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## Symposium I New Concepts and Advances in Photocatalytic Materials for Energy and Environmental Applications

### ABSTRACTS

#### Session I-1 - Design Elements and Advanced Concepts for Photo-functional Materials

##### I-1:IL01 Nanostructured Materials for Photocatalytic Energy Conversion Applications

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The main challenge in the field photocatalytic fuels production consists in the electronic structure engineering of photocatalytic materials able to harvest solar radiation producing electron-hole couples and ensure efficient charge separation for solar energy driven thermodynamically up-hill processes. In recent years we focused on the development of innovative photocatalytic materials, based on the engineering of their electronic structure, on solid solutions and heterojunctions produced by different techniques, on the modification of the surface properties by noble metals or co-catalysts to achieve increased charge separation. Innovative technologies, including RF magnetron sputtering and flame spray pyrolysis, together with electrochemical growth of nanotube (NT) arrays to obtain photoactive electrodes, have been explored with the final aim of producing photocatalytic systems in integrated form to be employed within devices for pure hydrogen production. In particular, recent results showed that the ordered 2D structure of the NT array confers them the photonic crystal properties with the formation of a photonic bandgap, the shift of which leads to a red shift of the activity threshold that allows harvesting and converting a larger portion of the solar spectrum.

##### I-1:IL04 Z-scheme over all Water Splitting on Rh/K4Nb6O17 Nanosheet Photocatalyst

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Developing a photocatalysis system to generate hydrogen from water is a topic of great interest for fundamental and practical importance. In this study, hydrogen production by a new Z-scheme photocatalysis water splitting system was examined over Rh modified K4Nb6O17 nanosheet and Pt/WO3 photocatalysts for H<sub>2</sub> evolution and O<sub>2</sub> evolution with I-/IO<sub>3</sub>- electron mediator under UV light irradiation. The H<sub>2</sub> evolution photocatalyst, Rh/K4Nb6O17 nanosheet with a slit like framework, was prepared by exfoliation of and proton exchange reaction. Pt/WO3 prepared by incipient-wetness impregnation method was used as O<sub>2</sub> evolution photocatalyst. The catalysts were characterized by powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy analysis (XPS), and ultraviolet-visible spectroscopy (UV-vis). These catalysts characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and ultraviolet-visible spectroscopy (UV-Vis). In this study, we developed a facile method of preparing K4Nb6O17 nanosheet containing Rh nanoparticles. Our results show that I- concentration and pH of reaction solution significantly influenced the photocatalytic activity. The combination of Rh modified K4Nb6O17 nanosheet with Pt/WO3 achieves a very high photoactivity (H<sub>2</sub>: 4240 μmol g<sup>-1</sup> h<sup>-1</sup> and O<sub>2</sub>: 1622 μmol g<sup>-1</sup> h<sup>-1</sup>).

##### I-1:L05 Iron Oxide-based Electrocatalysts for Water Oxidation at Neutral pH

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Various photocatalytic materials aiming at water splitting have been reported because produced hydrogen (H<sub>2</sub>) is attractive as a clean and renewable fuel. As for the water-splitting reaction, oxygen (O<sub>2</sub>) evolution reaction (OER) usually requires a large overpotential because it is intrinsically difficult to control the multielectron transfer process. Then the decreasing in the overpotential has been regarded as the critical issue and thus the development of an active and effective OER catalyst is required to enhance the water-splitting reaction. So far, iridium- or ruthenium-based catalysts have been enthusiastically investigated as OER catalysts. In place of them, we have tried to find the OER catalysts among earth-abundant metal oxides, such as iron oxides. We have found that the stabilization of Fe<sup>4+</sup> was responsible for the enhancement of OER activity. Base on the finding, we have investigated the OER activity of strontium ferrite (Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub>) and lanthanum-substituted Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub> (Sr<sub>2.6</sub>La<sub>0.4</sub>Fe<sub>2</sub>O<sub>7</sub>) to confirm the important role of Fe<sup>4+</sup> stability in the OER activity.

