

II.G.1 Nano-Architectures for 3rd Generation PEC Devices: A Study of MoS₂, Fundamental Investigations and Applied Research

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Fiscal Year (FY) 2011 Objectives

- Develop a high surface area, transparent conducting (TC) scaffold as a broadly applicable substrate for photoelectrochemical (PEC) devices, as well as a scalable route to fabricate them.
- Plan, develop, and perform synthesis and characterization, both physical and PEC, of nanoscale transition metal dichalcogenides.
- Correlate atomic scale characterization of dichalcogenides with performance to iteratively optimize materials for water splitting efficiency and stability.
- Merge TC and dichalcogenide materials to yield enhanced performance high surface area catalyst systems and demonstrate their efficacy under standard operating conditions.
- Correlate physical characterization results of complete device with its PEC performance to tune subsequent syntheses in an effort to optimize water splitting efficiency and photoelectrode stability.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(Y) Materials Efficiency

- (Z) Materials Durability
 (AA) PEC Device and System Auxiliary Materials
 (AB) Bulk Materials Synthesis

Technical Targets

The focus of this project is the development of a PEC device that incorporates a 3rd generation nanostructured absorber with a high aspect architecture support that enables efficient solar absorption and charge transport. If successful, this project will address the following DOE technical targets as outlined in the Multi-Year RD&D Plan.

TABLE 1. Progress towards Meeting Technical Targets for PEC Hydrogen Production

Characteristics	Units	2013 Target	2018 Target	2011 Status
Usable semiconductor bandgap	eV	2.3	2.0	1.8
Chemical conversion process efficiency	%	10	12	TBD
Plant solar-to-hydrogen efficiency	%	8	10	TBD
Plant durability	hr	1,000	5,000	TBD

TBD – to be determined

FY 2011 Accomplishments

- Developed a facile, scalable synthetic route to fabricate high surface area electrodes (HSEs) of transparent conducting oxide (TCO) materials.
- Electrochemically quantified relative enhancement of HSE surface area. Synthetic control garners 20-600 times surface area increase.
- Patent application pending for novel HSE fabrication method.
- Developed a facile, scalable, room temperature synthesis of quantum confined MoS₂ nanoparticles with bandgaps of 1.8 eV.
- Demonstrated accelerated stability of MoS₂ catalysts over 10,000 voltage cycles to simulate diurnal conditions.



Introduction

PEC water splitting is a promising route to produce high purity hydrogen (H₂) from a renewable resource [1].

Hydrogen produced in this manner represents a means of chemical storage of solar energy; the H_2 can potentially be used as a fuel. Current costs of H_2 production by photoelectrochemistry are not competitive with H_2 produced by the reformation of fossil fuels. However, a recent techno-economic analysis has shown that if high performance, stable, low-cost materials can be developed, the DOE target of \$2-\$4/gasoline gallon equivalent for dispensed hydrogen could be reached using solar photoelectrochemistry [2].

Development of high purity electrochemical H_2 generation systems requiring lower capital costs with sunlight as the sole energy input is the end goal of PEC water splitting research. Steps toward this goal include discovery and optimization of efficient, inexpensive, stable electrocatalysts, (photo)electrode materials, and high surface area electrode substrates on which to coat them. Integration of these components could result in a complete system capable of efficient, cost-effective, and sustainable production of solar-derived hydrogen.

Approach

Development of transparent HSEs to act as supports for both electrocatalyst and photoelectrode materials is an enabling technology at both the fundamental and applied research levels. In electrocatalysis, HSEs allow more electrocatalyst to be packed into a given area which increases the rate per projected area at which product is generated. For photoelectrochemistry, HSEs coated with ultra-thin layers of light absorbing material allow for more complete absorption of incoming light as compared

to flat electrodes – a major challenge in thin-film solar technologies (see Figure 1) [3]. Enabling ultra-thin layers to completely absorb solar photons is particularly advantageous as only a short distance needs to be traversed by photo-excited charges in order for them to reach the solid-liquid interface (for minority carriers) or the back contact (for majority carriers). This should yield much improved charge collection efficiency, translating to improved external quantum efficiency (QE). The end result is an enhanced overall performance due to greatly increased interfacial area.

