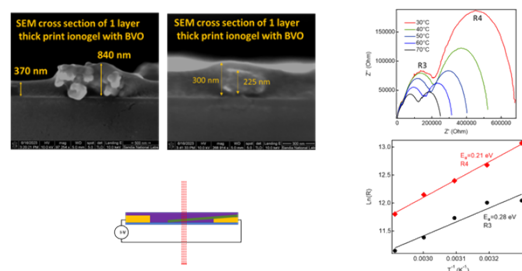
We focused on developing a mapping PEC, Raman, PL capability



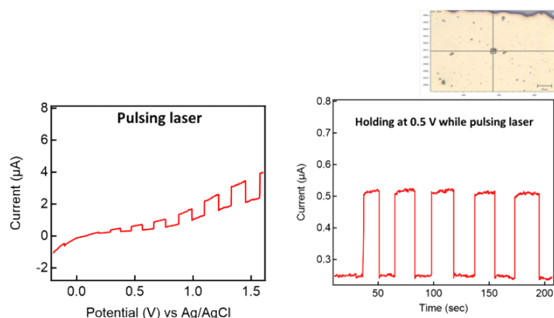
Ionogel with protic ionic liquid, dissolved H₂O enables water splitting



High ionic conductivity enables functional electrolyte at <100 nm thickness



PEC on a small cluster of BVO photocatalysts shows very high activity @532nm



First demonstration correlating PL/Raman/PEC