##### I-1:L07 Bismuth Vanadate-based Heterojunction Photoelectrodes for Photoelectrochemical Water Splitting: Synthesis and Characterisation

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The main aim of this study was to electrochemically synthesize and characterise bismuth vanadate (BiVO<sub>4</sub>) photoelectrodes for water splitting. The influence of electrodeposition duration and annealing temperature on the BiVO<sub>4</sub> nanocrystals structure were systematically studied. These were followed by advanced characterisation of the BiVO<sub>4</sub> photoelectrodes by using FE-SEM, EDX, XRD, UV-visible spectroscopy, PEC measurements and EIS analysis. Through this study, it was found that the electrodeposition duration of 4500s under air condition and heat treatment at 400°C were able to yield the highest photocurrent density of 1.02 mA/cm<sup>2</sup>. When the electrodeposited BiVO<sub>4</sub> thin films were subjected to different annealing temperatures, phase transitions will occur for tetragonal (528 K) and monoclinic (670 K). Through this study, it was found that the electrodeposition duration of 4500 s under air condition and annealing treatment at 400 °C were able to yield the highest photocurrent density of 1.02 mA/cm<sup>2</sup>. Finally, other BiVO<sub>4</sub>-based heterojunction photoelectrodes with various n-type semiconductors were coupled and formed in order to reduce the rapid recombination rate of electron-hole pairs.

##### I-1:IL08 Reflections on Rust: Iron Oxide Photoelectrodes for Solar Energy Conversion and Storage

**A. ROTHSCILD**, Department of Materials Science and Engineering, Technion – Israel Institute of Technology, Haifa, Israel

Large scale utilization of solar power requires affordable energy storage technology. Likewise, there is a need for renewable fuels to replace fossil fuels. These challenges can be achieved by splitting water into hydrogen and oxygen using solar power. The first and foremost challenge toward this goal is the development of stable, efficient and affordable photoelectrodes. Photoelectrodes for solar water splitting must employ a semiconductor material with exceptional stability against corrosion and visible-light absorption. On top of that, it should also be abundant, inexpensive and non-toxic. Iron oxide (hematite) is one of few materials meeting these criteria, but its poor transport properties and ultrafast charge carrier recombination present a challenge for efficient charge carrier generation, separation and collection. We explore an innovative solution to this challenge using ultrathin (20-30 nm) films on specular back reflector substrates. This simple design traps the light in otherwise nearly translucent ultrathin films, amplifying the intensity close to the surface wherein photogenerated charge carriers can reach the surface and split water before recombination takes place. This is the enabling key towards the development of high efficiency photoelectrodes.

**I-1:IL09 Hybrid Organic/Inorganic Assemblies with Tailored Photoelectro-chemical Activity: from Synthetic Aspects to Energy Applications**

**C. JANAKY**, A. VARGA, A. KORMANYOS, G. SAMU, University of Szeged, Hungary, K. RAJESHWAR, The University of Texas at Arlington, TX, USA

To efficiently harness the possible synergies, stemming from the combination of organic conducting polymers and inorganic semiconductors, sophisticated assembling methods are required to control the composition and morphology at the nanoscale. This talk focuses on how to use light-assisted methods in the synthesis of such hybrid materials. First, I will show examples on the photoelectrochemical deposition of conducting polymers (e.g., polypyrrole, polyaniline, PEDOT) on nanostructured inorganic semiconductor matrices, such as TiO<sub>2</sub> nanotube arrays and nanoporous WO<sub>3</sub>. In the second part of my talk, I will present our proof-of-concept study, demonstrating the in situ photocatalytic deposition of CdS nanoparticles on poly(3-hexylthiophene) (P3HT) nanofibers, exploiting the semiconducting nature of this polymer. We confirmed that both the particle size and the loading can be tuned by the deposition time. Photoelectrochemical studies revealed the facile transfer of photogenerated electrons from P3HT to CdS, as well as that of the holes from CdS to P3HT. It is believed that ensuring intimate contact between the components in these nanohybrids will open new avenues in various application schemes, e.g., solar energy conversion.

