

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

(Photo)electrocatalysis and Solar/Thermal Conversion

Moderators: Atasi Dan, National Institute of Standards and Technology (NIST), USA, Arnaud Le Febvrier, Uppsala University, Sweden, 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 Bi₂Te₃ 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 μ -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 termoeletrico e-Tattoo autossustentavel para mapeamento de temperatura" (2024) – Advanced Science

Printed Flexible μ -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 electro-deposited on the surface of as-prepared alloy. The obtained catalyst demonstrates excellent catalytic activity toward HER with a low

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overpotential of 28.4 mV at 10 mA cm⁻² and small Tafel slope of 42.1 mV dec⁻¹. Under a high current density of 500 mA 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 cm⁻², negligible voltage drops are demonstrated under both electrolyte conditions. The excellent HER performance and cost-effectiveness 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 excellent potentials of 1.25 V and 1.31 V at current densities of 10 mA cm⁻² and 100 mA 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 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 TiO₂ leads the Ultra-stable Visible-Light-Driven Photocatalytic H₂ 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 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@Ag0.5-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 $\mu\text{mol h}^{-1} \text{g}^{-1}$ and exceptional photocatalytic stability, with no degradation observed under visible light exposure for 96 hours. Compared to the hybrid material without Ag bonding (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

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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 m²/g, were synthesized via hydrothermal treatment methods to create nanoporous MOx (M = Cr, Fe, Co, Ni, Ce) and NiCo₂O₄ 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 CO₂ 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 CO₂ emission into atmosphere is a major issue to mitigate the current climate change. Moreover, be able to photo-convert CO₂ 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 CO₂, 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/O₂/CF₄ atmosphere. We demonstrated, that it is possible to obtain coatings of various crystallized compounds (Bi₇O₅F₁₁, BiO_{0.5}F₂, BiF₃...) 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 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^[1]. The CO₂ photoconversion measurements, performed at IFPEN, on these materials demonstrate a photon conversion efficiency close to the one of TiO₂ P25 from Degussa, but with a high selectivity to form CO (= 90% and 10% of H₂).

To go further, we now working on nanostructuring of these materials in order to increase the contact surface with CO₂ 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^[2]. These particles may be dispersed on porous support paving the way of high surface specific area system for CO₂ photoreduction.

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

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

4:40pm TS2-WeA-9 Effect of Crystallographic Texture on Dealloying Kinetics and Nanoporous Gold Thin Film Composition, *Ezgi Hatipoğlu*, Max-Planck Institut für Nachhaltige Materialien, Germany; *Ayman A. El-Zoka*, Imperial College London, UK; *Jochen Schneider*, Materials Chemistry, RWTH Aachen, Germany; *Baptiste Gault*, **Aparna Saksena** [a.saksena@mpie.de], Max-Planck Institut für Nachhaltige Materialien, Germany

With rising concerns regarding climate change, the demand for cleaner and sustainable fuels is increasing. Hydrogen is the most popular candidate for clean energy for a carbon-neutral economy. Hydrogen production via water splitting reaction is a promising route where catalysts play a vital role in improving the energy conversion efficiency of the reaction. Nanoporous metals offer an important platform for tailoring composition and surface-to-volume ratio, both aspects critical for applications in catalysis. Here, AgAu films were deposited at 400°C either (111)-textured or untextured. Upon chemical dealloying to form the nanoporous structure, atom probe tomography reveals that the textured film retains a higher Ag concentration within the nanoligaments, whereas the untextured film already exhibits coarsening, indicating a faster reaction kinetics, and a lower Ag content. Our study highlights the potential of microstructure engineering in tailoring the properties of nanoporous metals for possible future catalytic and electrochemical applications.

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