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Symposium FH
Advanced Photocatalytic Materials for Energy Transition, Solar-driven Chemistry and Environmental Applications

ABSTRACTS

Session FH-1 - Design Elements and Advanced Concepts for Photofunctional Materials

FH-1:IL01 **Electrochemical Oxygen & Chlorine Production: Enhancing Electro-catalytic Activity Using Atomic Layer Deposition**
M.R. HOFFMANN, Division of Engineering & Applied Science, California Institute of Technology, Pasadena, CA, USA

The economical generation of fuels and commodity chemicals from renewable electricity sources depends on the development of highly active electrocatalyst. Despite their advantages (e.g., facile product separation), the industrial use of heterogeneous electrocatalysts is still limited by current catalyst efficiency and selectivity. While many methods and design tools such as doping, strain induction, mixing metal oxides and others exist to improve the catalytic activity of heterogeneous electrocatalysts. However, the conventional methods are either limited by specific material parameters or by the ability to predict specific catalytic activity resulting from alteration of catalyst properties (e.g., doping). Thus, finding new tools to tune the intrinsic activity of catalysts represents a continuing challenge in the field of heterogeneous electrocatalysis. In our case, Atomic layer deposition (ALD) provides an attractive method for tuning electrocatalysts by precisely altering their surface charge densities. We applied TiO_2 *via* ALD to tune three heterogeneous electrocatalysts (IrO_2, RuO_2, and FTO) for the oxygen and chlorine evolution reactions (OER and CER). The electrocatalysts with ~3-30 ALD cycles of TiO_2 had measured overpotentials at 10 mA/cm^2 that were several hundred mVs lower than the uncoated, naked catalyst surfaces. In addition, controlled deposition of TiO_2 resulted in higher OER specific activities in 1 M H_2SO_4 (0.87 $mA/cm^2{}_{ECSA}$ at 350 mV η) than previously reported in the literature. The oxidation state of titanium and the potential of zero charge (E_{PZC}) were also shown to sensitive to the number of successive ALD cycles. These results suggest that with a controlled number of ALD cycles ≤ 30 the catalytic activity of electrocatalysts can be enhanced and at the same time protected against erosion and inactivation. Additional advances using Cobalt-doped Black TiO_2 nanotube electrodes will be presented.

FH-1:IL02 **Ultra-efficient Solar CO2 Conversion using Oxide Semiconductor Electrodes**
UNSEOCK KANG[1,2], SEUNG YO CHOI[1,2], HYE WON JEONG[1,2], GUANGXIA PIAO[1,2], DONG SUK HAN[3], **HYUNWOONG PARK**[1,2], [1]School of Energy Engineering, Kyungpook National University, Daegu, South Korea; [2]School of Architectural, Civil, Environmental, and Energy Engineering, Kyungpook National University, Daegu, South Korea; [3]Chemical Engineering Program, Texas A&M University at Qatar, Education City, Doha, Qatar

There is renewed interest in the photocatalytic and photoelectrochemical conversion of CO2 into value-added chemicals using various semiconductor particles and electrodes. Common CO2 reduction products are C1 chemicals (CO, HCOOH, CH3OH, and CH4) in aqueous media, while the production of C2-C4 hydrocarbons (e.g., C2H6 and C3H8) has also been reported. A number of solar-active materials have been reported, but they still suffer from low selectivity, poor energy efficiency, and instability, while failing to drive simultaneous water oxidation. This talk presents our recent studies on the solar CO2 conversion to value-added chemicals while using water as an electron donor in various photo-systems.
This research was supported by the Basic Science Research Program (2016R1A2B4007366), Korea Ministry of Environment as Waste to Energy-Recycling Human Resource Development Project (YL-WE-17-001).
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FH-1:IL03 **Nanocomposite Materials as Photoelectrodes in Solar Fuel Generation: Opportunities and Challenges**
C. JANAKY, E. KECSENOVITY, B. ENDRODI, University of Szeged, Szeged, Hungary

In this talk I will present the use of electrosynthetic (and photoelectrosynthetic) methods for preparing semiconductors on nanocarbon-modified electrode surfaces. I will show how electrodeposition can be used to tune composition, crystal structure, and morphology of the nanocomposites for targeted applications. Selected examples will be given for how these electrosynthesized hybrid assemblies can be deployed in various photoelectrochemical application schemes, most importantly CO2 conversion. I will present the controlled synthesis and photoelectrochemical behavior of Cu2O/CNT and Cu2O/graphene composites. A carefully designed, multiple-step electrodeposition protocol was developed that ensured homogeneous coating of the CNTs with the Cu2O nanocrystals. TiO2/3D graphene nanocomposites were also obtained in a similar manner. This enhanced charge transport property for the hybrids resulted in a drastic increase in the photocurrents measured for the CO2 reduction. In addition to this superior performance, long term photoelectrolysis measurements proved that the Cu2O/nanocarbon hybrids were more stable than the oxide alone. Taking these observations together, as a whole a general model will be presented on the role of the nanocarbon scaffold.