**I-1:IL10 Flexible Transparent Conductive Electrodes and Photocatalytic Conversion of CO<sub>2</sub> to CO Gas Sensor using Single Crystal Cu Thin Film**

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(Cu) thin films have been widely used as electrodes and interconnection wires in integrated electronic circuits, and more recently as substrates for the synthesis of graphene. However, the ultra-high vacuum processes required for high-quality Cu film fabrication, such as molecular beam epitaxy (MBE), restricts mass production with low cost. In this work, we demonstrated high-quality Cu thin films using a single-crystal Cu target and sputtering technique; the resulting film quality was comparable to that produced using MBE, even under unfavorable conditions for pure Cu film growth. The Cu thin film was epitaxially grown on an Al<sub>2</sub>O<sub>3</sub> (0001) substrate, and had high crystalline orientation along the (111) direction. Despite the 10<sup>-3</sup> Pa vacuum conditions, the resulting thin film was oxygen free due to the high chemical stability of the sputtered specimen from a single-crystal target; moreover, the deposited film had > 5 X higher adhesion force than that produced using a polycrystalline target. We applied the technique fabricating the single crystal thin film to the flexible transparent conducting electrodes, where a micromesh/nanomesh structure was fabricated on a polyimide substrate using UV lithography and wet etching. Hybrid Cu mesh electrodes were fabricated by adding a capping layer of either ZnO or Al-doped ZnO. The sheet resistance and the transmittance of the electrode with an Al-doped ZnO capping layer were 6.197 ohm/sq and 90.657 %, respectively, and the figure of merit was 60.502 × 10<sup>-3</sup> /ohm, which remained relatively unchanged after thermal annealing at 200 °C and 1,000 cycles of bending. We succeeded to fabricate Cu single crystal nanowire by the patterning of the single crystal Cu thin film grown on sapphire substrate, which shows less resistivity than bulk Cu even in nano scale and can be located where we want. We also applied Cu single crystal film to photo-catalytic conversion of CO<sub>2</sub> to CO by making homogeneous CuO film by oxidation.

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**I-1:IL12 Electron Trapping in Semiconductor Photocatalysis**

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A hypothesis proposed is that electron traps (ETs) in photocatalyst particles govern electron transfer and electron-hole recombination, i.e., photocatalytic activity: the higher the density of shallow ETs and the lower the density of deep ETs are, the higher the photocatalytic activity is. Although their structure is not clear, it is sure that appreciable ETs are there in metal oxides. It has been well known that metal oxides turn gray when reduced. Here, newly developed reversed double-beam photoacoustic spectroscopy (RDB-PAS) is reported as a powerful tool for ERDT (energy-resolved density of ETs) measurement. A brief explanation of the principle of RDB-PAS is (i) photoacoustic detection, using modulated LED light (first beam), of accumulation of electrons, i.e., ETs filling, from deeper to shallower level, using scanning continuous monochromatic light (second beam) to excite valence-band electrons directly to ETs, (ii) differentiating the resultant spectra from the longer wavelength side and conversion to absolute density of ETs with reference to results of the photochemical methods and (iii) plotting ERDT as a function of energy difference from the bottom of CB which is determined by ordinary PAS measurement of anatase titania samples.

**I-1:IL13 Doped Lanthanum Ferrite Perovskites: Promising Materials for Photocatalytic Applications**

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Perovskite-type transition metal oxides (TMOs) are semiconductors with a band gap narrow enough for efficient absorption of visible light. Therefore, they offer the possibility of using solar radiation or visible-light lamps for their activation, thus allowing the development of low cost photocatalytic applications. This is a strong advantage over the most used photocatalyst for environmental remediation, i.e. titanium dioxide, which instead absorbs UV light. One of the most used TMOs is lanthanum ferrite (LaFeO<sub>3</sub>). Generally, the functional properties of LaFeO<sub>3</sub> can be controlled either

by modulating structure and defectivity or by substitution of the metals into the crystal structure. Although modification is a quite simple task due to the versatility of this material, understanding the consequences of doping on the physico-chemical properties and on the photocatalytic activity still remains a challenging issue. In this work the effects of Sr and Cu doping on the physico-chemical and photoelectrochemical properties of LaFeO<sub>3</sub> are presented along with their influence on the photocatalytic activity in gas and liquid phases. In particular, the photocatalytic oxidation of 2-propanol and of 4-nitrophenol were investigated as model reactions in gas and liquid phases, respectively.

