Topical Symposium on Sustainable Surface Engineering
Room Town & Country D - Session TS2-2-ThM

Coatings and Surfaces for Renewable Energy Technology II

Moderators: Arnaud le Febvrier, Uppsala University, Sweden, **Marcus Hans**, RWTH Aachen University, Germany

8:00am **TS2-2-ThM-1 Energy-Efficient Hydrogen Production via Urea-Assisted Electrolysis Enabled by Linker-Engineered NiCo MOFs**, ***Thi Xuyen Nguyen [nguyenxuyen1511@gmail.com]***, *Hui-Chuan Chen, Jyh-Ming Ting,* National Cheng Kung University, Taiwan **INVITED**

Hydrogen (H_2) is widely recognized as a promising sustainable energy carrier for addressing the global energy crisis and achieving the net-zero carbon emission target. Among the various H_2 production strategies, urea-assisted electrochemical water splitting offers an energy-efficient route for H_2 production; however, the inherently sluggish six-electron urea oxidation reaction requires highly active electrocatalysts. Herein, we report a linker-engineering strategy in which the benzene dicarboxylate (BDC) linker of a NiCo-BDC metal-organic framework (MOF) is partially replaced by a redox-active dicarboxylferrocene (DFc) ligand to construct NiCo-MOF-DFc. The strongly coordinated DFc linker effectively modulates the electronic structure, enriching Ni^{3+} species, generating abundant oxygen vacancies, and inducing coordination asymmetry, thereby markedly enhancing urea oxidation activity. The NiCo-MOF-DFc catalyst delivers 100 mA cm^{-2} at a low potential of 1.33 V with excellent durability. Operando characterizations reveal that DFc facilitates rapid electron transfer, accelerates the transformation of the MOF into the catalytically active metal (oxy)hydroxide phase, and stabilizes the active sites. Density functional theory calculations further demonstrate that DFc weakens CO_2 adsorption and lowers the energy barrier of the rate-determining desorption step. An anion exchange membrane electrolyzer employing NiCo-MOF-DFc as the anode achieves 1000 mA cm^{-2} at a low cell voltage of 1.83 V and sustains stable operation for 500 h. Notably, the system requires only 48.6 kWh to produce 1 kg of H_2, representing over 10% lower energy consumption than conventional OER-based electrolysis, highlighting its strong potential for energy-efficient hydrogen production.

9:00am **TS2-2-ThM-4 Optimization of Tunable Interfacial Engineering in WOx/α-Fe_2O_3 Heterostructures via Dc Magnetron Sputtering for Enhanced PEC Activity and Carrier Transport Efficiency**, ***Carlos Gomes [c.e.gomes@ifsp.edu.br]***, *Mariane Murase Murase, Matheus Torres, Douglas Leite, Rodrigo Pessoa, Argemiro Sobrinho, André Pereira,* Instituto Tecnológico de Aeronáutica, Brazil

Transition metal oxide heterostructures are crucial for advancing sustainable energy technologies, demanding precise control over interfacial charge dynamics and long-term chemical stability. This work presents a systematic study on the fabrication and optimization of an Iron Oxide (α-Fe_2O_3) a visible-light absorber heterojunction with a Tungsten Oxide (WO_x) as an electron-transport layer, serving as a band alignment at the interface. Junction formation is a powerful strategy to overcome intrinsic limitations like poor charge transport and high surface recombination in semiconductors [1]. The staggered band alignment creates an internal electric field that promotes efficient separation of photogenerated electron(e^-)/hole(h^+) pairs and facilitates electron extraction, significantly reducing surface charge recombination [1,2].

The structures were fabricated using scalable DC Magnetron Sputtering, depositing the α-Fe_2O_3 layer over FTO glass (SnO_2/F) followed by the WO_x transport layer. The study investigates tunable surface engineering by systematically varying the WO_x deposition time to precisely control the layer's thickness and potentially its stoichiometry (WO_{3-x}), thereby modulating the electronic band alignment and transport efficacy.

Comprehensive characterization, including XRD, SEM, EIS, and CV, was employed to correlate layer thickness with interfacial structure. Analysis confirmed WO_x crystallization at 550°C, showing a direct relationship between peak intensity and deposition time. Deposition of an optimal WO_x layer enhanced Fe_2O_3 optical modulation, resulting in a 15% lower visible transmittance minimum (at ≈ 600 nm).

