## Wednesday Afternoon, May 14, 2025

# Topical Symposium on Sustainable Surface Engineering Room Palm 5-6 - Session TS2-WeA

# (Photo)electrocatalysis and Solar/Thermal Conversion Moderator: Arnaud Le Febvrier, Uppsala University, Sweden

2:00pm TS2-WeA-1 Flexible Thermoelectrics: Transforming Wearables, Space Exploration, and IoT, André Pereira [ampereira@fc.up.pt], University of Porto, Portugal INVITED

Flexible thermoelectric (TE) materials are at the forefront of advancing wearable electronics, space exploration, and the Internet of Things (IoT), offering a sustainable and efficient means of converting thermal gradients into electrical energy. Recent research has explored innovative designs and materials to overcome challenges in flexibility, efficiency, and scalability. A pivotal development is the radial flexible thermoelectric device powered by high-power laser beams, showcasing photo-thermoelectric conversion for wireless energy transfer. This approach provides a transformative solution for applications in space exploration, particularly for powering CubeSats and remote sensing systems.

Advances in hybrid thermoelectric materials have also driven significant progress. Nanostructured  $\mathrm{Bi_2Te_3}$  composites, integrated with polymer matrices like PVA, have demonstrated enhanced thermoelectric performance and printability. Devices fabricated with these materials achieve excellent mechanical flexibility and are well-suited for low-power wearable devices and printed electronics. The optimization of hybrid materials and ink formulations has enabled the realization of scalable, printable thermoelectric generators (TEGs) with customizable geometries.

Furthermore, the development of functional thermoelectric inks has opened avenues for high-throughput manufacturing of flexible  $\mu\text{-TEGs}.$  These devices exhibit improved thermoelectric properties, mechanical stability, and adaptability to various substrates, ensuring seamless integration into IoT sensor networks and wearable platforms. The interplay of material innovations, device architecture, and advanced manufacturing techniques underscores the potential of flexible thermoelectrics in addressing global energy challenges while enabling novel functionalities in emerging technologies.

This work highlights the role of multidisciplinary approaches in transforming the capabilities of thermoelectric devices, paving the way for their adoption in dynamic environments and applications demanding autonomy and efficiency.

#### Acknowledge:

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#### References:

M. Almeida "Touch Empowerment: Sistema termoelétrico e-Tattoo autossustentável para mapeamento de temperatura" (2024) – Advanced Science

Printed Flexible  $\mu$ -Thermoelectric Device Based on Hybrid Bi2Te3/PVA Composites

AL Pires, et al. ACS applied materials & interfaces 11 (9), 8969-8981

A Photo-Thermoelectric Twist to Wireless Energy Transfer: Radial Flexible Thermoelectric Device Powered by a High-Power Laser Beam

2:40pm TS2-WeA-3 Alloy/Phosphate Heterostructure as High-Performance Hydrogen Evolution Reaction Electrocatalyst, Yung Hsun Yen [N56124210@gs.ncku.edu.tw], National Cheng Kung University (NCKU), Taiwan; Thi Xuyen Nguyen, National Cheng Kung University (NCKU), Taiwan; Jyh Ming Ting, National Cheng Kung University (NCKU), Taiwan

With the rising demand for sustainable energy, the development of efficient electrocatalysts for the hydrogen evolution reaction (HER) has become increasingly important. Also, achieving cost-effective water electrolysis in industrial scale is crucial for large-scale green hydrogen production. In this study, we have investigated metal alloy/phosphate heterostructure HER electrocatalysts. Alloy is first synthesized using a two-step hydrothermal process, followed by thermal annealing. Phosphate is then electrodeposited on the surface of as-prepared alloy. The obtained catalyst demonstrates excellent catalytic activity toward HER with a low overpotential of 28.4 mV at 10 mA cm² and small Tafel slope of 42.1 mV dec¹. Under a high current density of 500 mA cm², the catalyst requires an *Wednesday Afternoon, May 14, 2025* 

only ultra-low overpotential of 186.3 mV.Stability tests using AEMWE having the heterostructure OER electrocatalyst are performed under 1 M KOH electrolyte and 1 M KOH + 0.3 M NaCl electrolytes.After 1000-h of test at 500 mA cm<sup>-2</sup>, negligible voltage drops are demonstrated under both electrolyte conditions. The excellent HER performance and cost-effective of the synthesized catalyst is highly desirable for real water splitting for sustainable hydrogen production.