**I-1:L14 Enhancing Photocatalytic Activity of TiO<sub>2</sub> by a Synergistic Effect between Plasmon Resonance in Ag Nanoparticles and Optical Interference**

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Development of plasmo-electronic-based nanostructures, such as photocatalysis, strongly depends on the understanding of carrier generation enhancement in an active semiconductor layer. We present original results obtained from assemblies of silver nanoparticles (Ag NPs) buried at few nm deep underneath the free surface of a thin titania (TiO<sub>2</sub>) layer. By using a properly sample architecture, we have taken simultaneous benefit of spectrally and spatially localized surface plasmon resonance, and optical amplification in order to enhance photon capture in the visible range. TEM and optical reflectance are used control the optical design. Plasmon-resonant Raman spectroscopy is originally used to analyze confinement of vibrations and electronic excitations in Ag NPs, the latter through the so-called "background" in SERS that gives here the signature of confined electron-hole excitations in the NPs. Moreover, the observation of mixed LO-plasmon modes in TiO<sub>2</sub> gives proof of coupling between injected carriers in the active semiconductor layer and its polar phonons. These substrates optimized so as to maximize the electromagnetic energy harvesting and carriers generation, show a high increase of the photocatalyst activity, but also appear promising for other plasmo-electronics based devices.

**I-1:L15 Ternary TiO<sub>2</sub>-Cu<sub>x</sub>S-Fly Ash System: Synthesis, Characterisation and Application in Adsorption and Photocatalysis**

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The wastewater from industrial processes has a multi-pollutants composition, thus their treatment (e.g. for re-use) often requires simultaneous/combined advanced processes as adsorption and photocatalysis. Therefore, the paper proposes a new approach based on the simultaneous photocatalysis and adsorption to remove a wide range of pollutants. This study aimed at developing an adsorption-photocatalysis system to treat industrial wastewater; additionally, as this industrial process is acceptable, photocatalysis exceeds the technical and economic main barrier: the use of UV radiation as activating agent and replace it with the VIS radiation or sunlight. A range of visible active composite photocatalyst based on the tandem TiO<sub>2</sub>-Cu<sub>x</sub>S-Fly ash composites were prepared by hydrothermal synthesis and photochemical precipitation. SEM, AFM, XRD, FT-IR, and UV-vis diffuse reflectance spectroscopy were used to characterise materials. Methylene blue, SDBS and Cd<sup>2+</sup> were selected as pollutants to evaluate the photocatalytic and adsorption ability of the composites. The pollutants degradation and adsorption mechanisms on the ternary composites were discussed based on experimental results.

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**I-1:IL16 Novel Functional Materials Applied to Photocatalysis**

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We would like to report the efficient study of Y<sub>2</sub>O<sub>3</sub> enhanced photocatalysis using novel Y<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> nanorod composite composition spreads. The highlights of this research are 1) successful fabrication of the sample using a combinatorial sputtering system without involving any special treatments, 2) systematic investigation of the coupling effect between Y<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> to achieve synergistic photocatalysis, and 3) opening an alternative novel application in photocatalysis for high-k materials. The composition variation and phase evolution across the sample were achieved through the well-controlled shutter moving strategy, which were verified using electron probe energy dispersive spectroscopy (XPS) and x-ray diffraction, respectively. XPS and UV-vis spectrometry measurements also complemented the composition variation results. The sample #6 (4 at% Y<sub>2</sub>O<sub>3</sub>-96 at% TiO<sub>2</sub>) was observed to exhibit the best photocatalytic efficiencies among all the samples under study, approximately 3.4 and 1.4 times higher than that of P25 and pure TiO<sub>2</sub> nanorods, respectively, suggesting the effectiveness of Y<sub>2</sub>O<sub>3</sub> incorporation. With the aid of PL analyses and the simple Y<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> energy band diagram, the charge carrier transport in the system was elucidated. The predominant factor to achieve synergistic photocatalysis for the sample #6 was justified to be electron migration along defective Y<sub>2</sub>O<sub>3</sub> nanorods to the sample surface. In addition, the photoelectrochemical stability and reusability of the sample #6 was also demonstrated. All the features suggested the sample #6 promising for the photocatalytic applications.