Such HSE structures require integration of materials that effectively absorb light to produce electronic charges that can efficiently drive the catalytic turnover of hydrogen and oxygen via water splitting. While high efficiency devices have been developed in this field [4], the costly processes and rare materials used in their production limit large scale deployment. Thus, it is imperative that new materials are discovered based on earth-abundant elements and produced using low cost methods. The approach used herein focuses on the development of MoS_2 , a material which decades ago was studied and not considered a promising candidate for solar PEC water splitting as it is limited by an inadequate electronic band structure as well as poor hydrogen evolution kinetics at its surface [5]. The approach herein is to use nanostructuring to improve the relevant bulk and surface properties of MoS_2 for (photo)electrochemical applications [6]. By synthesizing nanoparticles of MoS_2 , one can engineer the electronic band structure and light absorption properties through a quantum confinement effect [7], and expose edge sites for the improved catalytic turnover of hydrogen [8].

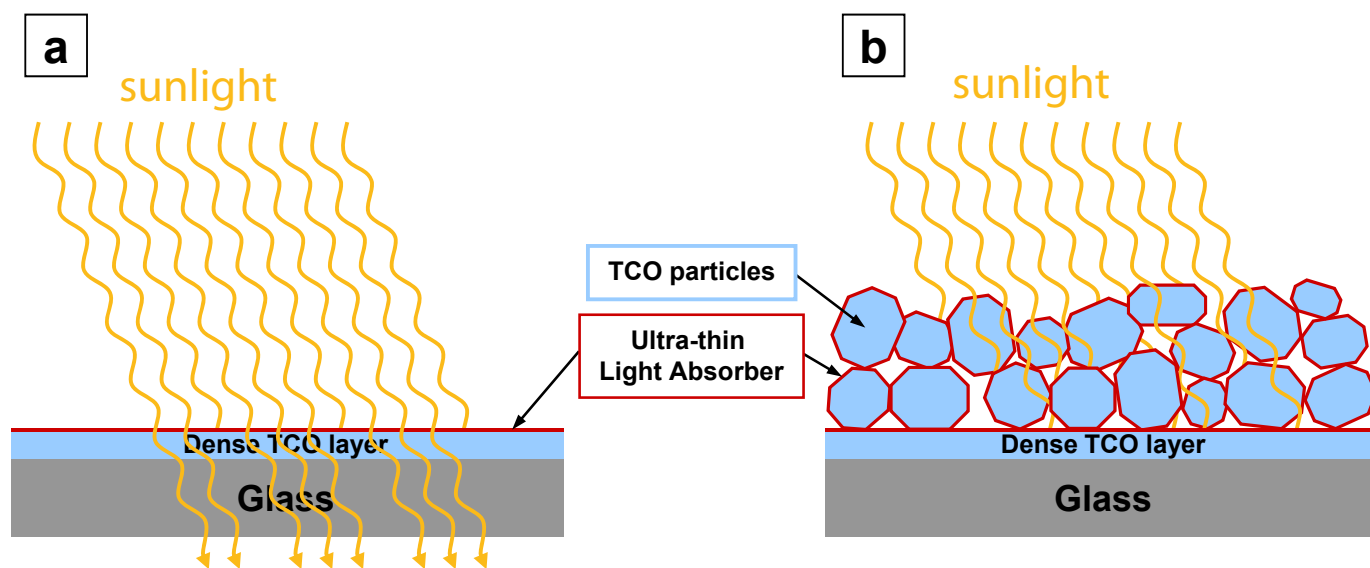


FIGURE 1. Quantum efficiency for photon-to-product conversion in PEC devices made from semiconductor absorber materials with poor electronic charge transport is maximized with ultra-thin semiconductor layers (a). However, the overall photon absorption (optical density) of these electrodes is typically very low (a), which limits the overall solar conversion efficiency. By conformally coating HSEs with ultra-thin absorber layers (b), the optical density is maximized while simultaneously maintaining high QE.