Functional performance such as stability and charge transfer dynamics was assessed, revealing that the WO_x (180s) sample's highest carrier number and lowest flat band voltage directly correlate with superior electrochemical performance (Specific Power under light and Specific Energy in the dark), suggesting that the improved electronic structure drives enhanced charge storage and transfer capabilities.

This research presents valuable insights into controlled thin film deposition and advanced surface engineering of robust oxide structures. These findings support the development of next-generation photoelectrochemical cells (PEC) for water splitting.

Keywords: WOx/α-Fe_2O_3, Heterojunction, DC Magnetron Sputtering, Thin Film Deposition, Advanced Surface Engineering.

[1] N. Al-Aisaee et al., *Solar Energy Materials and Solar Cells*, 263 (2023).

[2] B. Liu et al., (Review article on heterojunctions and charge separation mechanisms) (2025).

9:20am **TS2-2-ThM-5 Thermal Treatment Effects on the Structural and Optoelectronic Properties of Nb2O5 Thin Films Deposited by DC Magnetron Sputtering**, *Rodrigo Prado Medeiros Leite da Silva, Natali da Silva Barbosa, Bianca Sartori,* Instituto Federal de Educação, Ciência e Tecnologia de São Paulo, Brazil*; Lucas Diniz Araujo,* Aeronautics Institute of Technology (ITA), Brazil*; Carlos Eduardo Gomes,* Instituto Federal de Educação, Ciência e Tecnologia de São Paulo, Brazil*; Filipe Caldatto Dalan, André Luis de Jesus Pereira,* ***Argemiro Soares da SIlva Sobrinho [argemiro@ita.br]***, Aeronautics Institute of Technology (ITA), Brazil

The development of efficient semiconductor oxides for solar-driven energy conversion is a key step toward achieving a sustainable hydrogen economy. Transition-metal oxides such as TiO_2, WO_3, and Nb_2O_5 have emerged as promising photoactive materials due to their chemical stability and suitable band-edge alignment for photoelectrochemical (PEC) water splitting. Among them, niobium pentoxide (Nb_2O_5) is particularly attractive for its abundance, low toxicity, and tunable optoelectronic properties associated with oxygen-vacancy engineering. Understanding how deposition and post-treatment conditions affect its structure and charge-transport characteristics is therefore essential for optimizing its functional performance. In this work, Nb_2O_5 thin films were deposited by DC magnetron sputtering onto Si, glass, and FTO substrates and subsequently annealed at 300 °C, 400 °C, 500 °C, and 600 °C for eight hours under two controlled atmospheres: air at atmospheric pressure and vacuum (~10^{-2} Torr). The films were characterized by X-ray diffraction, Raman spectroscopy, UV–Vis transmittance, and electrochemical techniques to evaluate the influence of temperature and ambient on crystallization, defect formation, and electronic behavior. Structural analyses revealed a transition from amorphous to orthorhombic (Pbam) Nb_2O_5 above 500 °C, while vacuum-treated samples exhibited more pronounced oxygen-vacancy-related Raman features and a narrower optical band gap. Electrical impedance and cyclic-voltammetry results indicated reduced charge-transfer resistance for oxygen-deficient films, evidencing the beneficial role of substoichiometry in enhancing carrier mobility. These results demonstrate that both annealing temperature and atmosphere strongly modulate the structural and optoelectronic properties of sputtered Nb_2O_5, providing valuable guidelines for tailoring its performance in PEC and photocatalytic applications.

10:20am **TS2-2-ThM-8 Interface-Driven Evolution and Electrochemical Behavior of CuO/WO_X Heterostructures Deposited by Magnetron Sputtering**, *Rafael Leal, Giovana Fazenda, Helen Barros, David Graves, Filipe Dalan, Mariane Murase, Marcilene Gomes,* Aeronautics Institute of Technology (ITA), Brazil*; Douglas Leite,* Aeronautics Institute of Technology, Brazil*; Argemiro Silva-Sobrinho,* ***André Pereira [andreljp@ita.br]***, Aeronautics Institute of Technology (ITA), Brazil

