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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:IL02 Solar Fuel Generation Enhanced by Surface Plasmon Resonance

**NIANQIANG WU**, Department of Mechanical & Aerospace Engineering, West Virginia University, Morgantown, WV, USA

This presentation will discuss the concept, design principles and applications of plasmonic metal-semiconductor composites. This talk will describe that surface plasmon resonance (SPR) enhances the solar energy conversion of semiconductors by three underlying mechanisms such as light scattering/trapping, plasmon-induced resonance energy transfer (PIRET) and hot electron injection. The roles of each mechanism that play in the solar energy conversion are dependent on the strength of plasmon and the coupling of the metal with the semiconductor. This presentation will demonstrate the effort to tailor the plasmonic properties and the composite structure to maximize the solar energy conversion efficiency.

##### 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 H2 evolution and O2 evolution with I-/IO3- electron mediator under UV light irradiation. The H2 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 O2 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. Based 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:L06 Water Splitting Semiconductor Photoanodes

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

The long term stability is the critical issue that conditions application of semiconductor materials in photo-electrochemical water splitting devices. This is the reason why the choice of the semiconductors intended to operate as water oxidation photo-anodes is actually restricted to a few metal oxides. However, none among those materials, able to absorb a significant portion of solar light, exhibits band-edge energy levels that match those of hydrogen and oxygen evolution reactions. Neither tungsten trioxide, nor bismuth vanadate and still less hematite ferric oxide have the positions of the conduction band edges more negative than the H<sub>2</sub> evolution potential, a condition necessary to perform unassisted water splitting. Consequently, continuing efforts are devoted to minimize the bias voltage required to perform visible light-driven photo-oxidation of water. These efforts include, among others, development of new electrocatalysts and incorporation into photo-anodes of plasmonic metal nanostructures. Recent advances regarding the most

investigated photoanode materials: WO<sub>3</sub> (E<sub>g</sub> = 2.5 eV) ; BiVO<sub>4</sub> (E<sub>g</sub> = 2.4 eV) and hematite Fe<sub>2</sub>O<sub>3</sub> (E<sub>g</sub> = 2.2 eV) will be discussed.

**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. Though 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**

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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:L10 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.

1. W. K. Kim, et al., and Se-Young Jeong, *Scientific Reports* 5, 10715 (2015). 2. J. Y. Kim et al., and Se-Young Jeong, *Scientific Reports* 4, 05450 (2014). 3. S. Lee et al., Cheol Seong Hwang, and Se-Young Jeong, *Scientific Reports* 4, 6230 (2014). 4. Y. C. Cho et al., G. W. Lee, and Se-Young Jeong, *CrystEngComm*, 16 7575 (2014)

**I-1:L11 Hybrid Nanostructured Materials for the Harvesting and Conversion of Solar Energy**

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Biochar-based photocatalysts have been prepared from biomass derivatives and studied in photocatalytic processes concerning with environmental remediation such as phenol and methylene blue photodegradation, and in clean energy production such as hydrogen photoproduction. A careful design of the pyrolysis/activation processes permits to control both the texture and chemistry surface of carbons. Biomass precursor is a master key to control both the crystalline framework and optical and electrical properties of photoactive semiconductors such as TiO<sub>2</sub>, ZnO and Nb<sub>2</sub>O<sub>5</sub>. In addition, the influence of heteroatoms-doped biochars and the influence of noble metal upon TiO<sub>2</sub>-based photocatalysts will be also presented. Finally, a single synthetic route will be showed to obtain C-doped semiconductor hollow spheres to be employed as electrodes in solar cells. In conclusion, results showed that biomass-derived materials are an alternative for the harvesting of solar energy to be employed in metal-free and semiconductor-free photocatalysts and in solar cells.

#### 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:IL14 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:IL15 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.

