

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

### (Photo)electrocatalysis and Solar/Thermal Conversion

**Moderators:** Dr. Atasi Dan, National Institute of Standards and Technology (NIST), USA, Dr. Arnaud Le Febvrier, Uppsala University, Sweden, Prof. Carlos Tavares, University of Minho, Portugal

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  $\text{Bi}_2\text{Te}_3$  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  $\mu$ -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 termoelectrico e-Tattoo autossustentável para mapeamento de temperatura” (2024) – Advanced Science

Printed Flexible  $\mu$ -Thermoelectric Device Based on Hybrid  $\text{Bi}_2\text{Te}_3$ /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 electro-deposited 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  $\text{cm}^{-2}$  and small Tafel slope of 42.1 mV  $\text{dec}^{-1}$ . Under a high current density of 500 mA  $\text{cm}^{-2}$ , the catalyst requires an 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  $\text{cm}^{-2}$ , 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**, Rwei 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  $\text{cm}^{-2}$  and 100 mA  $\text{cm}^{-2}$ , 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  $\text{cm}^{-2}$ . 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  $\text{TiO}_2$  leads the Ultra-stable Visible-Light-Driven Photocatalytic  $\text{H}_2$  Production**, Tsan-Yao Chen [chencaeser@gmail.com], Fan-Gang Tseng, National Tsing Hua University, Taiwan; Jyh-Pin Chou, National Taiwan University, Taiwan

Atomic Ag cluster bonding is utilized to enhance the interface between PF3T nanoclusters and  $\text{TiO}_2$  nanoparticles. At an optimized Ag loading of 0.5 wt% (Ag/ $\text{TiO}_2$ ), the Ag atoms are uniformly dispersed on the  $\text{TiO}_2$  surface, generating a high density of intermediate states within the bandgap. This forms an efficient electron channel between the terthiophene groups of PF3T and  $\text{TiO}_2$  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  $\text{TiO}_2$ . These features enable a remarkable  $\text{H}_2$  production efficiency of 16,580  $\mu\text{mol h}^{-1} \text{g}^{-1}$  and exceptional photocatalytic stability, with no degradation observed under visible light exposure for 96 hours. Compared to the hybrid material without Ag bonding ( $\text{TiO}_2$ @PF3T), the  $\text{H}_2$  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.  $\text{CoCrFeNi}$  and  $\text{MnCrFeNi}$ , 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  $\text{CoCrFeNi}$  and  $\text{MnCrFeNi}$  films, shifting it from a (2+1) electron pathway in as-deposited films to either a 4- or 2-electron pathway

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in anodized films. These changes are attributed to modifications in active 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  $100 \text{ m}^2/\text{g}$ , were synthesized via hydrothermal treatment methods to create nanoporous MOx (M = Cr, Fe, Co, Ni, Ce) and  $\text{NiCo}_2\text{O}_4$  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  $10 \text{ mA}/\text{cm}^2$ ), 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  $\text{H}_2\text{O}_2$  production using nanoporous transition metal oxides, air, water, and KOH.

**4:20pm TS2-WeA-8 Bi-Based Photocatalysts Obtained by Reactive Sputtering for the  $\text{CO}_2$  Photoreduction – from Thin Films and Composites to Nanoparticles**, *Angélique Bousquet* [[angelique.bousquet@uca.fr](mailto: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  $\text{CO}_2$  emission into atmosphere is a major issue to mitigate the current climate change. Moreover, be able to photo-convert  $\text{CO}_2$  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  $\text{CO}_2$ , 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  $\text{Ar}/\text{O}_2/\text{CF}_4$  atmosphere. We demonstrated, that it is possible to obtain coatings of various crystallized compounds ( $\text{Bi}_7\text{O}_5\text{F}_{11}$ ,  $\text{BiO}_{0.5}\text{F}_2$ ,  $\text{BiF}_3$ ...) depending on the injected flow rates of  $\text{O}_2$  and  $\text{CF}_4$  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 heterojunctions 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 photodegradation 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  $\text{CO}_2$  photoconversion measurements, performed at IFPEN, on these materials demonstrate a photon conversion efficiency close to the one of  $\text{TiO}_2$  P25 from Degussa, but with a high selectivity to form CO (= 90% and 10% of  $\text{H}_2$ ).

To go further, we now working on nanostructuring of these materials in order to increase the contact surface with  $\text{CO}_2$  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 succeeded for the first time to use it in reactive mode to obtain dispersion of spherical, 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  $\text{CO}_2$  photoreduction.

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

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

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