**I-1:L17 Micro-TiO<sub>2</sub> as Photocatalyst for New Ceramic Surfaces Activated via Digital Printing**

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Nowadays pollution is one of the biggest concerns of both the public and different governments because it is risky for the safety of the every habitat. Among the AOPs, photocatalysis is one of the most promising and TiO<sub>2</sub> is the best semiconductor able to oxidize pollutants; especially, it can be applied on materials: TiO<sub>2</sub>-photocatalytic surfaces might play a major role in cleaning environments. Industrial photocatalytic tiles are commercially available but the classical preparation consists in the deposition of TiO<sub>2</sub> by airless spray, sometimes without a good powder's distribution. The digital printing was exploited as a new tool to manufacture photocatalytic tiles even of very large size, in order to solve this issue. Crucial is the use of micro-TiO<sub>2</sub> instead of nano: some tests on the animals have reported that NPs are dangerous and the high difficulty of handling is not convenient in industrial uses. The surface of the photoactive slabs was analyzed by HR-SEM showing an excellent uniformity. Photocatalytic degradation tests performed in air using both NO<sub>x</sub> and VOCs molecules confirm the good performances of the tiles to tackle the environment pollution.

**I-1:L18 Designing Bimetallic Reduction Co-catalysts – Correlating Atomic Structure with Properties**

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Correlating structure and function is fundamental for the design of functional materials. Specifically, the atomic rearrangement within a nanoparticle has a direct effect on its properties and overall performance as a building block. While synthetic efforts have succeeded in producing diverse complex materials, the rational design of new materials is still a challenge. Our approach is using atomic resolution transmission electron microscopy to unravel the atomic structure of the particle, therefore allowing the understanding of the growth process and the origin of the functionality of the structures. We believe that by doing so, design rules can be offered to optimize the available nanoparticles for their

designated role as functional units. The above-mentioned rationale was used for understanding the enhanced activity of Au-Pd metal tips on seeded rods of CdSe@CdS, by studying the effects of structure both on efficiency and stability. I will show that a structure of Au@alloy is the most efficient photocatalyst and also more stable in longer illumination times (50 hours). The degradation mechanisms will be unraveled and potential strategies to prevent them will be suggested. In addition, I will present the evolution of the structures through the synthesis stages, showing how that atomic re-construction of the particles during the initial synthesis of the structures might have detrimental consequence on their stability.

#### I-1:L19 Nanoplasmonics-assisted Degradation of Pollutants and Oxidation of Glycerol under Visible Light

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Many approaches were used for new solar energy harvesting. An especially attractive approach is based on the use of sunlight to drive chemical reaction (1). In this context Plasmonic nanostructures of noble metals have been attracting significant attention due to their ability to interact with light from visible to near IR range through the creation of resonant surface plasmon (2). Recent studies have shown that plasmonic nanostructures can be used to drive chemical model reaction with visible light where nanoparticles (NPs) act as the light absorber and the catalytic active site (3). This behavior is attributed to the plasmonic effect of gold nanoparticles (GNPs) which can concentrate the energy of visible light and convert it into heat (5). Consequently, photoexcited GNPs can act as efficient nanosources of light, heat and energetic electrons (4). The recent advances in the comprehension of local properties of GNPs have led to development of the plasmonic assisted catalysis approach which has been applied to a large variety of reactions (4, 6). Here we report the feasibility of this "nanoplasmonic" catalysis on an industrial and environmental application reaction. First, we studied the photocatalytic degradation of Bisphenol A (BPA) under visible irradiation (laser source and LED). We investigate the coupling between Plasmonic GNPs and catalyst supports such as TiO<sub>2</sub>, ZnO and Al<sub>2</sub>O<sub>3</sub> on the photodegradation reaction of BPA. The experimental investigations have shown extremely fast and complete photodegradation of organic pollutants in water (7). Secondly, the oxidation of glycerol (co-product of biodiesel production) in the presence of supported GNPs under visible irradiation and atmospheric pressure at room temperature was demonstrated. The conversion of glycerol was 89% after 2 h of reaction at ambient temperature. Experimental results indicate that oxidation was induced by excited gold nanoparticles and that organic acids such as glyceric acid and tartaric acid are appropriate as essential products in the oxidation reaction. The reaction does not occur in the absence of laser irradiation. In comparison to previous experiments our approach is characterized by many aspects: (a) Coupling nanothermal effect and catalytic effect of nanoparticles offers the potential of studying the oxidation of glycerol under sunlight (b) Coupling hot electrons effect of MNPs and catalyst support offers the potential of studying the degradation of BPA under sunlight (c) The oxidation of glycerol was carried out in the absence of macroscopic heating and atmospheric pressure (d) The photodegradation of BPA is complete after 12 min using visible source of light.

