

## Functional Thin Films and Surfaces Room Pacific D - Session C3-1-ThM

### Thin Films and Novel Surfaces for Energy I

**Moderators:** Dr. Clío Azina, RWTH Aachen University, Germany, Prof. Carlos Tavares, University of Minho, Portugal

8:40am **C3-1-ThM-3 Tailoring Surface Reactivity of Perovskite Oxides for Water Oxidation**, *Kelsey Stoerzinger*, Oregon State University, USA INVITED  
The intermittent nature of renewable energy sources requires a clean, scalable means of converting and storing energy. One Earth-abundant storage option is water electrolysis: storing energy in the bonds of O<sub>2</sub> and H<sub>2</sub>, and later extracting electricity by the electrochemical reaction of gasses in a fuel cell. Nickel oxides are notably active for oxygen electrocatalysis in alkaline solutions, and the perovskite structure (ANiO<sub>3</sub>) in particular. I will present studies of model oxide electrodes grown by pulsed laser deposition (PLD) and molecular beam epitaxy (MBE) on single crystal substrates that display a known crystallographic orientation, strain, surface area, and path for charge transport. Electrochemical measurements on these heterostructures can establish the intrinsic activity of oxide catalysts in a way that cannot be realized with polydisperse nanoparticle systems, and we use these findings to rationally design the nickelate composition and structure to maximize activity. Additional insight into the mechanism of the oxygen evolution reaction (OER) is obtained from spectroscopic probing of adsorbates with ambient pressure X-ray photoelectron spectroscopy (AP-XPS), pH dependence of activity, and measurements of oxygen isotope exchange. This fundamental understanding aids in the design of active, earth-abundant electrocatalysts for efficient conversion of renewable energy into chemical fuels.

9:20am **C3-1-ThM-5 The Influence of Sb Doping on the Local Structure and Disorder in Thermoelectric ZnO:Sb Thin Films**, *J. Ribeiro, F. Rodrigues, F. Correia*, University of Minho, Portugal; *A. Kuzmin*, University of Latvia; *E. Alves, N. Barradas*, University of Lisbon, Portugal; *O. Bondarchuk*, International Iberian Nanotechnology Laboratory, Portugal; *A. Welle*, Karlsruhe Institute of Technology (KIT), Portugal; *Carlos Jose Tavares*, University of Minho, Portugal

Thermoelectric transparent ZnO:Sb thin films were deposited by magnetron sputtering, with Sb content varying between 2-14 at.%. As evidenced from X-ray diffraction analysis, the films crystallize in the ZnO wurtzite structure for lower levels of Sb-doping, developing a degree of amorphization for higher levels of Sb-doping. Temperature-dependent (10-300 K) X-ray absorption spectroscopy studies of the produced thin films were performed at the Zn and Sb K-edges to shed light on the influence of Sb doping on the local atomic structure and disorder in the ZnO:Sb thin films. The analysis of the Zn K-edge EXAFS spectra by the reverse Monte Carlo method allowed to extract detailed and accurate structural information in terms of the radial and bond angle distribution functions. The obtained results suggest that the introduction of antimony to the ZnO matrix promotes static disorder, which leads to the partial amorphization with very small crystallites (~3 nm) for large (12-14 at.%) Sb content. Rutherford backscattering spectrometry (RBS) experiments enabled the determination of the in-depth atomic composition profiles of the films. The film composition at the surfaces determined by X-ray photoelectron spectroscopy (XPS) matches that of the bulk determined by RBS, except for higher Sb-doped ZnO films, where the concentration of oxygen determined by XPS is lower near the surface, possibly due to the formation of oxygen vacancies that lead to an increase in electrical conductivity. Traces of Sb-Sb metal bonds were found by XPS for the sample with the highest level of Sb-doping. Time-of-flight secondary ion mass spectrometry obtained an Sb/Zn ratio that follows that of the film bulk determined by RBS, although Sb is not always homogeneous, with samples with lower Sb content (2 and 4 at.% of Sb) showing a higher Sb content closer to the film/substrate interface. From the optical transmittance and reflectance curves, it was determined that the films with the lower amount of Sb doping have higher band-gaps, in the range of 2.9 – 3.2 eV, while the partially amorphous films with higher Sb content have lower band-gaps in the range of 1.6-2.1 eV. Albeit the short-range crystalline order (~3 nm), the films with 12 at.% of Sb have the highest Seebeck coefficient (~56 mV/K) and a thermoelectric power factor of ~0.2 mW·K<sup>-2</sup>·m<sup>-1</sup>.