*This research was supported by a grant of the Romanian National ANCS UEFISCDI project PNII-PT-PCCA-2013-4-0726*

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

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We would like to report the efficient study of Y2O3 enhanced photocatalysis using novel Y2O3-TiO2 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 Y2O3 and TiO2 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% Y2O3-96 at% TiO2) 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 TiO2 nanorods, respectively, suggesting the effectiveness of Y2O3 incorporation. With the aid of PL analyses and the simple Y2O3-TiO2 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 Y2O3 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-TiO2 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 TiO2 is the best semiconductor able to oxidize pollutants; especially, it can be applied on materials: TiO2-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 TiO2 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-TiO2 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 NOx 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 TiO2, ZnO and Al2O3 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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**I-1:L20 A New Strategy to synthesize TiO<sub>2</sub> Mesocrystals with Superior Photocatalytic Activity**

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Mesocrystals are a new class of solid materials, which is built of crystallographically oriented nanocrystals. Usually, mesocrystals are formed by a bottom-up self-assembly process. Recently, we developed a new top-down strategy to prepare TiO<sub>2</sub> mesocrystals using topotactic transformation reactions of ammonium oxofluorotitanates. The morphologies and building structures of the TiO<sub>2</sub> mesocrystals can be adjusted by the precursors. Due to the presence of F<sup>-</sup>, most products are built of TiO<sub>2</sub> nanocrystals with dominantly exposed {001} facets. The unique structures lead to superior photocatalytic activities, which is close to 3 times of that of P25. Because of their large sizes (300 nm ~ 100 μm), it is very easy to remove these TiO<sub>2</sub> mesocrystals from the reaction system via centrifugation or filtration. This is very good for their applications in practice.

**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.

*This work is supported by the National Science Foundation of the United States of America.*

**I-2:IL04 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:L07 Optical Characterization of CdTe highly doped with Antimony

**S. COLLINS**, I. KHAN, V. EVANI, C. FERIKIDES, University of South Florida, Tampa, FL, USA

Understanding and controlling p-type doping in CdTe cells is critical in improving the cell voltage and ultimately efficiency. This study uses low-temperature photoluminescence (PL) to investigate the defect bands of polycrystalline CdTe films, which were doped with antimony (Sb). The films in this study were deposited using the Elemental Vapor Transport technique (EVT). The amount of Sb vapors used for the deposition of the thin films corresponded to 125,000 and 250,000 ppm. The films were grown mostly under conditions of excess Cd, in order to create Te-vacancies 1V<sub>Te</sub> for Sb to occupy Sb<sub>Te</sub>. Three Cd/Te vapor ratios (1.0, 2.0 and 3.0) were used for this study. The PL spectra for all films were comprised of 3 main impurity bands: 1.1eV, 1.4eV and 1.57eV. It has been previously suggested that the 1.1eV defect is associated with a deep donor-acceptor pair, having 1V<sub>Te</sub> as the donor. The 1.1eV peak, was only observed in the doped films and the intensity of this band increased, with Sb concentration. The 1.4eV band was quenched in films with the higher Cd/Te ratio, supporting the well-known association of this band with VCd. These results suggest that Sb was successfully incorporated in CdTe while Cd vacancies were quenched as expected under Cd-rich deposition conditions. Further deconvolution and data analysis has been performed to calculate activation energies and to determine transition types, and is presented at the conference.

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

**D. OLLIS**, Chemical Engineering Department, North Carolina State University, USA

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,  $\beta_{SV}$ ,  $\beta_{SL}$ , 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 photoelectrodes. It is observed that when recombination occurs under short circuit conditions the charge-collection efficiency determined from small-perturbation methods is overestimated, and this effect becomes more pronounced with increasing recombination losses under short circuit conditions. We propose a simple method to detect whether recombination losses at short-circuit are important. ZnO is an interesting material for application in the dye-sensitized solar cell (DSSC) related to the large variety of low-temperature synthesis methods that allow for easy manipulation of the morphology and texture of the material, which may affect the dye bonding, dye coverage, and injection efficiency, the electron transfer kinetics to the solution, and the trap state distribution. Using these materials, we have compared the electron transport and recombination properties using small-signal perturbation techniques.

#### I-2:IL10 TiO<sub>2</sub> Nanostructures for Energy and Environmental Applications

**M. WARK**, Institute of Chemistry, Carl von Ossietzky University Oldenburg, Oldenburg, Germany

TiO<sub>2</sub> thin films with highly ordered mesoporosity were proven to be ideal photocatalysis systems in which photo- or electrodeposited co-catalyst can be in intimate contact with the light-absorbing material. Several highly active systems for pollutant degradation and H<sub>2</sub> generation from water splitting were developed. For example it was found that with a 4-layer mesoporous anatase film (thickness about 750 nm) 10<sup>-5</sup> mol/L of the non-steroidal anti-inflammatory drug Diclofenac in water, which is about 10-100 times the concentration typically found in principal wastewater, can be completely degraded within only 2 hours. Loading of the films with highly dispersed noble metal nanoparticles enhances the activity drastically so that very low film thicknesses of only about 150 nm are sufficient. Quite often high porosity of the TiO<sub>2</sub> is even more important than highest crystallinity. For water splitting grain boundaries should be avoided, thus mesoporous TiO<sub>2</sub> films thicker walls formed by the evaporation-induced self-assembly (EISA) process are advantageous over films with walls constructed of nanoparticles via the brick-and-mortar approach. Several strategies

to gain visible light activity will be discussed as well in the lecture.

