Topical Symposium on Sustainable Surface Engineering
Room Town & Country D - Session TS4-2-ThA

Coatings and Surfaces for Thermoelectrical Energy Conversion and (Photo)electrocatalysis II

Moderators: Clio Azina, RWTH Aachen University, Germany, **Carlos Tavares**, University of Minho, Portugal

1:20pm **TS4-2-ThA-1 Two-Dimensional Ruddlesden–Popper Phase of B-site substituted $Ca_{n-1}Mn_{n-3}Nb3O_{3n+12-}$ (n=4,5,6) Perovskite Nanosheets Integration with Chlorella vulgaris for Electrochemical Water Splitting***, Yao-Yuan Chang (m56111135@gs.ncku.edu.tw), C. Chang, Y. Su,* National Cheng Kung University (NCKU), Taiwan

Two-dimensional (2D) perovskite nanosheets have emerged as potential candidates for hydrogen production and spintronic devices due to their large surface area, special optical, electric, magnetic, and structural properties. In this study, we synthesized 2D Ruddlesden–Popper (RP) phase perovskite nanosheets $Ca_{n-1}Mn_{n-3}Nb_3O_{3n+1}^-$ (n=4,5,6) to tune their physicochemical properties and catalytic performances via soft chemistry process. In this configuration, manganese (Mn) partially substitutes niobium (Nb) at the B-site within the niobate perovskite lattice structure exhibited positive influences in water splitting applications.The combination of CMNO nanosheets with Chlorella on the photoelectrode surface has demonstrated improved photoelectrochemical performance, especially for CMNO (n=6) nanosheet.This research contributes to the future outlook for sustainable energy solutions by unique properties of 2D perovskite oxide nanomaterials in conjunction with bio-inspired components.

Keywords: two-dimensional, Ruddlesden–Popper phase perovskites, Chlorella vulgaris, water splitting,magnetic

1:40pm **TS4-2-ThA-2 Multifunctional Materials for Emerging Technologies***, Federico Rosei (federico.rosei@units.it),* University of Trieste, Italy **INVITED**

This presentation focuses on structure property/relationships in advanced materials, emphasizing multifunctional systems that exhibit multiple functionalities. Such systems are then used as building blocks for the fabrication of various emerging technologies. In particular, nanostructured materials synthesized via the bottom–up approach present an opportunity for future generation low cost manufacturing of devices [1]. We focus in particular on recent developments in solar technologies that aim to address the energy challenge, including third generation photovoltaics, solar hydrogen production, luminescent solar concentrators and other optoelectronic devices. [2-40].

References

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2:20pm **TS4-2-ThA-4 Enhanced Photoelectrochemical Water Splitting on $ZnCo_2O_4$ Electrodes in Chloroplasts Driven by Spin Injection***, Chien-Yu Lin (n56111453@gs.ncku.edu.tw), Y. Su,* National Cheng Kung University (NCKU), Taiwan

This work demonstrated the photoelectrochemical water splitting efficiency of spinel-structured $ZnCo_2O_4$ on carbon paper substrate as photoelectrode and also coating on chloroplasts. $ZnCo_2O_4$ is p-type transition metal oxide semiconductor and could be synthesized by hydrothermal method and different annealing temperature, showing nanoparticles in morphology. Furthermore, we extracted the chloroplasts from chlorella to make it coat on $ZnCo_2O_4$ electrodes as protection layer, which also could be boosting the photosynthesis reaction when the water splitting process goes on. We observed the applied bias photon-to-current efficiency (ABPE) by changing spin quantum states, and the chloroplasts photoelectrochemical water splitting cell shows a splendid efficiency of hydrogen production. Accordingly, the device can be successfully applied on energy storage and conversion, suggesting the great potential of the applications in electronic, catalysis, and solar applications.