Results

One of the primary results of this project has been the development of an extremely high surface area TCO substrate that can be used with a wide variety of devices—namely those employed for PEC water splitting. In demonstrating this new development for the very first time, we have concurrently developed a synthetic route applicable to large-scale fabrication of HSE TCO electrodes. These TCOs include indium tin oxide (ITO), fluorine doped tin oxide (FTO), aluminum zinc oxide and many other well utilized electrode materials in the PEC, photovoltaic and electrochemical fields. The synthetic route involves spray deposition of a two part mixture containing solid TCO powder (~1-100 μm diameter particles) and TCO sol-gel precursors in an acidified ethanolic solvent, followed by heat treatment. Figure 2a exhibits a schematic representation of the resulting film morphology. The amount of mixture sprayed onto the appropriate conductive substrate controls the final surface area of the HSE. These TCO HSEs are capable of enabling PEC materials to simultaneously address three of the DOE technical barriers for Production

(Y, AA, AB). Compared to more classical HSE fabrication techniques such as lithographic patterning, spray deposition offers significant cost savings and scalability – absolute necessities for an emerging solar energy technology seeking to generate copious domestic fuel.

The key performance criteria for TCO HSEs are three fold: surface area, electrical conductivity and transparency to visible light. Our proof-of-principle HSEs spray fabricated from ITO have demonstrated excellent performance in all three categories. Figure 2b reveals their optical transparency and Figures 2c and 2d show the general morphology as viewed by a scanning electron microscope (SEM). The faceted geometric shapes seen by SEM indicate good crystallinity of the ITO which translates into superior electrical conductivity while the porous, open network results in high surface area. This surface area is quantified by performing electrochemical capacitance (EC) measurements in 1.0 M NaOH (Figure 3). Here we see the EC of a planar, commercial ITO film compared to spray deposited HSEs of controllably higher surface area. The capacitance current, which is proportional to surface area, is read as the oxidative current at 0.3 V vs. saturated

SEM

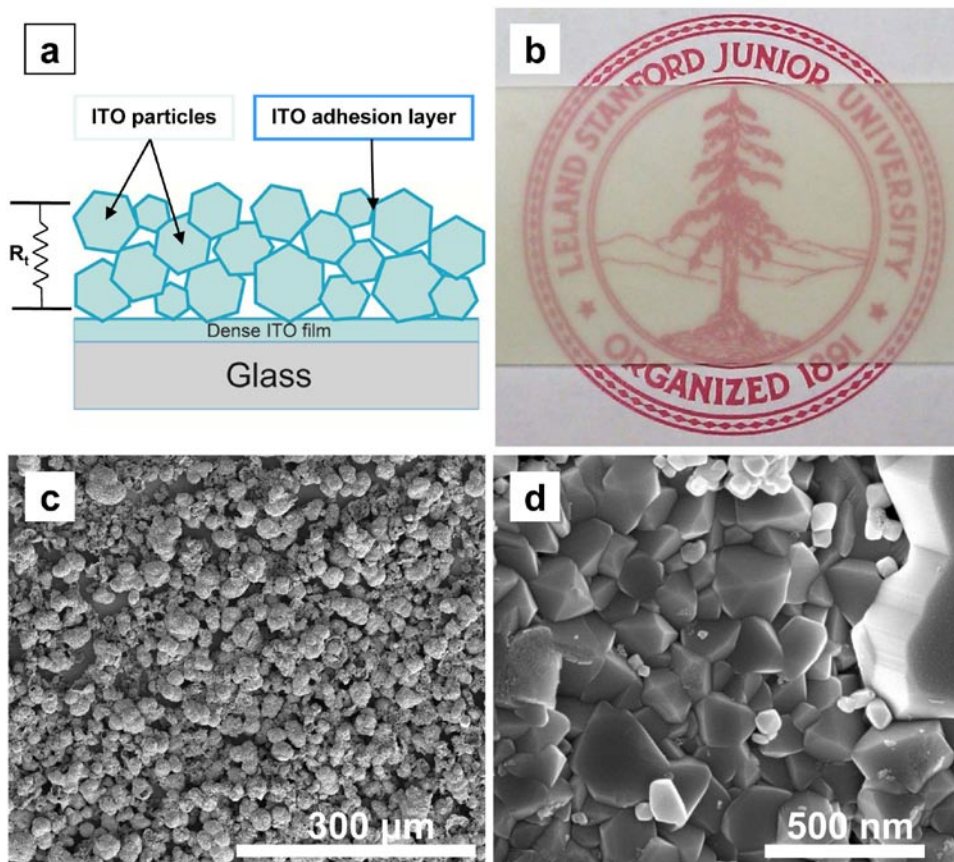


FIGURE 2. A schematic cross section (a) and optical photograph showing transparency (b) of the ITO HSE. SEM images show the textured particulate HSE surface (c) and the crystallinity of the ITO adhesion layer (d).