9:40am **C3-1-ThM-6 An Economic Experimental Approach to Optimize the Microstructure and Thermoelectric Performance of ZnSe Thin Films**, *Khalid Mahmood*, Department Of Physics, Government College University Faisalabad, Pakistan

Current study demonstrated the growth of good quality, smooth surface ZnSe thin films by an economic and safer thermal evaporation method. The quality of grown thin films was modulated by varying the source to substrate distance (SSD) from 5-15 cm with a step of 5 cm during the thermal evaporation process. XRD scans indicated the pure phase formation and SEM analysis has confirmed the uniformity and smooth surface growth of these deposited thin films. Crystallite size is found to be increased from 28.73-40.18 nm with the increase in source to substrate distance. Raman analysis has further confirmed the cubic phase crystalline nature of these films. Transport properties such as the electrical conductivity, Seebeck coefficient [https://www.sciencedirect.com/topics/physics-and-astronomy/seebeck-effect] and power factor were observed to be varied with source to substrate distance. The highest values of Seebeck coefficient, electrical conductivity and power factor (260 μV/C, 4.1 S/cm and 2.21344 x 10<sup>-6</sup> W/mK<sup>2</sup> respectively) were achieved by varying SSD.

10:00am **C3-1-ThM-7 The Influences of Plasmonic Resonance and Coupling Effect on Photocatalysis of MoS<sub>2</sub>/Gold Hybrid Nanoparticles for Hydrogen Production**, *Yi-Hsueh Chen, J. Ruan*, National Cheng Kung University (NCKU), Taiwan

Hydrogen energy is clean and more friendly to our environment, which drives scientists around the world to look for materials able to catalyze hydrogen production. MoS<sub>2</sub> has been recognized as the most efficient photocatalyst for hydrogen evolution among non-noble metals. In particular, MoS<sub>2</sub> nanosheets exposed lots of active sites for the attachment of proton and later reduction reactions, and the efficiency is better than other bulk materials. Unfortunately, the absorption wavelength of MoS<sub>2</sub> nanosheets is only within the UV region. Visible light accounts for 95% of sunlight and UV light occupies only 5%. It is vital for photocatalysts to be able to efficiently harvest visible light. The absorption of visible light is able to cause strong localized surface plasmon resonance (LSPR) of gold nanoparticles (AuNPs), which has been widely investigated able to promote the performance of MoS<sub>2</sub> as a photocatalyst. However, the desired dispersion patterns of AuNPs for the optimization of surface plasmon resonance are less achievable. As an approach to maximize the amount of energy absorbed from the sunlight, we aim to design and fabricate hybrid particles composed of AuNPs and MoS<sub>2</sub> nanosheets with the control of coupling effect of among AuNPs. Through the achieved adjustment of separation distances among AuNPs, we are able to clarify the required condition for the best effect LSPR to absorb visible light and thus to optimize the efficiency of electron transition from AuNPs to MoS<sub>2</sub> nanosheets, which largely enhances desired hydrogen production.

To prove the influence of local surface plasmonic resonance and coupling effect to achieve hot electron transfer and reflect in hydrogen production, we fabricated a plasmonic nanostructure with gold nanoparticles (Au NPs) / MoS<sub>2</sub> nanosheets. The distribution of Au NPs fabricated by a steric hindrance of PVP to avoid the characteristic that colloidal particles tend to agglomerate during precipitation. In the MoS<sub>2</sub>-generated portion, the PVP segment originally attached to the gold surface is squeezed out by grafting the MoS<sub>2</sub> precursor thiourea, so that MoS<sub>2</sub> grows directly on the gold and maintains a specific spacing between the Au NPs on MoS<sub>2</sub> nanosheets.

10:20am **C3-1-ThM-8 Self-Reconstruction of Sulfate-Containing High Entropy Sulfide for Exceptionally High-Performance Oxygen Evolution Reaction Electrocatalyst**, *Thi Xuyen Nguyen, Y. Su, C. Lin, J. Ting*, National Cheng Kung University (NCKU), Taiwan

Novel earth abundant metal sulfate-containing high entropy sulfides, FeNiCoCrX<sub>2</sub> (where X = Mn, Cu, Zn, or Al), have been synthesized via a two-step solvothermal method. We show that sulfate-containing FeNiCoCrMnS<sub>2</sub> exhibits superior OER activity with exceptionally low overpotential of 199, 246, 285, and 308 mV at current densities of 10, 100, 500 and 1000 mA cm<sup>-2</sup>, respectively, and surpassing its unary-, binary-, ternary-, and quaternary-metal counterparts. The electrocatalyst yields exceptional stability after 12000 cycles and 55 h of durability even at a high current density of 500 mA cm<sup>-2</sup>. Various *in-situ* and *ex-situ* analyses were used to investigate the self-reconstruction of the sulfides during the oxygen evolution reaction (OER) for the first time. The resulting metal (oxy)hydroxide is believed to be the true active center for OER. The remaining sulfate also contributes to the catalytic activity. Density function theory calculation is in a good agreement with the experimental result. The

# Thursday Morning, May 25, 2023

extraordinary OER performance of the high entropy sulfide brings a great opportunity for desirable catalyst design for practical applications.