Heterostructures composed of copper and tungsten oxides have drawn increasing attention for solar-driven photoelectrochemical (PEC) hydrogen generation due to their complementary optical and electronic properties [1]. The interface between p-type CuO and n-type WO_x plays a critical role in charge separation and carrier transport; however, its efficiency strongly depends on the structural order and chemical composition of the WO_x layer [1,2]. In this work, CuO/WO_x heterostructures were fabricated entirely by DC magnetron sputtering. CuO films were first deposited onto FTO substrates and annealed at 450 °C for 2 h to promote crystallization and improve adhesion. WO_x overlayers were then deposited for 1, 5, and 10 min, followed by post-annealing at 450 °C for 2 h to obtain crystalline layers; as-deposited samples were kept amorphous. The WO_x layer thickness, determined by profilometry and ellipsometric modeling, increased linearly with deposition time (~15 nm min^{-1}), while the refractive index was slightly higher for crystalline samples, indicating greater density and lower porosity. Structural and vibrational analyses revealed distinct interface behaviors. For crystalline WO_x layers, Raman and XRD showed that samples with 5 and 10 min deposition underwent interdiffusion at the interface, forming $CuWO_4$, whereas the 1 min sample exhibited a substoichiometric WO_x layer. In contrast, amorphous WO_x overlayers preserved only CuO peaks. Electrochemical measurements confirmed the correlation between structure and functionality. Cyclic voltammetry and impedance spectroscopy revealed that crystalline samples containing $CuWO_4$ exhibit lower charge-transfer resistance and higher photocurrent under illumination, while amorphous heterostructures display slower carrier dynamics and greater capacitive behavior. The electrochemically active surface area (ECSA), estimated from non-faradaic capacitive current, was significantly larger for crystalline samples, particularly those with $CuWO_4$, indicating an increased density of electroactive sites and enhanced charge accumulation capability. Overall, the controlled formation of $CuWO_4$ or substoichiometric WO_x interlayers offers a promising strategy to improve PEC efficiency and long-term stability of CuO-based photoelectrodes for sustainable hydrogen generation.

Acknowledgments

We acknowledge the financial support from FAPESP (Grant No. 2022/02994-2) and CNPq (Grant No. 302823/2025-5).

[1] X. Wen et al., ACS Appl. Nano Mater. 7 (2024) 14936–14945. DOI: 10.1021/acsanm.4c00769.

[2] M. Castaneda Mendoza et al., Materials 18 (2025) 2896. DOI: 10.3390/ma18122896.

10:40am **TS2-2-ThM-9 Unlocking the Potential of Medium-Entropy Prussian Blue for Superior Electro-Fenton Oxidation***, **Sheng-Wei Lin [alec97622964@gmail.com]**, Jyh-Ming Ting,* National Cheng Kung University (NCKU), Taiwan

Electro-assisted advanced oxidation processes, such as the electro-Fenton (EF) process, are gaining intensive attention recently. This work investigates the application of a medium-entropy Prussian blue analogue (designated as 3M-PBA) as a heterogeneous EF catalyst for the removal of organic pollutants from water. EF process can overcome the drawbacks of conventional Fenton process, such as the limited pH range and poor reusability. In this work, the 3M-PBA catalyst further enhances the EF performance by providing multiple redox-active sites, which accelerate electron transfer and improve structural stability during operation.

The phase, morphology, oxidation state, charge-transfer behaviour, hydroxyl-radical generation efficiency, and EF degradation performance were characterized using several techniques. UV-Vis spectroscopy analysis shows a continuous decrease in the characteristic TC absorption peak at 357 nm with time, confirming the molecular breakdown. The 3M-PBA catalyst achieves a high TC removal within a short time under an applied potential (0.6 V vs. Ag/AgCl). Iron leaching remains below 0.4 ppm throughout the five cycles, indicating strong structural integrity and environmental safety.

Keywords: electro-Fenton, high-entropy PBA, charge transfer, catalyst stability, wastewater treatment

11:00am **TS2-2-ThM-10 Non-Precious Metal Phosphide/Sulfide Heterostructure Electrocatalyst for SOR***, **Jian-An Wu [tommy772222@gmail.com]**, Jyh-Ming Ting,* National Cheng Kung University (NCKU), Taiwan

With the increasing discharge of wastewater containing sulfur compounds from various industries, the need for efficient sulfur removal and recovery is becoming more urgent. The Sulfion Oxidation Reaction (SOR), which converts sulfide ions (S^{2-}) into elemental sulfur (S_8), which is common for industrial use. Unlike the conventional oxygen evolution reaction (OER), which is thermodynamically challenging and energy-consuming, SOR operates at a much lower potential (-0.48 V vs. RHE), making it a more energy-efficient alternative for sulfur oxidation. Furthermore, the added economic value makes SOR an attractive option for wastewater treatment, as it reduces the need for costly disposal methods while turning a pollutant into a resource.