calomel electrode (SCE) (linear region) on Figure 3a. The relative ratio of capacitances or surface areas (roughened vs. planar) is termed roughness factor (RF) and is plotted against square root of scan rate for several typical spray films in Figure 3b. For the HSEs, capacitance charging is limited by solute diffusion at higher scan rates and the RF appears smaller. Therefore, extrapolation of the data to zero scan rate yields the true RF values. The EC data presented here shows HSEs that have RFs ranging from 250 to 800 relative to the planar ITO film. We have succeeded in fabricating films with RFs from ~20-800 via spray deposition, the right order of magnitude for roughness needed to maximize performance according to our calculations.

Electronic resistance measurements of these spray films indicate that resistance in the transverse direction, R_p , (see Figure 2a) is $\sim 1 \Omega/10 \mu\text{m}$, or only about 10Ω for the average film thickness. This resistance is superb given the low cost, low quality fabrication method employed.

We have just begun to coat these HSEs with ultra-thin layers of semiconductor material including manganese oxide and iron oxide, two excellent absorbers of visible light. The challenge here is that these absorber materials are performance limited by electronic charge transport. Therefore, ultra-thin layers will help facilitate extraction of photogenerated charge carriers to the back contact (the TCO) with a high QE. By conformally coating the HSEs with that same ultra-thin layer of absorber material we can combine the high QE carrier extraction of an ultra-thin layer with full absorption of incoming light because of the many layers coated across the high surface area. This device design has an optical density equivalent to an absorber layer X times thicker where X is proportional to the RF of the HSE.

Using an entirely room temperature synthetic procedure, we have produced nanoparticles of MoS_2 only several nanometers in size that exhibit a visible shift in light absorption towards lower wavelengths (Figure 4a) with an estimated bandgap of $\sim 1.8 \text{ eV}$ for the smallest nanoparticles as a result of quantum confinement. Transmission electron microscopy (TEM) reveals a range in nanoparticle size from 2.4 to 8.3 nm. In addition, PEC measurements of these nanoparticles have shown that they possess proper conduction and valence band alignments relative to the hydrogen and oxygen evolution potentials to enable unassisted water splitting.

We have also studied the long-term performance of highly nanostructured MoS_2 as an electrocatalyst for hydrogen evolution at current densities relevant to efficient solar conversion ($\sim 10 \text{ mA/cm}^2$). By carefully controlling the extent of thermal sulfidization treatments, we can optimize the growth of ultra-thin MoS_2 shell structures that are only a few nm thick at temperatures as low as 200°C on a high aspect ratio MoO_3 nanowire core support. These catalysts remain stable over ten thousand voltage cycles that simulate the diurnal conditions of solar irradiation (Figure 4b). Furthermore, they exhibit this stability in strongly acidic environments, a feature not possessed by other Earth-abundant hydrogen evolution catalysts such as nickel.

Conclusions and Future Directions

In order to reach our goal of developing a fully operational PEC water splitting device, we have been developing a 3rd generation light absorber material (MoS_2) while also producing a TC scaffold onto which it can be incorporated. We have achieved the following:

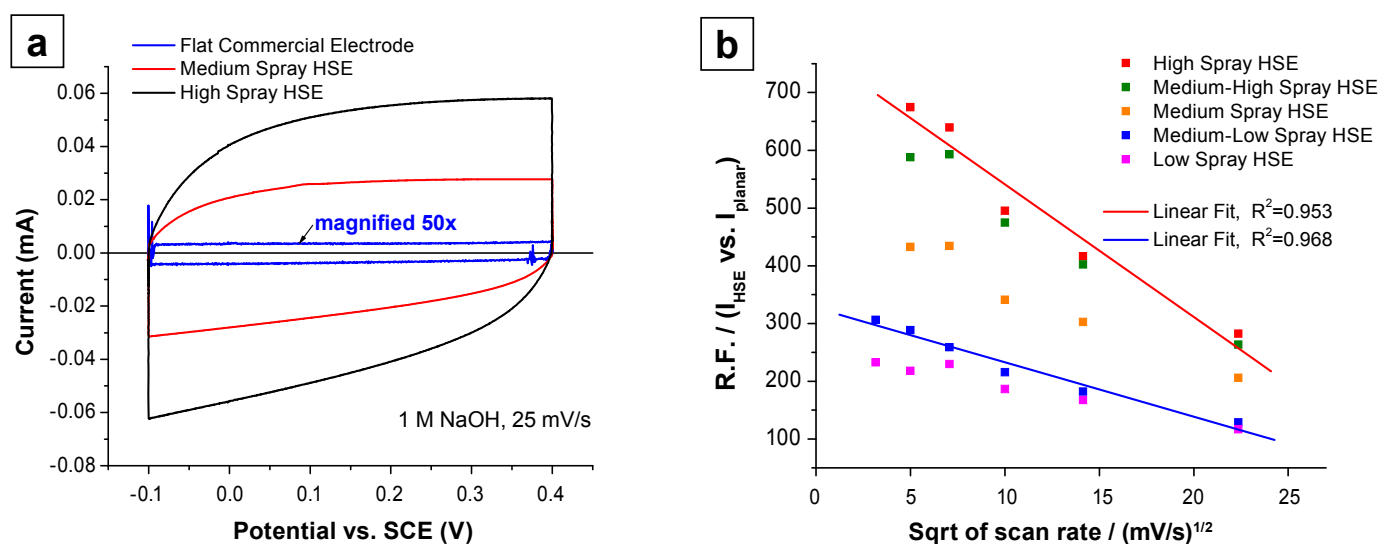


FIGURE 3. Advanced cyclic voltammograms (a) swept from -0.1 to 0.4 V vs. SCE where the scan is held at each vertex potential for 30 seconds. The third in a series of scans for each electrode is shown. Roughness factor as a function of square root of scan rate (b). Linear fits of two sample data sets are shown.