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### Session I-2 - Understanding Fundamentals of Photoinduced Processes and Charge Transport

#### I-2:IL01 Understanding Charge Transfer Processes on Metal Oxide Surfaces through Laser Flash Photolysis Analysis

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During the last decade great attention has been paid to the synthesis of different semiconductors possessing high photocatalytic activities, whereas fundamental studies concerning the underlying photocatalytic processes have rarely been executed. The knowledge of these processes is, however, of utmost importance for the understanding of the photocatalytic reaction mechanism and thus for a better design of photocatalytic systems. In the present study, the dynamics of charge carriers photogenerated in TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, NaTaO<sub>3</sub>, and in Ba<sub>5</sub>Ta<sub>4</sub>O<sub>15</sub> nanoparticles have been investigated using diffuse reflectance laser flash photolysis. Upon laser excitation of TiO<sub>2</sub> nanoparticles (anatase, rutile, brookite) at 351 nm in air the transient absorption of the trapped holes was observed, while the trapped electrons could only be detected in the presence of electron donors indicating that holes are trapped faster than electrons. Due to the higher driving force the conduction band electrons subsequently rather undergo recombinations with these trapped holes instead of forming less stable Ti<sup>3+</sup> centers. Following laser excitation of hematite trapped holes and trapped electrons could be observed simultaneously with the former exhibiting shorter lifetimes due to bimolecular disproportionation processes.

#### I-2:IL02 Charge-carrier Dynamics in Photocatalytic Processes

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The photocatalytic activity of TiO<sub>2</sub> compounds is related to the creation and the evolution of charge-carriers in the photocatalyst. Thus, 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 TiO<sub>2</sub>, Time Resolved Microwave Conductivity (TRMC) may be used. It is a contactless method, based on the measurement of the change of the microwave power reflected by a sample induced by laser pulsed illumination. In this work, monophasic and biphasic TiO<sub>2</sub> powders (anatase, rutile and brookite) with numerous morphologies have been synthesized using various methods (hydrolysis, thermohydrolysis, hydrothermal, microwave), with different precursors and additives. The photocatalytic activity of TiO<sub>2</sub> samples has been studied by photodegradation of phenol and formic acid in water. The electronic properties have been followed by TRMC. In each case, the relation between titania modification, charge-carrier dynamics (electronic properties) and photocatalytic activity has been investigated. It has been shown that a strong influence of structural parameters and morphology on photoconductivity and photoactivity is observed.

#### I-2:IL03 Role of Reduced Graphene Oxide in Promoting the Photoelectro-chemical Responses of 1D Oxide-0D

**Chalcogenide Nanocomposites**

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A fundamental driver that determines the performance of photoactive inorganic materials in a solar-driven process, is charge transport. Carbon additives have been examined extensively as a candidate materials to perform such a process. However the integration of these materials with the photoactive materials can be tricky, especially when the photoactive components show dimensionality and aspect ratios. This work outlines a strategy that can be implemented to assemble a 1D oxide – 0D chalcogenide and a carbon-based charge transporting agent to demonstrate multifunctional applications. As a case study, the focus here will be on 1D large bandgap oxides such as TiO<sub>2</sub> and ZnO along with 0D CdX (X=S,Se) using reduced graphene oxide as the charge transporting agent. Select physical, surface, and optical properties of these compounds will be presented. It will be shown that the photoinduced charges generated in the chalcogenides are transported effectively by the reduced graphene oxide. These interesting heterostructures can find applications in photoelectrochemical processes and photocatalysis.

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**I-2:L04 Mimicking in Photocatalysis the Photosynthesis Z Scheme with one Monophasic Material**

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Based on our DFT results we have proposed in recent years, intermediate band (IB) single-phase materials which may couple two low energy photons to achieve a higher energy excitation (like in nature's Z-scheme), providing wider spectral response and higher efficiency in photovoltaic or photocatalytic systems. We have realized the concept in some of these cases with transition metal-substituted main group sulfides. Thus substituting In by V in In<sub>2</sub>S<sub>3</sub> (having gap=2.0 eV) extends its photon absorption to <1.6 eV, and its spectral response in an aqueous HCOOH photo-oxidation test is extended equally. This is not due to band gap narrowing: this material has photoluminescence (PL) of emitted 2.0 eV photons not only if irradiated with E>2.0 eV photons (as for In<sub>2</sub>S<sub>3</sub>), but also with the same <1.6 eV photon range, i.e. upconversion occurs. Also, the thus induced PL intensity grows linearly, not quadratically, with incident light intensity, which is explained by IB partial filling. Same principle should be utilizable in H<sub>2</sub> photogeneration.