FH-1:IL04 **Role of Electron Traps in Photocatalysis: Identification and Characterization of Metal Oxide Particulate Photocatalysts**
BUNSHO OHTANI, Institute for Catalysis, Hokkaido University, Sapporo, Japan

From the beginning of history of photocatalysis studies, particulate photocatalysts, used in the studies and discussed in the papers, have not been identified. However, who can identify a powder in an unlabeled bottle/package found in a laboratory? How can evaluate the fluctuation in quality of a sample prepared in a routine procedure? X-ray diffraction (XRD) pattern and/or specific surface area data may give some physical properties. Are those sufficient to identify the sample? In the field of organic synthesis, it is accepted that showing reasonable fit of elemental composition and NMR data with theoretical value and authentic one, respectively, can be identification of a product. Such a difference in identification for molecules and particles must be due to the existence of surface on particles, and therefore, composition and bulk structure of particles cannot be enough to identify. Here we report energy-resolved distribution of electron traps (ERDT), which may be located predominantly on the surface, measured for titania and the other metal-oxide powders and propose the distribution can be a finger print of powder for identification and a sole possible structural parameter closely related to the photocatalytic activities of metal-oxide powder samples.

FH-1:IL05 **Mechanistic Aspects of Photocatalysis - Control of Photoinduced Redox Processes**
W. MACYK, M. KOBIELUSZ, M. TROCHOWSKI, M. SUROWKA, M. PACIA, J. KUNCEWICZ, Faculty of Chemistry, Jagiellonian University in Kraków, Kraków, Poland

Photocatalytic activity may be enhanced through a smart engineering of photocatalysts resulting in tuning their redox properties. Surface modification, doping, co-precipitation may be involved to reshape the density of electronic states (DOS) of semiconductors. This, in turn, reflects in changed redox properties (energy of electrons and holes), the fundamental factors governing the interfacial electron transfer to and from the adsorbed reactants. DOS, determined by spectroelectrochemical approach, can be shaped, e.g., by thermal treatment, atomic layer deposition, surface functionalization. Examples of such engineering will be discussed in the context of photocatalytic reactions, including O2 and CO2 reduction. For instance, Fe(III) species influenced the morphology and therefore DOS of synthesized TiO2, even if iron species were not introduced into the crystal lattice of titania. A particular improvement of the photocatalytic activity was achieved for materials with a low iron content (0.01%mol Fe). Beside commonly discussed mechanisms (photo-Fenton processes, charge separation, photosensitization, etc.) iron species can indirectly affect the photocatalytic activity of TiO2, acting as steering factors influencing crystal phase composition and therefore its redox properties.

FH-1:IL06 **The Photochemical Reactivity of Polar Surface Domains on Non-polar Surfaces**
G.S. ROHRER, P.A. SALVADOR, Carnegie Mellon University, Dept. of Materials Science and Engineering, Pittsburgh, PA, USA

Polar semiconductors have recently received significant attention because their internal fields separate photogenerated electron-hole pairs and reduce recombination. On surfaces with polar domains, electrons are attracted to positively terminated domains where they promote reduction reactions and holes are attracted to negatively charged domains where they promote oxidation. We have found that polar domains can be created on the surfaces of non-polar materials, including BiVO4, WO3, and SrTiO3. In the cases of WO3 and BiVO4, polarity arises from the flexoelectric effect. On SrTiO3, polarity arises from polar terminations on different terraces. For SrTiO3, it is possible to control the fraction of the surface terminated by positive or negative charges by annealing the surfaces in environments with an excess or deficit of strontium. In this talk, the use of polar domains to control photochemical reactions on the surfaces will be described.

FH-1:IL07 **Nano-graphitic Templates and Hierarchical Nanostructures in Multi-functional Electrocatalysts for the Artificial Leaf**
G. VALENTI, A. BONI, M. MARCACCIO, S. RAPINO, M. IURLO, **F. PAOLUCCI**, University of Bologna, Bologna, Italy; P. FORNASIERO, M. PRATO, University of Trieste, Italy; M. BONCHIO, University of Padua, Italy

Nanomaterials are nowadays at the forefront of materials science research. The design and realization of hierarchical nanoarchitectures, in which selected components are arranged to leverage their expected mechanistic functions are obtaining a wide range of applications, from the aerospace industry to bio-medicine, and as benchmarks for many catalytic reactions. Carbon-based nanomaterials have been the main actors of nanotechnology since their very first discovery, and their unique morphological/electronic properties are particularly suited to be used in electrocatalytic applications. CNTs and graphene are indeed ideal supports in catalysis as they have an optimal electronic conductivity and provide percolation routes for charge transfer reactions to occur. The integration of nanocarbons into hierarchical materials is an effective strategy to further boost the potentiality of nanostructured catalysts. We will show that, once embedded within nanoarchitectures made of multi-wall carbon nanotubes or graphene and metal oxide shells, the catalytic properties of nanoclusters (1,2) and metal nanoparticles (3,4) can be dramatically enhanced according to mechanisms which likely involve the concerted and synergic participation of all component building blocks in the electrocatalytic steps.