#### I-2:IL11 Photocatalytic Activation of Biomaterials

K.H. CHEUNG, P. KOSHY, M.B. PABBRUWE, C.S. SORRELL, School of Materials Science and Engineering, UNSW Australia, Sydney, NSW, Australia

Photocatalytic materials generally are activated by ultraviolet radiation. However, it is less well known that clinical doses of X-radiation are adequate to activate biocompatible and photocatalytic oxides, such as TiO<sub>2</sub>, when implanted in the body in the form of bulk materials or coatings. Anodised coatings of TiO<sub>2</sub> on Ti and biomedical-grade Ti alloy have been produced as a function of voltage and time and characterised in terms of chemistry, mineralogy, and microstructure. They have been subjected to varying doses X-radiation and the photocatalytic activity has been assessed in terms of the decomposition of different organic materials.

#### I-2:IL12 Analysis of the Dynamics in Composition of Pt and Ni/NiO promoted SrTiO<sub>3</sub> in Overall Water Splitting

G. MUL, Mesa+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

In this presentation I will show that various co-catalysts, frequently reported to be active in the overall water splitting reaction, change their chemical composition in the first hours after initiation of illumination. When SrTiO<sub>3</sub> is equipped with a Pt co-catalyst prepared by photo-deposition in oxidative conditions, a strong O<sub>2</sub> evolution transient occurs before hydrogen production is observed, assigned to in situ reduction of PtOx to metallic Pt. Interestingly, doping of SrTiO<sub>3</sub> with Rh cations, results in a significantly lower O<sub>2</sub> evolution transient, and higher average steady state oxidation state of Pt co-catalyst particles, which negatively affects the efficacy in water splitting. Another frequently studied co-catalyst for SrTiO<sub>3</sub> is Ni/NiO. In particular the structure performance relation of the active Ni species has been frequently discussed in the literature. I will provide novel insight on the basis of transient productivity, this time in hydrogen evolution, and will propose an important role of in situ formation of NiOOH in stimulating hydrogen formation. Implications of these findings are that structure activity correlations reported in the literature on the basis of characterization of as-prepared catalysts should be considered preliminary.

#### I-2:IL13 Metal Oxides for Photoelectrochemical Water Splitting and Environmental Remediation

S. CARAMORI, V. CRISTINO, N. DALLE CARBONARE, F. RONCONI, C.A. BIGNOZZI, G. LONGOBUCCO, L. PASTI, A. MOLINARI, Department of Chemical and Pharmaceutical Sciences, University of Ferrara, Ferrara, Italy; R. ARGAZZI, CNR/ISOF c/o Department of Chemical and Pharmaceutical Sciences, University of Ferrara, Ferrara, Italy

Metal oxide semiconductors play a central role as photoanodes for the photooxidation of water, thanks to the fulfillment of some fundamental requirements which include the absorption of near UV-Visible photons, the favorable position of their valence band edge with respect to the O<sub>2</sub>/H<sub>2</sub>O potential and stability in aqueous electrolytes under oxidizing conditions within appropriate pH intervals. The photoelectrochemical properties and the charge transfer dynamics of materials based on WO<sub>3</sub> (both anodized and sol-gel), BiVO<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> will be described in photoelectrochemical water splitting processes and in the OH radical mediated degradation of impervious emerging contaminants. The molecular sensitization of WO<sub>3</sub> and SnO<sub>2</sub> by cationic perylenes characterized by strongly oxidizing ground state redox potentials, aimed at the realization of molecular driven solar fuel production will also be considered.