2:40pm **TS4-2-ThA-5 Piezoelectricity-Assisted Photocatalyst of BiOBr-Based Composites on a Flexible Substrate***, Thi Nghi Nhan Nguyen (nghinhan2410@gmail.com), K. Chang,* National Cheng Kung University (NCKU), Taiwan

A novel 3D network of BiOBr flakes was grown on carbon fiber (CF) substrates through a straightforward chemical deposition process. The BiOBr-based composites served as catalysts for photodegradation and as photoelectrodes for photoelectrochemical cells. The p-n junction formation was determined by Mott–Schottky measurements which was also confirmed through high-resolution transmission electron microscopy and X–ray photoelectron spectroscopy. The piezoelectric properties of BiOBr were verified using piezoresponse force microscopy. The photoelectrochemical performance of samples was assessed through various techniques, including linear sweep voltammetry, chronoamperometry [https://www.sciencedirect.com/topics/chemistry/chronoamperometry], amperometry andcyclic voltammetry. Under simultaneous illumination and mechanical pressure, the Ag_2O/BiOBr composite demonstrated a photocurrent of approximately 20.0 mA cm^{-2} at 1.23V, showcasing a remarkable enhancement over 4 and 20 times compared to individual BiOBr and Ag_2O, respectively. The maximum applied bias photon to current efficiency values of Ag_2O/BiOBr composite with external stress was approximately 2.7 % at 0.9V. Additionally, a glucose sensor based on Ag_2O/BiOBr composite exhibited a high sensitivity of 400 μA cm^{-2} mM^{-1}, within a detection glucose range of 0.1–12 mM. The Ag_2O/BiOBr-based photolectrodes showed excellent stability and repeatability in glucose detection. Furthermore, the CuS/BiOBr composite displayed outstanding performance in TC degradation. The effectiveness of the BiOBr composites was attributed to the p-n junction formation, piezoelectric potentials, substantial active surface area and advantageous band positions.

3:00pm **TS4-2-ThA-6 Hydrothermal Synthesis of p-Ag_2O/n-$BaTiO_3$ Heterojunctions for Visible-light Photocatalytic Application***, Yen-Lun Chiu (0953065268v@gmail.com), K. Chang, S. Han,* National Cheng Kung University (NCKU), Taiwan

Perovskite-nanostructured films are attractive because of their excellent characteristics. Different kinds of properties can be obtained, e.g., dielectric properties, piezoelectricity, and thermoelectricity, from different materials. With the hydrothermal fabrication, the perovskite materials can be synthesized in a facile way with lower power consumption. However, studies on this topic directly through hydrothermal processes for the fabrication of perovskite-nanostructured films are still lacking. In this study, well-aligned (Ba,Sr)TiO_3 nanorod arrays composited with p-AgBr were synthesized through the hydrothermal reaction for visible-light piezo-photocatalytic application. The hydrothermal parameters, including concentrations of precursor solutions, reaction time, temperatures, different types of ion species, and the surfactants used for the reaction, were manipulated. X-ray diffraction and transmission electron microscopy were employed to determine the phase and microstructure of the resultant samples. The amplitude of the piezoresponse (d_{33}) was measured through a piezoresponse force microscope for the materials. The photoelectrochemical activity of the samples were also studied for related applications. An energy band diagram was constructed to elucidate a potential mechanism for the remarkable activity.

Keywords: perovskite-nanostructured films, hydrothermal, (Ba,Sr)TiO_3 nanorod arrays, p-AgBr, piezo-photocatalysis

3:20pm **TS4-2-ThA-7 Advances in Piezo-Photothermal Effect Enhanced Photocatalytic Activities of Heterostructure Composites***, Van Ty Tran (tranvanty108@gmail.com), D. Chen,* National Cheng Kung University (NCKU), Taiwan