FH-1:IL08 **Advanced Organic/Inorganic Hybrid Materials Derived from Tunable Si-based NanoBuilding Blocks**
S. DIRE', E. CALLONE, M. D'ARIENZO, B. DI CREDICO, R. SCOTTI, F. RIBOT, University of Trento, Dept. Industrial Engineering, Trento, Italy; University of Milano-Bicocca, Dept. Materials Science, Milano, Italy; Université Pierre et Marie Curie, CMCP, UMR7574 -UPMC / CNRS / Collège de France, Paris, France

Polysiloxanes and silsesquioxanes obtained from hydrolysis-condensation of organoalkoxysilanes of the type R'nSi(OR)4-n with different R' organic functions and OR alkoxy groups find wide application in the field of protective and functional coatings, matrices for embedding organic and biochemical compounds, catalysis, optics and electronics. The design of synthesis and processing parameters plays a key-role in driving the siloxane network development. In particular, the NanoBuilding Blocks (NBBs) approach is employed for the preparation of organic/inorganic (O/I) hybrid materials with the aim of fine-tuning the crosslinking degree, the extent and chemical nature of O/I interfaces and, as a consequence, the structure-related properties. To this purpose only a deep understanding of oligomers growth and assembling and the knowledge of NBBs structural features can direct the synthesis toward materials with desired functionalities. In this frame, NBBs have been recently exploited to develop novel photoactive coatings including TiO2 nanoparticles (NPs) with tailored morphology. This strategy meets the challenge of tailoring photocatalytic and mechanical properties simultaneously, granting the transfer of the intrinsic peculiarity of NBBs and TiO2 NPs to the final advanced materials.

FH-1:L09 Transient Behavior of Ni/NiO Modified Mg:SrTiO3 in Photocatalytic Overall Water Splitting

KAI HAN, B. MEI, G. MUL, University of Twente, Enschede, The Netherlands

SrTiO3 is known as a promising photocatalyst for driving overall water splitting under UV light illumination. However, feasible co-catalysts, such as Pt or Ni/NiO, are still required to drive the reaction. In this contribution we will discuss three aspects crucial to design this photocatalyst. More specifically it will be shown that: 1) Changes in the NiOx oxidation state through transformation of Ni(OH)2 to NiOOH are in agreement with observed transient H2 evolution profiles, leading to an active Ni/NiO modified SrTiO3 composite photocatalyst; 2) Electronic modification of SrTiO3 by Mg incorporation into the perovskite structure causes drastic improvements to the initial transient and steady state photocatalytic water splitting efficiency; 3) We will discuss strategies to stabilize Ni/NiO modified Mg:SrTiO3 by photodeposition of CrOx from Cr(VI) containing solutions.

FH-1:L10 Coupling Between Enzymes and a Photoactive Sulphide for Photoproduction of H2 and O2

C. TAPIA, **J.C. CONESA**, A.L. DE LACEY, M. PITA, Inst. de Catálisis y Petroleoquímica, CSIC, Madrid, Spain; S. SHLEEV, Biomed. Sci., Fac. Health & Society, Malmö University, Malmö, Sweden

Solar fuel generation is a much studied subject, as it may facilitate a renewable energy-based economy. The best known light absorbing semiconductor proposed to this aim, TiO2, is active, stable and inexpensive, but can only convert UV light. Sulphides like In2S3 and SnS2, with bandgaps of respectively 2.0 and 2.2 eV, have shown better photo-activity with visible light and higher stability against photocorrosion (in oxidative abatement of organics) than the toxic compound CdS. Here we report the photocatalytic H2 production in aqueous suspension combining a Ni-Fe hydrogenase enzyme (no precious or heavy metal being involved) and In2S3, as well as the photon-assisted electrochemical generation of O2 using an electrode containing In2S3 as light absorber and a Cu-based laccase enzyme (also with no heavy or precious metal) acting as catalyst to evolve O2 from water with good faradaic efficiency. Thus for the first time a visible light absorbing semiconductor plus enzyme combination is shown to photoevolve O2 from water. Since InsS3 hyperdoped with vanadium has shown ability to achieve the coupling of low energy photons to produce a higher electronic excitation (like in the Z-scheme of photosynthesis), this opens possibilities to generate solar fuels using the whole visible spectrum.