#### I-2:IL14 Organic Photoelectrochemical Cells for Selective Redox Reactions

A. GUERRERO, Institute of Advanced Materials (INAM), Universitat Jaume I, Castelló, Spain

Organic photoactive materials are promising candidates for generation of solar fuels in terms of efficiency and cost. However, their low stability in aqueous media constitutes a serious problem for technological deployment. Here, we present organic photocathodes for generation of hydrogen in aqueous media with outstanding stability. The device relies on the use of water resistant selective contacts, which protect the photoactive layer.[1] An insoluble cross-linked PEDOT:PSS hole selective layer avoids delamination of the film and an electron selective TiO<sub>x</sub> layer in contact with the aqueous solution electrically communicates the organic layer with the hydrogen evolving catalyst (Pt). Tuning the thickness of the TiO<sub>x</sub>/Pt layer leads to a trade-off between the highest photocurrent reported for this system (~1 mAcm<sup>-2</sup>) and stable hydrogen generation of 6 μmol h<sup>-1</sup>cm<sup>-2</sup>. The high photocurrent limit approaches to our recently demonstrated results in non-aqueous solvents where obtained photocurrents are close to the theoretical maximum.[2] 1. M. Haro, C. Solis, G. Molina, L. Otero, J. Bisquert, S. Gimenez and A. Guerrero, *The Journal of Physical Chemistry C*, 2015, 119, 6488-6494. 2. A. Guerrero, M. Haro, S. Bellani, M. R. Antognazza, L. Meda, S. Gimenez and J. Bisquert, *Energy & Environmental Science*, 2014, 7, 3666.

#### I-2:L15 Band Engineering of Titanium Dioxide Relevant to Solar Cells and Photocatalysis

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The electronic band engineering of TiO<sub>2</sub> is fundamental for photocatalysis, solar cells and solar fuel generation. The position of conduction band (CB) edge controls the driving force for photocatalytic hydrogen evolution from water, potential of dye-sensitized solar cell (DSC) and recombination blocking in perovskite solar cells. The staggered alignment in mixed anatase/rutile phases is assumed to enhance photocatalytic activity, but it is unclear whether the CB of rutile or that of anatase is higher. XPS and most DFT simulations support the former, but the flat-band potential measurements provide just opposite results. The controversy can be explained by taking into account the adsorption of OH<sup>-</sup> and H<sup>+</sup> from the electrolyte solution on the electrode surface. XPS indicates that the CB edge of (001)-anatase is upshifted by 0.1 eV referenced to (101)-anatase in agreement with the DFT calculation [3] and with the electrochemical flatband potentials (upshift of CB by 60 meV).

*This work was supported by the Grant Agency of the Czech Republic (contract No. 13-07724S).*

### Session I-3 - Design Approaches for Advanced Applications

#### I-3:IL01 Efficient Solar Driven Water Splitting using a Bipolar Membrane to enable pH-gradients

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The conversion of solar energy into a chemical fuel, such as hydrogen, is a promising route to enable a sustainable and clean energy future. Multiple designs for this conversion have been proposed, ranging from separate photovoltaic and electrolysis cells (PV-EC) to direct photo-electrochemical (PEC) fuel production technologies. However, efficient operation of (photo-)electrodes and catalysts depends on the electrolyte's pH. Differences in optimal pH conditions for each element seriously challenges the practical applicability of a solar fuel device. To ease the combination of suitable electrodes and catalysts, a solar-assisted design with a bipolar membrane (BPM) was demonstrated [1]. This BPM dissociates water into H<sup>+</sup> and OH<sup>-</sup>, which maintains an acidic cathodic compartment and an alkaline anodic compartment. We demonstrate the practical operation of a BPM for direct photo-assisted hydrogen production, as well as for photovoltaic driven electrolysis. Our experimental results show a voltage over the BPM very close to its thermodynamic minimum, a stable pH difference for several days and a solar-to-hydrogen efficiency of >10%, showing the efficacy of bipolar membranes in developing a practical solar fuel device.

1. Vermaas, Sassenburg and Smith, *J.Mat.Chem.A*, 2015,3, 19556-62

**I-3:IL02 Development of Photocatalyst Sheet for Unassisted Sunlight-driven Water Splitting**

**T. HISATOMI**, K. DOMEN, The University of Tokyo, Tokyo, Japan; Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPCChem)

Photocatalytic water splitting has been studied as a means of renewable solar hydrogen production [1]. It is necessary to activate narrow band gap semiconductors to achieve a sufficient solar-to-hydrogen energy conversion efficiency (STH) with reasonable quantum efficiencies. Z-scheme water splitting based on two-step excitation is suited to utilizing long-wavelength photons because the energy required to drive each photocatalyst can be lowered than overall water splitting on single photocatalytic materials. The authors' group recently developed photocatalyst sheets consisting of a hydrogen evolution photocatalyst and an oxygen evolution photocatalyst embedded into a conductive layer [2]. The photocatalyst sheets exhibited significantly higher activity in Z-scheme water splitting than the corresponding photocatalyst powder suspensions owing to the presence of the conductive layer that facilitated the electron transport between the photocatalysts. In this talk, the factors controlling the activity of the photocatalyst sheets will be discussed. Our recent effort in the development of photocatalyst sheets using photocatalysts with narrow band gap energies will also be presented.