Herein, we have synthesized a non-precious metal phosphide/sulfide heterostructure catalyst with conductive backbone and abundant active site on the surface. The catalyst demonstrates an exceptional SOR performance in 1M KOH with 1M Na_2S, achieving a low potential of 0.278V at 100 mA cm^{-2} and 0.368V at 300 mA cm^{-2}, and a lower onset potential.

Keywords:Sulfion Oxidation Reaction (SOR), transition-metal based catalyst, heterostructure

11:20am **TS2-2-ThM-11 Defect-Engineered Copper-Based Materials for Electrocatalytic Nitrate Reduction***, **Ting- Chun Hung [jim8965976@gmail.com]**, Jyh-Ming Ting,* National Cheng Kung University (NCKU), Taiwan

Electrochemical nitrate reduction reaction (NO_3RR) has emerged as a promising strategy for simultaneously addressing nitrate pollution and producing valuable ammonia via a carbon-free process. Ammonia is an important chemical feedstock, widely used in fertilizer production, and offers advantages such as an alternative energy source for replacing hydrogen due to its ease of storage and transport.

For NO_3RR, copper-based materials are known to be highly active catalysts by facilitating the conversion of nitrate (NO_3^-) to nitrite (NO_2^-), which is the rate-determining step. In this study, novel Cu-based heterostructure nanosheets rich in oxygen vacancies (Ov) were investigated as an effective electrocatalyst for NO_3RR. The catalyst was synthesized via a hydrothermal method, followed by chemical reduction for controlled creation of Ov. The catalyst exhibits excellent NO_3RR performance, achieving a Faradaic efficiency of ~95% at -0.2 V vs. RHE, a high ammonia yield rate of 0.92 mmol h^{-1} cm^{-2}, and outstanding stability over 1000 hours, demonstrating both superior activity and long-term durability. Density functional theory calculation was performed to support the experimental data.

Keyword: Electrochemical nitrate reduction, heterostructures, oxygen vacancy, high ammonia yield rate

Author Index

Bold page numbers indicate presenter

— B —
Barros, Helen: TS2-2-ThM-8, 1
— C —
Caldatto Dalan, Filipe: TS2-2-ThM-5, 1
Chen, Hui-Chuan: TS2-2-ThM-1, 1
— D —
da Silva Barbosa, Natali: TS2-2-ThM-5, 1
da SIlva Sobrinho, Argemiro Soares: TS2-2-ThM-5, **1**
Dalan, Filipe: TS2-2-ThM-8, 1
de Jesus Pereira, André Luis: TS2-2-ThM-5, 1
Diniz Araujo, Lucas: TS2-2-ThM-5, 1
— F —
Fazenda, Giovana: TS2-2-ThM-8, 1
— G —
Gomes, Carlos: TS2-2-ThM-4, **1**
Gomes, Carlos Eduardo: TS2-2-ThM-5, 1
Gomes, Marcilene: TS2-2-ThM-8, 1
Graves, David: TS2-2-ThM-8, 1
— H —
Hung, Ting- Chun: TS2-2-ThM-11, **2**
— L —
Leal, Rafael: TS2-2-ThM-8, 1
Leite, Douglas: TS2-2-ThM-4, 1; TS2-2-ThM-8, 1
Lin, Sheng-Wei: TS2-2-ThM-9, **2**
— M —
Murase, Mariane: TS2-2-ThM-8, 1
Murase, Mariane Murase: TS2-2-ThM-4, 1
— N —
Nguyen, Thi Xuyen: TS2-2-ThM-1, **1**
— P —
Pereira, André: TS2-2-ThM-4, 1; TS2-2-ThM-8, **1**
Pessoa, Rodrigo: TS2-2-ThM-4, 1
Prado Medeiros Leite da Silva, Rodrigo: TS2-2-ThM-5, 1
— S —
Sartori, Bianca: TS2-2-ThM-5, 1
Silva-Sobrinho, Argemiro: TS2-2-ThM-8, 1
Sobrinho, Argemiro: TS2-2-ThM-4, 1
— T —
Ting, Jyh-Ming: TS2-2-ThM-1, 1; TS2-2-ThM-10, 2; TS2-2-ThM-11, 2; TS2-2-ThM-9, 2
Torres, Matheus: TS2-2-ThM-4, 1
— W —
Wu, Jian-An: TS2-2-ThM-10, **2**