Session FH-2 - Understanding Fundaments of Photoinduced Processes and Charge Transport

FH-2:IL01 Atomic Level In situ Microscopy and Spectroscopy of Photocatalyst for Water Splitting

D. HAIBER, Q. LIU, T. BOLAND, **P. A. CROZIER**, Arizona State University, Tempe, AZ, USA

Photocatalytic generation of solar fuels such as hydrogen is a potential path for solar energy utilization. To improve performance of photocatalysts, many fundamental materials questions on the nature of the processes taking place must be addressed. An important step in developing an improved understanding on the functioning of inorganic photocatalysts is to determine structure-reactivity relations at the nanometer and atomic level. We have developed in situ electron microscopy approaches to investigate the behavior of photocatalytic materials under conditions related to water splitting. This approach allows us to apply photon, gas, and thermal stimuli to photocatalysts to identify the surface structural motifs and their evolutions under photochemical stimuli. For oxides like TiO2, the role of oxygen vacancy generation on the surface properties is described. On exposure to water and light (or the electron beam), surface hydroxylation is observed. Interfacial systems such as TiO2/CeO2 and functionalized polymeric systems such as C3N4 permit visible light absorption and may also be exploited in water splitting applications.

FH-2:IL02 Role of Radical Species and Interparticle Electron Transfer in Photocatalysis

D. BAHNEMANN, Institut fuer Technische Chemie, Gottfried Wilhelm Leibniz Universitaet Hannover, Hannover, Germany

Various free radical species have been suggested to be involved - often as key intermediates - in photocatalytic processes with oxygen centered radicals (ROS, i.e., Reactive Oxygen Species) such as the hydroxyl and the superoxide radical seemingly being the most important candidates. Direct detection of these very reactive radicals is usually very difficult, hence, mostly indirect evidence is presented by various authors to prove their formation in photocatalytic systems. The presentation will focus on time resolved kinetic studies as well as on spectroscopic investigations concerning these radical species. Photocatalytic systems are often formed from semiconductor nanoparticles and it has been shown that they are forming three-dimensional structures through self-assembly processes. Following the absorption of one photon by one of these nanoparticles within this network results in the formation of an exciton and subsequently an electron/hole pair. Both, the exciton but also the individual charge carriers are readily transported throughout this nano particulate network until they will finally encounter a particle were they can (and will!) interact with adsorbed donor or acceptor molecules resulting in the observed photocatalytic process. The antenna mechanism will be discussed.

FH-2:IL03 Enhancing Photoelectrochemical Water Splitting Performance using Hematite Anode through Doping and Morphology Control

XIN ZHAO, **ZHONG CHEN**, School of Materials Science and Engineering, Nanyang Technological University, Singapore

Photoelectrochemical (PEC) water splitting to generate hydrogen fuel is a promising route to solve energy and environmental issues by means of storing the intermittent and inexhaustible solar energy in the form of chemical bonds. Hematite (α-Fe2O3) is a promising anode material for PEC water splitting due to its excellent stability in the photocatalytic environment. However, the poor conductivity and short hole diffusion length have limited its energy conversion efficiency. Doping with a higher valence metal to the Fe site, and / or generating oxygen vacancies are able to improve the electron conductivity. In the meantime, creating nanorod structure could improve the transport of charge carriers by reducing the travel distance and in the same time increase the reaction sites. In this talk, we will present our latest understandings of the role of Ti-doping, oxygen vacancy, and a technique to maintain the nanorod morphology of Ti-doped hematite film through understanding the influence of Ti-precursor concentration on the morphology change. The photoelectrochemical performance of the Ti-doped nanorod hematite was optimized through analyzing the limiting factor of the performance. Our systematic investigation indicates that the electron transport is a limiting factor for the PEC performance of hematite. Maintaining the nanorod structure can be realized by replenishing the Ti precursor during the nanorod growth. Subsequent nitrogen treatment to generate oxygen vacancies has further increased the photocurrent of the nanorod structure.

FH-2:IL04 **Mechanistic Aspects of Photocatalytic CO2 Reduction**

M. DILLA, A. MATEBLOWSKI, S. RISTIG, Max-Planck-Institute for Chemical Energy Conversion, Muelheim/Ruhr, Germany; N. MOUSTAKAS, T. PEPPEL, **J. STRUNK**, Leibniz Institute for Catalysis (LIKAT), Rostock, Germany

In spite of roughly 40 years of research, no process has yet been developed that allows a photocatalytic recycling of CO2 (+H2O) to platform chemicals on an industrial scale. Knowledge of mechanistic aspects, and consideration of reaction engineering approaches, may allow a targeted optimization of the photocatalyst and the reaction conditions. This approach is exemplified for TiO2 as photocatalyst. In a high-purity batch reactor CH4 and CO are the main products of a reaction of CO2+H2O. CH4 formation can only occur after intermediates with a C-C bond have been formed. When the reaction is run in continuous flow, CH4 is the only detected product. Product formation is optimal at rather low CO2 concentration, and physisorbed H2O is sufficient to carry out the reaction. Product formation shows a square-root dependence on light intensity. The presence of O2 completely hinders CH4 formation. Due to a limited number of active sites or charge carriers, and the competing back reaction, TiO2 can thus never be an industrially viable option. Consequently, new material concepts and reaction conditions (e.g. CO2+H2) are studied to overcome the small product yields.