3:00pm TS2-WeA-4 Ni-Co Based Catalysts for the Upcycling of Polyethylene Terephthalate, Ruei Chi Lin [a0979116476@gmail.com], National Cheng Kung University (NCKU), Taiwan; Thi Xuyen Nguyen, National Cheng Kung University (NCKU), Taiwan; Jyh Ming Ting, National Cheng Kung University (NCKU), Taiwan

Plastic waste management represents a critical environmental issue. Electrochemical upcycling of polyethylene terephthalate PET waste into high-value chemicals has received great attention recently. However, the development of highly active and selective catalysts remains challenging. In this study, we have developed a noble metal-free Ni-Co based electrocatalyst, synthesized via a hydrothermal method, for ethylene glycol oxidation reaction (EGOR). The EG is derived from PET. With its high surface area and tunable electronic structure, the obtained catalyst exhibits an excellent potentials of 1.25 V and 1.31 V at current densities of 10 mA cm<sup>-2</sup> and 100 mA cm<sup>-2</sup>, respectively. PET is effectively transformed into potassium terephthalate with excellent Faradaic efficiency and selectivity under high current density. Meanwhile, zero-gap membrane electrode assembly closed-loop flow reactor has been used to achieve outstanding stability of PET upcycling in PET hydrolysis at 100 mA cm<sup>-2</sup>. This work highlights the excellent potential for electro-reforming PET plastic waste into valuable chemicals with simultaneous reduced-cost hydrogen production.

3:20pm TS2-WeA-5 Single Atom Ag Bonding between PF3T nanocluster and TiO<sub>2</sub> leads the Ultra-stable Visible-Light-Driven Photocatalytic H<sub>2</sub> Production, Tsan-Yao Chen, Fan-Gang Tseng, National Tsing Hua University, Taiwan; Jyh-Pin Chou, National Taiwan University, Taiwan; Sun Wei Tse, Taiwan: National Tsing Hua University. [ym1015139@gmail.com], National Taipei University of Technology, Taiwan Atomic Ag cluster bonding is utilized to enhance the interface between PF3T nanoclusters and TiO2 nanoparticles. At an optimized Ag loading of 0.5 wt% (Ag/TiO2), the Ag atoms are uniformly dispersed on the TiO2 surface, generating a high density of intermediate states within the bandgap. This forms an efficient electron channel between the terthiophene groups of PF3T and TiO2 in the hybrid composite (denoted as T@Ag05-P). The enhanced interface broadens the photon absorption bandwidth and facilitates core-hole splitting by enabling photon-excited electrons (from excitons in PF3T) to inject into the conduction band (CB) of TiO2. These features enable a remarkable H2 production efficiency of 16,580 µmol h<sup>-1</sup> g<sup>-1</sup> and exceptional photocatalytic stability, with no degradation observed under visible light exposure for 96 hours. Compared to the hybrid material without Ag bonding (TiO2@PF3T), the H2 production yield and stability improve by 4.1-fold and 18.2-fold, respectively, representing the best performance among similar materials with comparable component combinations and interfacial reinforcement strategies. This innovative bonding approach opens new opportunities for advancing photocatalytic hydrogen production technologies.

3:40pm TS2-WeA-6 Transition Metal-Based Electrocatalysts for Sustainable Oxygen Reactions in Green Energy Applications, Emma Björk [emma.bjork@liu.se], Linköping University, IFM, Sweden INVITED

Water splitting and recombination are pivotal processes in the transition toward green, renewable, and fossil-free energy production. These reactions are limited by the kinetics of the oxygen reactions—the Oxygen Evolution Reaction (OER) and the Oxygen Reduction Reaction (ORR)—which creates a significant demand for efficient electrocatalysts. Efforts are focused on developing abundant, cost-effective alternatives to the noble metal catalysts currently in use. In this presentation, the possibility to use transition metal oxides, e.g. Co, Ni, and Mn oxides, as oxygen catalysts will be discussed.

The first part will cover multicomponent films, e.g. CoCrFeNi and MnCrFeNi, as catalytically active, corrosion-resistant coatings. The films were synthesized via magnetron sputtering and subsequently subjected to electrochemical activation through anodization, enhancing their catalytic activity towards both ORR and OER. Anodization also altered the ORR mechanism in CoCrFeNi and MnCrFeNi films, shifting it from a (2+1) electron pathway in as-deposited films to either a 4- or 2-electron pathway in anodized films. These changes are attributed to modifications in active

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sites and film structure. Substituting Co with Mn slightly improved OER performance but did not affect the ORR activity significantly.