Nanostructured MoS₂

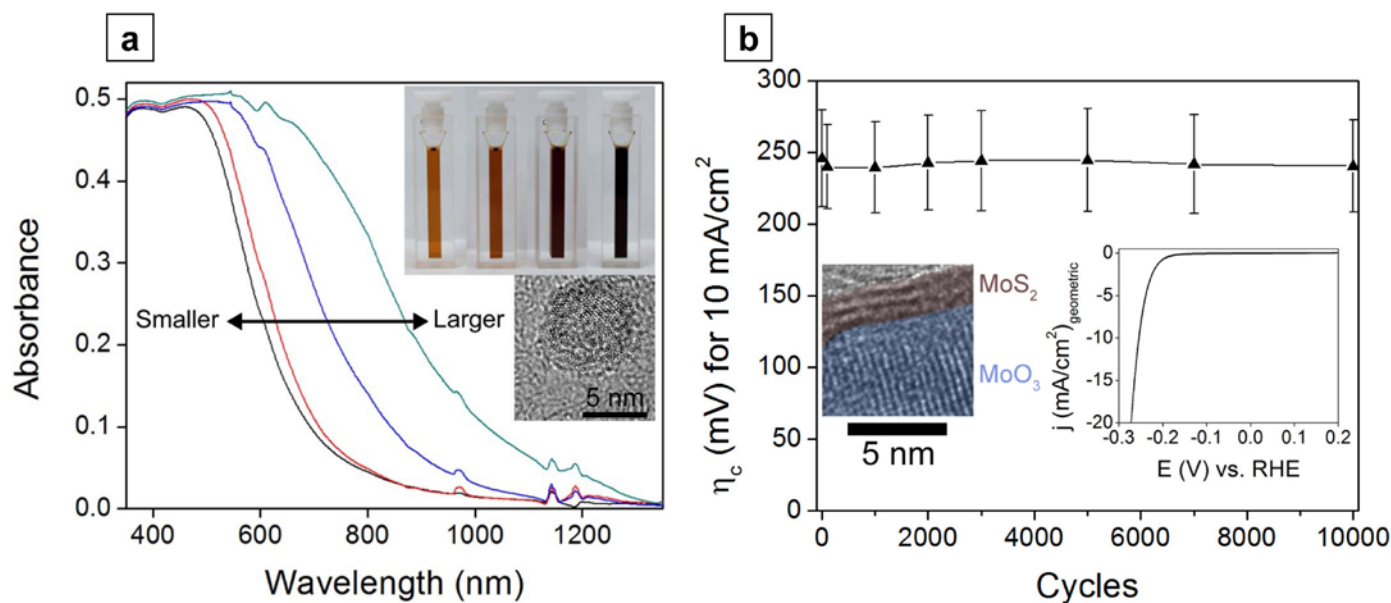


FIGURE 4. Spectroscopy, microscopy, and electrochemical performance of nanostructured MoS₂. Ultra-violet visual absorbance (a) of quantum confined MoS₂ nanoparticles with an inset photograph of solutions containing nanoparticles of increasing size towards the right, and an example TEM image of the nanoparticles. Electrochemical stability (b) of ultra-thin MoS₂ shell structures surrounding a MoO₃ core, assessed as a function of overpotential required to drive 10 mA/cm² of current density over the course of 10,000 potential cycles from -0.3 to 0.2 V vs. the reference hydrogen electrode. The inset shows a TEM image of the core-shell structures along with a cyclic voltammogram detailing their electrochemical performance for the hydrogen evolution reaction.

- A low-cost, scalable, facile route to fabrication of high surface area transparent conducting electrodes has been developed and a patent application is pending.
- Physical and electronic characterization of these electrodes indicates roughness factors of ~20-800 and electrical conductivity commensurate with requirements for PEC and many other electronic applications.
- Developed bandgap engineered nanoparticles of MoS₂ which possess the correct energetic for water splitting.
- Demonstrated long-term stability of highly nanostructured MoS₂ hydrogen evolution catalysts.

The next step in our work is the incorporation of nanostructured materials and thin films into our HSE platforms. We will accomplish this task through various objectives:

- Incorporate MoS₂ nanoparticles into the HSE and characterize their water splitting properties with respect to light absorption, charge transport, and stability.
- Demonstrate the broad applicability of the HSE platform for various other PEC materials.

Special Recognitions & Awards

1. DOE Hydrogen and Fuel Cells Program R&D Award to Prof. Thomas F. Jaramillo (PI).

Patents Issued

1. Arnold J. Forman, Zhebo Chen, and Thomas F. Jaramillo, "Synthesis of High Roughness Factor Transparent Conducting Oxide Thin Films" (patent application pending).

FY 2011 Publications/Presentations

1. J. Forman, Zhebo Chen, and Thomas F. Jaramillo, "Synthesis of High Roughness Factor Transparent Conducting Oxide Thin Films" (manuscript in preparation).
2. Zhebo Chen, Dustin Cummins, Benjamin N. Reinecke, Ezra Clark, Mahendra K. Sunkara, and Thomas F. Jaramillo, "MoS₂ Coated MoO₃ Nanowires: Active, Stable, and Earth-abundant Catalysts for Hydrogen Evolution in Acid" (submitted March 2011).
3. Zhebo Chen, Jakob Kibsgaard, and Thomas F. Jaramillo, "Nanostructuring MoS₂ for Photoelectrochemical Water Splitting," *Proc. SPIE*, Vol. 7770, 77700K-6 (2010).
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5. Thomas F. Jaramillo, Zhebo Chen, Shin-Jung Choi, Jesse Benck, and Jakob Kibsgaard, Nano-architectures for 3rd generation PEC devices: A study of MoS₂, fundamental investigations and applied research, DOE EERE Annual Merit Review, Crystal City, VA. May 12, 2011.

6. Zhebo Chen, Jakob Kibsgaard, Jesse Benck and Thomas F. Jaramillo, "Nanostructured MoS₂ for Solar Hydrogen Production," 2011 Spring Meeting of the Materials Research Society, San Francisco, CA. April 29, 2011.
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6. Our applied research on the photoelectrochemistry of MoS₂ is funded through this program; our more fundamental research on MoS₂ is currently supported by Center on Nanostructuring for Efficient Energy Conversion (CNEEC) at Stanford University, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001060.
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