FH-2:IL05 **Recent Advances in the Search of Effective Materials for Photo-electrochemical Water Splitting**

J. AUGUSTYNSKI, Centre for New Technologies, University of Warsaw, Warsaw, Poland

Implementation of a semiconductor material in solar light-driven photo-electrochemical water splitting device requires combination of effective visible light absorption, suitable band energetics and long-term stability of the photo-material. In the case of semiconductors intended to operate as oxygen evolution photo-anodes, the actual choice is restricted to a few metal oxides that are both resistant against photo-corrosion in aqueous solutions and able to capture a significant portion of visible light. However, none of those photo-materials including tungsten trioxide (WO_3), bismuth vanadate ($BiVO_4$) or hematite ferric oxide (Fe_2O_3) have the positions of the conduction band edges more negative than the hydrogen evolution potential, a condition necessary to perform unassisted water splitting. For this reason, continuing efforts are devoted to minimize the bias voltage required to perform visible light-driven water splitting in a tandem device combining the photo-electrolyser with connected in series photovoltaic cell. These efforts include, in particular, modification of the semiconductor oxides by doping, development of new water oxidation electro-catalysts and incorporation into photo-anodes of plasmonic metal nanostructures to improve light capture and charge generation. Large recent improvements in the photo-electrochemical performance of one of the important photo-anode materials, WO_3, operating within blue-green part of the solar spectrum will be discussed.

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FH-2:L06 **Conduction Band Engineering in TiO2 and SnO2: Photocatalysis, Solar Fuel and Solar Cells**

L. KAVAN, J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic

The electronic band structure of TiO_2 or SnO_2 is of fundamental implication for applications in electrochemistry, photoelectrochemistry and photocatalysis. The position of conduction band (CB) edge controls the reductive photocatalytic reactions (e.g. hydrogen evolution from water or CO_2 reduction), potential of dye-sensitized solar cells and recombination blocking in perovskite solar cells. The electron collecting electrodes in perovskite solar cells with both planar and mesoscopic architectures, require the development of nanometer-thin blocking layers. They selectively transport electrons from the photabsorber to the back contact, and, at the same time, prevent recombination of these electrons with hole conductor. The low-temperature ALD-grown TiO_2 and SnO_2 layers are of particular interest for this application. Amorphous SnO_2 films are pinhole-free for thicknesses down to 2 nm. Their excellent blocking behavior allows photoelectrode design with even thinner electron selective layers; thus minimizing resistance losses. The compact nature and blocking function of thin SnO_2 films is not perturbed by annealing at 450 °C which is a significant benefit compared to TiO_2 and other amorphous ALD oxides. Amorphous and crystalline ALD SnO_2 films substantially differ in their flatband (and conduction band) positions.

FH-2:L07 **Electron Transfer and Energy Transfer in Heterogenous Photocatalysis**

F. PARRINO, L. PALMISANO, Dipartimento di Energia, Ingegneria dell'Informazione e Modelli Matematici (DEIM), Università degli Studi di Palermo, Palermo, Italy

When an electronically excited species A* interacts with a species B in its ground state, both an energy transfer and an electron transfer may occur due to an initial orbital overlap or to dipole-dipole interactions. These fundamental reactions are closely related both conceptually and mechanistically. However, despite the qualitative similarities at the initial stage of interaction, the two processes become quantitatively different along with the reaction coordinate, and different factors may address the occurrence of one or the other of them. Nevertheless, distinguishing between energy and electron transfer is often a hard task in heterogeneous photocatalytic complex reactions. In fact, the two mechanisms can afford the same products, and consecutive reactions or adsorptive phenomena makes it difficult to differentiate them.

Heterogeneous photocatalysis is generally considered based on electron transfer reactions. However, rare examples such as singlet oxygen generation or some isomerization reactions are reported in literature to be energy transfer induced processes. This work will report some of these cases, and in particular will focus on the importance of the energy transfer mechanism in photocatalysis.