This study focusses on developing heterostructure composites to enhance the efficiency of piezoelectric and photothermal-assisted photocatalytic processes for pollutant degradation and photoelectrochemical water splitting. The $Ag_2O/BiFeO_3$ and CuS/MoS_2 composites were fabricated through a hydrothermal method. The morphologies and microstructures of the samples are analyzed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy. The composites exhibit a low band gap, indicating their capacity to absorb light in the Vis-NIR range. The conductive type of the samples and p-n junction formation is determined through Mott Schottky (M-S) measurements. The formation of a p-n junction facilitates the separation of electron-hole pairs, thereby improving the efficiency of the photocatalyst. Additionally, the induced piezoelectric potential in the piezoelectric material promotes photocatalytic activity by reducing the recombination of photogenerated charges. Under irradiation, the generated heat further supplies kinetic energy to photogenerated carriers, enhancing reaction rates in photocatalytic processes. The piezoelectric composite demonstrates the ability to produce •O^{2-}, •OH, and h^+ through photocatalysis, effectively degrading pollutants like tetracycline (TC) and Rhodamine B (Rh B) through oxidation. The degradation efficiency of the TC solution was further increased to 95% for CuS/MoS_2 composite in 30 min, which was higher than that of individual components. Moreover, The Ag_2O/$BiFeO_3$ heterostructure exhibited excellent photocatalytic degradation of Rhodamine B and TC, and photoelectrochemical water splitting activity.

4:00pm **TS4-2-ThA-9 Photoelectrochemical Properties of Chlorophyll Coating on Cu_2O Photocatalyst by Mediating Charge Transfer Characteristic***, **Yu-Teng Wu (wuyuteng22@gmail.com)**, Y. Su,* National Cheng Kung University (NCKU), Taiwan

Metal oxide semiconductors have impressive applications in the field of photo electrochemistry. This study utilizes electrochemical deposition to generate nano-thin films of cuprous oxide, applying them in green energy sources. During the photoelectrochemical (PEC) process, cuprous oxide faces issues of instability and insufficient durability due to photo-induced corrosion in aqueous solutions. To address this, the natural photosensitizing material chlorophyll is adhered to enhance charge transfer efficiency and provide a better surface electric field distribution. Additionally, the chlorophyll layer effectively isolates the aqueous solution from direct contact with cuprous oxide, enhancing sample stability. Detailed research results, including atomic force microscopy (AFM) and electrostatic force microscopy (EFM) surface electric field analyses, along with electrochemical methods, confirm that Chlorophyll/Cu2O exhibits superior stability and durability, enhancing the overall value of this PEC cell.

4:20pm **TS4-2-ThA-10 Ligand Modified Bimetallic Metal-Organic Frameworks Electrocatalysts for Urea Oxidation Reaction***, **Hui Chuan Chen (jace52112@gmail.com)**,* National Cheng Kung University (NCKU), Taiwan*; T. Nguyen,* National Cheng Kung University (NCKU), Taiwan, Viet Nam*; J. Ting,* National Cheng Kung University (NCKU), Taiwan

In the quest for energy efficiency, electrocatalytic urea oxidation reaction (UOR) is a promising alternative to oxygen evolution reaction (OER) due to the favorable thermodynamics, meanwhile, it is also an environmentally friendly strategy.

In this regard, metal-organic framework (MOF) materials have the advantages of high specific surface area, high porosity, structural adjustability, etc., providing abundant metal active sites to achieve high efficiency electrocatalytic performance. However, due to the poor conductivity of MOF, the charge transfer ability is limited. In order to improve the shortcoming, ligand having redox activity is introduced. This ligand can not only adjust the synergistic effect of metal clusters and organic ligands to increase the charge transfer ability, but also can be an additional adsorption sites to promote the adsorption/desorption ability of intermediates. In this study, we report ligand modified bimetallic MOF synthesized via a low temperature hydrothermal method, this optimized bimetallic MOFs exhibits an outstanding UOR performance with high catalytic activity, low resistance and excellent electrochemical stability.

Keywords: MOFs, urea oxidation reaction (UOR), electrocatalyst

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