The films also demonstrated excellent corrosion resistance in alkaline and neutral chloride environments, attributed to the formation of a protective oxide layer. The corrosion performance was influenced by film composition and structure, particularly grain size. For example, lattice distortion in CoCrFeNi enhanced resistance in NaCl, while smaller grain sizes improved the corrosion resistance in KOH.

The second part of the talk focuses on increasing catalytic activity of transition metal oxides by introducing nanoporosity to enhance the number of active sites. Nanoporous materials, which often have specific surface areas exceeding 100 m²/g, were synthesized via hydrothermal treatment methods to create nanoporous MOx (M = Cr, Fe, Co, Ni, Ce) and NiCo<sub>2</sub>O<sub>4</sub> oxygen electrocatalysts. Optimizing pore size in nanoporous NiO revealed a critical balance between the number of active sites and the diffusion of reactants and products. NiO with a pore size of 3.3 nm achieved the lowest overpotential (335 mV at 10 mA/cm²), outperforming a commercial Ir/C catalyst under similar conditions.

The different ORR pathways on the various catalysts enable product selectivity, and we have designed electrochemical cells for an oxygen pump, hydroxyl radical generation, and H2O2 production using nanoporous transition metal oxides, air, water, and KOH.

4:20pm TS2-WeA-8 Bi-Based Photocatalysts Obtained by Reactive Sputtering for the CO<sub>2</sub> Photoreduction – from Thin Films and Composites to Nanoparticles, Angélique Bousquet [angelique.bousquet@uca.fr], Sara Ibrahim, Jean-Michel Andanson, Pierre Bonnet, Institut de Chimie de Clermont-Ferrand, France; Mireille Richard-Plouet, Institut des Matériaux, France; Maryline Le Granvalet, Institut des Matériaux de Nantes, France; Sébastien Roth, Audrey Bonduelle, Institut Français du Pétrole, Energies Nouvelles, France

To reduce the  $CO_2$  emission into atmosphere is a major issue to mitigate the current climate change. Moreover, be able to photo-convert  $CO_2$  into more valuable species and form clean solar fuels and molecules would be a step forward to the industry decarbonation. Among the photocatalysts investigated to photoreduce  $CO_2$ , Bi-based materials have demonstrated their interest to selectively form CO, a molecular building block which can further be used to obtain methanol, acetic acid, aldehyde and even fuels...

In this study, we investigated the deposition of Bismuth oxyfluoride thin films by reactive radiofrequency magnetron sputtering of a pure Bi target in Ar/O<sub>2</sub>/CF<sub>4</sub> atmosphere. We demonstrated, that it is possible to obtain coatings of various crystallized compounds (Bi<sub>7</sub>O<sub>5</sub>F<sub>11</sub>, BiO<sub>0.5</sub>F<sub>2</sub>, BiF<sub>3</sub>...) depending on the injected flow rates of O2 and CF4 reactive gases. More interesting, is the possibility to form composites of these compounds with a controlled content of metallic Bismuth nanodomains by reducing the reactive gas flow rates. Hence, we obtained in one step heterojonctions that presents enhanced photocatalytic activities thanks to potential plasmonic effect. The composition, structure and morphology of these coatings were studied by XRD, Raman spectroscopy, XPS, TEM and SEM. Their optical properties, especially their band gap, were determined from UV-visible spectroscopy and ellipsometry. Experiments of photodegration of pollutants into water shows that an optimum of metallic content has to be found to enhance the photocatalytic properties of the Bi-based materials<sup>[1]</sup>. The CO<sub>2</sub> photoconversion measurements, perforned at IFPEN, on these materials demonstrate a photon conversion efficiency close to the one of TiO<sub>2</sub> P25 from Degussa, but with a high selectivity to form CO (= 90% and 10% of H<sub>2</sub>).

To go further, we now working on nanostructuration of these materials in order to increase the contact surface with CO<sub>2</sub> gas using an original method: the reactive sputtering onto liquid. If this technique was already investigated to form dispersion of metallic nanoparticles into liquid, we suceeded for the first time to use it in reactive mode to obtain dispersion of sperical, well-crystallized oxyfluoride nanoparticles with a mean size ranging from 6 to 8 nm and presenting a photocatalytic response<sup>[2]</sup>. These particules may be dispersed on porous support paving the way of high surface specific aera system for CO<sub>2</sub> photoreduction.

[1] S. Ibrahim, et al., 2023, hal-04037069v1.

[2] S. Ibrahim, et al., Nanoscale, 15, 2023, 5499 - 5509

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