FH-2:IL08 **Studying Mobile Charge-Carriers in Photocatalytic Particles by Time Resolved Microwave Conductivity: Recent Developments**

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The knowledge of the relation existing between charge-carrier lifetimes and material structural parameters can help to understand the mechanisms leading to the photoactivity. To follow the charge-carrier dynamics in semi-conductors, the variation of the conductivity after illumination must be determined. Time Resolved Microwave Conductivity (TRMC) is a contactless method, based on the measurement of the microwave power reflected by a sample induced by laser pulsed illumination. The signal obtained by this technique allows to follow directly, on the nanosecond time scale, the decay of the number of electrons and holes after a laser pulse by recombination or trapping of the charge-carriers. TRMC has been used to analyse the influence of TiO2 morphology and texture on charge-carrier lifetimes. The effect of nanostructured mono and bimetallic deposits on commercial TiO2 has also been studied. The influence of various parameters on TRMC signal has been followed. The maximum signal value as function of the excitation energy shows different behaviours under visible or UV irradiation. P25 dye sensitization with pigments is evidence by a very strong TRMC signal under visible light. The signal obtained on P25 under different atmospheres evidences a strong influence of O2 on the decay.

FH-2:L09 **Probing Local Atomic Structural Variations in Bulk and on Surfaces of TiO2 Anatase Nanoparticles**

QIANLANG LIU, T. BOLAND, P.A. CROZIER, Arizona State University, Tempe, AZ, USA

TiO2 in the anatase form is a widely studied photoactive material, which has shown interesting photocatalytic behaviors for water splitting. The surface and bulk structures of a photocatalyst are crucial to the reactivity, especially when defects such as oxygen vacancies are present, as they influence charge transfer and recombination. In this work, aberration-corrected transmission electron microscopy (TEM) is used in the so-called negative Cs imaging condition (NCSI) to observe the atomic structures of anatase nanoparticles, in vacuum and exposed to near-reaction conditions. In this NCSI mode, both Ti and O atomic columns can be imaged, and local lattice distortions as well as oxygen column intensity variations have been observed. In order to better understand these structural motifs, molecular dynamics simulations have been employed. Vacancies are introduced into the bulk as well as on the surface and the system is allowed to relax. Local atomic disorder is tracked around the defect sites. The resulting structures are then simulated and compared with experimental images to determine the relationship between vacancies and local lattice distortions.

FH-2:L10 **Aloof-beam EELS as a Non-destructive, Surface-sensitive Probe for Photocatalyst Nanostructures**

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Transmission electron microscopy and related techniques are important tools for characterizing water splitting photocatalysts at the nano- or atomic-level. Monochromated electron energy-loss spectroscopy (EELS) now enables optical, electronic and vibrational properties to be characterized at the nanoscale, by detecting subtle features in the vibrational and bandgap regions of the spectrum. Due to the long-range nature of the incident electron's electric field, low-energy excitations can still be accessed with the beam outside the specimen. Moreover, in this "aloof beam" configuration, surface interactions are enhanced while high-energy ionizations pathways are suppressed offering a surface-sensitive, non-destructive characterization tool for nanostructured materials. Here, we develop an aloof beam EELS technique to probe bandgap states on oxide nanoparticles’ surfaces when exposed to water. Excitation of resonance cavity modes is observed when applying this technique on oxide particles such as TiO2. In graphitic carbon nitrides, amine content is believed to regulate charge transfer by stabilizing a disordered, defective in-plane structure. Using aloof-beam EELS, we show that amine and cyanide defects vary throughout the structure.

FH-2:IL11 **Photocarrier Transport and Transfer in Emerging Transition Metal Oxide Photoelectrodes**

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Thin film transition metal oxide semiconductors are actively investigated as efficient, durable, and scalable photoelectrodes for direct conversion of solar energy to chemical fuel. However, efficiencies of these systems typically fall far short of the thermodynamic limits. Here, we investigate the function and limitations of an emerging class of semiconductor photoanode, copper vanadate (CVO), different phases of which were recently identified to be photoelectrochemically active and to have bandgaps of 1.8–2.0 eV. As a starting point, we use X-ray and optical spectroscopies to provide a comprehensive portrait of electronic structure. Building on these results, we identify specific loss mechanisms in the bulk and at interfaces by quantifying the spatial charge collection efficiency, which provides a depth profile of function within the material. By quantifying loss mechanisms associated with recombination, background doping, and surface Fermi level pinning as a function of composition, we shed light on the roles played by different constituent elements on energy conversion and identify specific strategies for improving performance of emerging transition metal oxide photoelectrodes.