**I-2:IL05 Molecular Electrets: Effects of Localized Fields on Photo-induced Charge Transfer**

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Controlling charge transfer at a nanoscale and molecular level is fundamental for electronic and energy applications. Electrets, materials that possess ordered electric dipoles, present an excellent choice for a source of fields that could guide flows of charges. Electrets, however, are dielectrics, unable to efficiently mediate long-range charge transduction. To overcome this challenge, we undertake bioinspired approaches. Adopting principles from bioenergetics and combinatorial proteomics, we design macromolecular electrets comprising de novo non-native aromatic amino acids that are capable of holding charges. While the electrets still possess large intrinsic dipoles originating from ordered amide and hydrogen bonds, the aromatic moieties along the electret backbones provide pathways for efficient long-range charge transfer. The bioinspired electrets rectify charge transfer. The dipoles play a key role in the charge-transfer rectification. For charge recombination, however, the spin-density distribution of the radical-ion forms of the non-native residues prevails the rectification and opposes the dipole effects. This somewhat surprising finding presents unexplored venues for controlling charge transfer that could prove essential for multiscale design of electronic materials.

**I-2:IL06 Interfacing Light Absorbers with Catalysts for Enhanced Photo(electro)catalysis**

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The development of photochemical systems capable of mimicking the natural photosynthesis by driving useful chemical transformations has attracted significant interest motivated by the need to secure the future supply of clean and sustainable energy. The activity of such systems is typically determined by efficient separation of photogenerated charges at well-designed interfaces introducing gradients of electrochemical potential. Assembling different materials in form of hybrid or composite architectures can therefore lead to highly enhanced photoconversion efficiencies. The talk will focus on our recent research on fabrication of hybrid photoanodes for water splitting and their interfacing with metal oxide-based co-catalysts (IrO<sub>x</sub>, CoO<sub>x</sub>) for oxygen evolution. The high quality of coupling between the light absorber and the electrocatalysts is crucial for both activity and stability of the hybrid photoanodes. Visible light-induced photooxidation of water to dioxygen at moderate bias potentials has been demonstrated. In particular, the advantages and drawbacks of different co-catalyst deposition routes and the role of photoelectrochemical and advanced spectroscopic techniques for elucidation of the mechanism of the photo(electro)catalytic action will be discussed in detail.

**I-2:L08 Kinetics of Photocatalytic, Self-cleaning Surfaces: Connecting Contaminant Removal to Contact Angle Evolution**

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The ISO test method for photocatalyst activity of self-cleaning surfaces involves measurement of the air-water-solid contact angle (CA) (1) to determine when a contaminated, hydrophobic surface is clean, as determined by achieving a sufficiently small CA value. The contact angle for a flat surface is related to the solid-vapor (SV), solid-liquid (SL) and vapor-solid (VS) interfacial energies,  $\beta_{SV}$ ,  $\beta_{SK}$ , and  $\beta_{VS}$ , respectively, by the Young-Dupre equation (2):

$$\beta_{SG} - \beta_{SL} - \beta_{VG} \cos(\theta) = 0$$

The vapor(air)-liquid energy is known, and the solid-gas and solid-liquid interfacial energies depend on the solid surface composition. Hydrocarbon deposits on flat TiO<sub>2</sub> surfaces may involve configurations of monolayers (3), ridges (4), or multi-layer islands (5). This paper extends our earlier models of reaction kinetics for self-cleaning, photocatalytic surfaces (6) to predict contact angle ( $\theta$ ) evolution vs. time.

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**I-2:IL09 Charge Transport and Recombination in Nanostructured Materials for Photoelectrochemical and Solar Cells**

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The electronic properties of nanostructured photoelectrodes determine the performance of a variety of devices, including several types of third generation solar cells. We report here on the commonly unaccounted for effect of recombination under short-circuit conditions on the charge transport and recombination dynamics in nanostructured