10:40am **C3-1-ThM-9 Hydrothermal-Based Synthesis of Piezo-Composite Thin Films and Their Applications**, *Thi Nghi Nhan Nguyen, K. Chang*, National Cheng Kung University, Taiwan

Piezoelectric materials have shown key characteristics for engineering and electrochemical applications, such as in sensors and actuators. The heterojunction has been investigated to prove the feasibility of the built-in electric field, which promotes the improvement of photocatalytic efficiency and the piezoelectric nanogenerator (PNGs) applications. In this research, detailed studies focused on piezo-composite thin films and their relative piezo-applications were reported. BiFeO<sub>3</sub> (BFO) microplates were grown on the ZnO nanorod array using the hydrothermal method, effectively reducing excess electrons in the ZnO layer. The BFO-ZnO composite act as a power generation source under a force from a motor stepper or external resources such as human hands and a pen. The output voltages and currents of the fabricated PNG were measured. The results clearly demonstrate the effectiveness of the BFO-ZnO heterostructure for realizing high performance, revealing the high durability and stability of devices. The piezo-photocatalytic application such as piezo-photodegradation and piezo-photoelectrochemical water splitting were studied under light irradiation and external stress. Moreover, the piezotronic effect on the performance of the BiOBr/Carbon fibers-based glucose sensor was systematically investigated under various glucose concentrations. The BiOBr/Carbon fibers exhibited a large surface area and low band gap, facilitating improved electrochemical reactivity toward glucose oxidation. The piezo-electrochemical results indicated that the piezotronic effect significantly increased the sensitivity as well as improved the sensing resolution of the BiOBr/Carbon fibers-based glucose sensors. The working mechanism of coupling the piezoelectric effect and photoexcitation in composite has been proposed based on the analysis of the band energies in the heterojunctions. This work demonstrates a promising approach to improve the sensitivity and generally improve the performance of the PNGs, glucose sensors, and the photocatalytic activities of composites.

11:00am **C3-1-ThM-10 A Comparative Study of the Thermochemical Performances of VO<sub>2</sub> Films Obtained by Air Oxidation of V and VN Precursors**, *D. Pilloud, A. Garcia-Wong, F. Capon, Jean-François Pierson*, Institut Jean Lamour - Université de Lorraine, France

Thanks to its metal-to-insulator transition (MIT) temperature not so far from the ambient one, thermochromic VO<sub>2</sub> exhibits great potentiality in smart coatings devoted to energy purposes. Among the different methods to synthesize thermochromic VO<sub>2</sub> films, reactive sputter deposition remains one of the most suitable for cost-effective industrial-scale production. For a few decades, increasing attention has been paid to a fast and relatively simple approach based on two steps to produce thermochromic VO<sub>2</sub> thin films: synthesis of a vanadium thin film followed by its oxidation at moderate temperatures (often less than 500 °C). Recently, we have revealed that the oxidation of vanadium nitride (VN) thin films also give rise to the formation of thermochromic VO<sub>2</sub>. This work aims to compare the thermochromic properties of VO<sub>2</sub> films achieved after thermal air oxidation of V and VN thin films prepared by sputtering deposition from an elemental vanadium target. For both precursors, short-time air annealing (from 60 to 300 seconds) was performed at 550 °C. X-ray diffraction and Raman spectroscopy depicted that the thermal oxidation domain allowing the formation of the thermochromic VO<sub>2</sub> phase was enlarged for VN compared to V precursor films. These results were confirmed by electrical measurements of the resulting oxides in the temperature region that encompass the MIT of thermochromic m-VO<sub>2</sub>. Finally, a particular focus was made on the oxides of the VN series in terms of their infrared properties. The results indicate that the oxidation of VN precursor allows the synthesis of monoclinic VO<sub>2</sub> films with high purity displaying good thermochromic performances (IR contrast of 63%, electrical switch of ~ 2 decades) with narrower hysteresis widths (< 9.3 °C) as compared to those obtained by vanadium films oxidation, making VN precursor of particular interest for industrial upscaling.