FH-2:L12 **A Comparative Study on Defect-rich and Defect-free O-incorporated 1T-MoS2 Nanosheets for Visible-light Photocatalytic H2 Evolution**

XIA TAO, XIAOHONG ZHANG, NAN LI, JIAOJIAO WU, State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, China

Structure and phase engineering in low-cost and earth-abundant MoS2 materials has been widely explored in catalytic domains, yet a comparative study of defects capable of significant affecting the photocatalytic H2 evolution reaction (HER) in the MoS2-based catalytic system is rather limited. We herein report two kinds of hydrothermal-synthesized MoS2 nanosheets i.e. defect-rich and defect-free O-incorporated 1T-MoS2 nanosheets (denoted as DRM and DFM), in which the incorporation of O and the formation of the 1T phase in DRM and DFM are introduced to improve the intrinsic activity and conductivity of MoS2. The as-prepared DRM and DFM as cocatalysts then were integrated with CdS nanorods to form two photocatalytic heterostructures i.e. DRM-C and DFM-C through simple ultrasonic and agitation treatments. A carefully comparative study on DRM and DFM demonstrates that the DRM cocatalyst exhibits the more abundant defects in the basal plane and edges, and thus leading to the higher density of active sites beneficial to the photocatalytic HER. Besides, the favorable band position of DRM relative to DFM could contributes to the injection of the photo-excited electrons from CdS into the CB of DRM. As a result, the optimized 20 wt% DRM-C exhibits an extraordinary visible-light (λ > 420 nm) photocatalytic H2 production rate of 132.4 mmol h-1 g-1, obviously higher than that of 20 wt% DFM-C (102.1 mmol h-1 g-1). Interestingly, such an impressive activity of 20 wt% DRM-C is demonstrated to be superior to that of pure CdS (20 mmol h-1 g-1) and conventional Pt/CdS (89 mmol h-1 g-1). To the best of our knowledge, this DRM-C photocatalyst shows the advanced visible-light-driven HER performance among reported MoS2/CdS composites.

Session FH-3 - Design Approaches for Advanced Applications

FH-3:IL01 **Design Rules for Photoactive Materials for Photo Electrochemical Solar Energy Conversion**

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For an effective conversion of solar energy to a chemical fuel a number of elementary processes as well as their coupling to each other must be optimized without severe losses in the number and the chemical potential of the originally generated electron-hole pairs. Light absorption coupled to efficient charge carrier generation and separation may be realized by thin film semiconductor devices - preferentially using buried tandem or multijunction solar cells in a photoelectrochemical arrangment - which may provide broad band quantum efficiencies close to 1. Alternatively, Janus type photocatalysts may be chosen which favour vectorial electron-hole pair transport into opposite directions. Subsequently, H2 and O2 from H2O must be formed by electron and hole transfer reactions with minimized loss of chemical potential. This will only be possible if the involved charge transfer steps are coupled to selective multi electron transfer catalysts without loss in the chemical potential of the minority carriers and their photocurrent. Technologically feasible solutions seem to be possible for water splitting and H2-generation, as we will show with a number of investigations performed recently combining electrochemical investigations with surface science studies.

FH-3:IL02 **Strategies for Stable Water Splitting via Protected Photoelectrodes**

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Hydrogen is the simplest solar fuel to produce and we shall give a short overview of the strategies for various tandem devices. The large band gap semiconductor needs to be in front, but apart from that we can chose to have either the anode in front or back using either acid or alkaline conditions. Since most relevant semiconductors are very prone to corrosion the advantage of using buried junctions and using protection layers offering shall be discussed. In particular we shall show how doped TiO2 is a very generic protection layer for both the anode and the cathode. Next, we shall discuss the availability of various catalysts for being coupled to these protections layers and how their stability and amount needed may be evaluated. Examples of half-cell reaction using protection layers for both cathode and anode will be discussed though some of recent examples both under both alkaline and acidic conditions. Notably NiOx promoted by iron is a material that is transparent, providing protection, and is a good catalyst for O2 evolution. Finally we shall also discuss the possibility of making high energy density fuels by hydrogenation of CO2 instead of hydrogen evolution. We shall give a brief status of what limits our current catalysts today and discuss the way forward.

FH-3:IL03 **Transient Phenomena in Photocatalysis, as Studied by Ultrafast FTIR Measurements**

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Developing of new, highly efficient, photocatalytic materials depends to large extent on better understanding of the physical and chemical phenomena occurring right after photon absorption. Over the years two major techniques have been utilized, using pulsed lasers beams for excitation: time Resolved Microwave Conductivity (TRMC) and UV-Vis absorption and fluorescence spectroscopy. Here we present a third method for studying the excitation of photoactive and, in particular, photocatalytic materials. The method is based on measuring time resolved changes (5 nanoseconds in resolution) in the IR spectra photocatalytic materials following excitation by a pulsed 355 nm laser beam. In the presentation, the fundamental pros and cons of the method will be described. Results for several photocatalysts (g-C3N4, BiVO4, ZnS, BiOCl) will be presented, revealing spectral transient changes that are sensitive to the phase of the photocatalyst and to its preparation procedure. Results will be compared with theory and will be correlated with photocatalytic measurements and with measurements made by other techniques.