11:20am **C3-1-ThM-11 Revolutionizing Concentrated Solar Thermal Power Technology: Developing Self-Cleaning Mirrors with TiO<sub>2</sub> Films**, *Nafsika Mouti, V. Terziyska, N. Kostoglou*, Montanuniversität Leoben, Austria; *A. Kaidatzis, M. Arfanis*, National Centre of Scientific Research "Demokritos", Greece; *A. Eliades, K. Milidonis*, The Cyprus Institute, Cyprus; *K. Giannakopoulos*, National Centre of Scientific Research "Demokritos", Greece; *C. Mitterer*, Montanuniversität Leoben, Austria

Concentrated Solar Thermal (CST) technologies constitute a promising approach for harnessing the power of the sun to drive high-temperature thermal processes of interest, such as a power block for electricity generation, high-temperature industrial process heat or high-temperature solar chemistry applications. The Light Collection and Concentration Sub-system (LCCS) of a CST plant is responsible for collecting the direct solar radiation and concentrating it onto the active surface of a receiver system, where the thermal energy conversion takes place. The LCCS use mirrors (usually of parabolic shape) to concentrate the sunlight onto the receiver, however, the accumulation of dust and other particles (e.g. mirror soiling) on the mirrors has a direct effect on the efficiency of the LCCS. To address this issue, the Nano4CSP project with partners from Austria, Greece and Cyprus focuses on the development of self-cleaning CST mirrors using TiO<sub>2</sub> films. TiO<sub>2</sub> is a well-known photocatalyst, capable of breaking down dirt and other contaminants upon exposure to sunlight, making it a suitable material for creating self-cleaning surfaces. Within this study, sputtering has been successfully used to deposit TiO<sub>2</sub> films on CST mirrors at room temperature under various growth conditions. The deposited films with thicknesses in the range of 10 to 1000 nm have been extensively characterized using scanning electron microscopy with energy-dispersive X-ray spectroscopy, X-ray diffraction, Raman spectroscopy, optical measurements, nanoindentation, nanoscratching and field tests. Films with a dominant anatase phase have been found to show self-cleaning properties, thus improving the mirrors efficiency. Additionally, doping of TiO<sub>2</sub> films with N<sub>2</sub> and Zr has been evaluated, to improve the transparency and photocatalytic properties and to maximize the performance of the mirrors. The obtained results indicate that sputter deposition represents a promising method for producing self-cleaning CST mirrors, since it allows a precise control over the thickness and uniformity of the films, as well as the ability to apply them at room temperature, thus reducing costs and increasing efficiency for the necessary large area deposition on mirror surfaces. The findings of this research can have a significant impact on the further development of CST technology and its widespread implementation in larger scales, increasing the cost competitiveness of such plants by reducing the operational and maintenance costs and the associated water consumption for mirror cleaning.

## Author Index

**Bold page numbers indicate presenter**

— A —

Alves, E.: C3-1-ThM-5, **1**  
Arfanis, M.: C3-1-ThM-11, **2**

— B —

Barradas, N.: C3-1-ThM-5, **1**  
Bondarchuk, O.: C3-1-ThM-5, **1**

— C —

Capon, F.: C3-1-ThM-10, **2**  
Chang, K.: C3-1-ThM-9, **2**  
Chen, Y.: C3-1-ThM-7, **1**  
Correia, F.: C3-1-ThM-5, **1**

— E —

Eliades, A.: C3-1-ThM-11, **2**

— G —

Garcia-Wong, A.: C3-1-ThM-10, **2**  
Giannakopoulos, K.: C3-1-ThM-11, **2**

— K —

Kaidatzis, A.: C3-1-ThM-11, **2**  
Kostoglou, N.: C3-1-ThM-11, **2**  
Kuzmin, A.: C3-1-ThM-5, **1**

— L —

Lin, C.: C3-1-ThM-8, **1**

— M —

Mahmood, K.: C3-1-ThM-6, **1**  
Milidonis, K.: C3-1-ThM-11, **2**  
Mitterer, C.: C3-1-ThM-11, **2**  
Mouti, N.: C3-1-ThM-11, **2**

— N —

Nguyen, T.: C3-1-ThM-8, **1**; C3-1-ThM-9, **2**

— P —

Pierson, J.: C3-1-ThM-10, **2**  
Pilloud, D.: C3-1-ThM-10, **2**

— R —

Ribeiro, J.: C3-1-ThM-5, **1**  
Rodrigues, F.: C3-1-ThM-5, **1**  
Ruan, J.: C3-1-ThM-7, **1**

— S —

Stoerzinger, K.: C3-1-ThM-3, **1**  
Su, Y.: C3-1-ThM-8, **1**

— T —

Tavares, C.: C3-1-ThM-5, **1**  
Terziyska, V.: C3-1-ThM-11, **2**  
Ting, J.: C3-1-ThM-8, **1**

— W —

Welle, A.: C3-1-ThM-5, **1**