FH-3:L04 **New Strategy for Micro-plastic Degradation: Green Photocatalysis Using a Protein-based Porous N-TiO2 Semiconductor**

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Plastics are extensively applied in a wide gamma of applications. Until 2015, approximately 6300 Mt of plastic waste had been generated. Unfortunately, most of this waste (79%) goes to landfills or the environment, leading to plastic introduction into continental and seawater in form of microplastics. These can be consumed by marine organisms across the trophic levels and act as a medium to concentrate and transfer persistent, bio-accumulative, and toxic substances. Then, they cause toxic effects in both the organisms that consume them and at higher trophic levels. Furthermore, plastics can cause cancer and neurological affections in humans. Here, for the first time, photocatalysis was used for the degradation of polyethylene microplastics. A N-TiO2 derived from Cristaria plicata proteins was used and proteins acted as N source and pore-forming agent. Results suggest that porous N-TiO2 promotes degradation of microplastics in terms of wt. loss and FTIR bands reduction. Furthermore, solid photocatalysis (microplastic/N-TiO2 composites) is more effective than the aqueous process (dispersed microplastics in contact with a N-TiO2 film) due to the effective exploitation of the surface area of the photocatalyst by increasing the contact between the pollutants and N-TiO2.

FH-3:L05 **Optical Emission from Catalytic Combustion of MeOH/air on Yb2O3 Supported Metal Catalysts**

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The catalytically induced luminescence, also known as cataluminescence, is a new and possibly efficient way to transform fuels to electricity via efficient light generation and its conversion by photovoltaics. Our approach to demonstrate this phenomenon is the catalytic combustion of methanol over metal catalysts supported on oxides. As a valuable oxide support with the right luminescent properties, we chose Yb2O3, which has strong selective emission from Yb f-electrons around 1000nm. The support was doped with metallic nanoparticles such as copper, palladium, and ruthenium. All studied catalytic systems showed a high conversion yield of CH3OH oxidation to CO2 and H2O. Differences in the catalytic activities of the different metals are the onset temperatures for significant conversion. Copper is active at elevated temperatures only above roughly 350°C. In parallel to the catalytic conversion, the optical emission was measured which was also similar in all studied systems at elevated temperatures. The results obtained from these measurements showed that combustion takes place on the metallic nanoparticle without direct energy transfer to the support (Yb2O3) resulting in a low efficiency of light emission above 1000nm required for electricity production by Si-photovoltaic cells.

FH-3:IL06 **Modelling of Solar Water Splitting Devices**

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Modelling can efficiently and actively support the choice of the most interesting conceptual design pathways, material choices, and operating approaches to PEC devices. Here, I will discuss modeling of two different approaches to cheap solar hydrogen production: i) relying on the utilization of concentrated irradiation and smart thermal management, and ii) relying on the use of semiconductor particle-based photoelectrodes (PEs) fabricated by scalable dipping procedures. Modeling for concentrated PEC (CPEC) devices requires the incorporation and solution of the energy conservation equation. We have developed a corresponding 2D model of CPEC which I will review and use to guide the design of CPEC and to predict simple controlling strategies to CPEC that can mediate disturbances to the system (e.g. component degradation and irradiation variations). Modeling of complicated particle-based PEs, on the other hand, requires full 3D multi-scale device models accounting for the morphological details of the nano-scale. I will show how we utilized nano-tomography to obtain the exact nano-scale morphology and how this morphology is incorporated into direct pore-level modeling to predict inhomogeneity in the variable fields and corresponding underutilization of parts of the PE.

FH-3:IL07 **Coupling Peroxidase Enzymes with Photocatalytic Hydrogen Peroxide Production**

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Inspired by the natural photosynthesis pathway photobiocatalysis combines two powerful catalytic tools which harmonize together since both operate under mild conditions. The consolidation of their advantages can lead to highly sustainable chemical processes. The use of enzymes offers highly selective and efficient reactions. However, industrial utilization is often limited by their requirement of expensive cofactors. Photocatalysis offers the possibility for (re-)generation of cofactors without creating any wasteful byproducts and by using light as the only energy source. Peroxidases have the advantage that their cofactor, H2O2, is economically priced and can be easily synthesized. The challenge for utilization of peroxidases is their poor stability against H2O2. This problem can be overcome by employing in-situ generation techniques that guarantee a constant but low concentration. The production of H2O2 by heterogeneous photocatalysts such as titanium dioxide directly from oxygen and water under illumination with UVA-light is well known. The concentration achieved is characterized by a relatively low steady-state concentration. The proposed photobiocatalytic system enables a homogeneous supply of hydrogen peroxide and avoidance of detrimental concentration peaks.