[1] Hisatomi et al., *Chem. Soc. Rev.* 2014, 43, 7520. [2] Wang et al., *J. Catal.* 2015, 328, 308.

**I-3:L03 Quasi-1D Black Titanium Oxide Nanostructures for Water Splitting Applications**

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Quasi-1D titanium oxide nanostructures synthesized by Pulsed Laser Deposition (PLD) were developed and studied as photoanodes for photoelectrochemical water splitting. An explorative combined approach to improve TiO<sub>2</sub> performance was investigated, i.e. extension of the photoresponse to the visible range as well as optimization of morphology and structure to increase light harvesting and quantum efficiency. This was pursued by varying the deposition atmosphere (from pure O<sub>2</sub> to Ar/O<sub>2</sub> or Ar/H<sub>2</sub>), and by substituting/combining the air annealing process (necessary to induce crystallization to the anatase phase) with Ar/H<sub>2</sub> annealing, to induce reduction/hydrogenation (the so-called black titania). SEM, Raman spectroscopy and UV-vis-IR spectroscopy were employed to understand the material morphology, structure and optical properties. A photoluminescence background and a tail absorption towards the visible emerged for hydrogen-treated samples. Photocurrent measurements under solar simulator illumination showed a noteworthy increase of photocatalytic response for the Ar/O<sub>2</sub> deposited samples followed by a double air+Ar/H<sub>2</sub> thermal treatment. These findings could be ascribed to the combination between an optimized nanoscale morphology and oxygen vacancy-related tail states in the bandgap.

**I-3:IL04 A Stand Alone Artificial Photosynthesis of Formate from Carbon Dioxide and Water**

**HYUNWOONG PARK**, School of Energy Engineering, Kyungpook National University, Daegu, Korea

There is renewed interest in the photocatalytic and photoelectrochemical conversion of CO<sub>2</sub> into value-added chemicals using various semiconductor particles and electrodes. Common CO<sub>2</sub> reduction products are C<sub>1</sub> chemicals (CO, HCOOH, CH<sub>3</sub>OH, and CH<sub>4</sub>) in aqueous media, while the production of C<sub>2</sub>-C<sub>4</sub> hydrocarbons (e.g., C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>) 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 CO<sub>2</sub> conversion to value-added chemicals while using water as an electron donor in various photo-systems [1-4].

[1] S.K. Choi, U. Kang, S. Lee, D.J. Ham, S.M. Ji, and H. Park, *Advanced Energy Materials* 4 (2014) 1301614. [2] H. Park, H.-H. Ou, A.J. Colussi, and M.R. Hoffmann, *Journal of Physical Chemistry A* 119 (2015) 4658. [3] U. Kang, S.K. Choi, D.J. Ham, S.M. Ji, W. Choi, D.S. Han, A. Abdel-Wahab, and H. Park, *Energy & Environmental Science* 8 (2015) 2638. [4] H. Park, H.-H. Ou, U. Kang, J. Choi, and M.R. Hoffmann, *Catalysis Today*, accepted.

**I-3:L05 Sculpting Photocatalysts on the Nano Scale**

**L. AMIRAV**, Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa, Israel

The solar-driven photocatalytic splitting of water into hydrogen and oxygen is a potential source of clean and renewable fuels. However, four decades of global research have proven this multi-step reaction to be highly challenging. The design of effective artificial photocatalytic systems will depend on our ability to correlate the photocatalyst structure, composition, and morphology with its activity. Here, I will present our strategies, and most recent results, in taking photocatalyst production to new and unexplored frontiers. I will focus on unique design of innovative nano scale particles, which harness nano phenomena for improved activity, and methodologies for the construction of sophisticated heterostructures. I will demonstrate how vital is the ability to characterize our hybrid nanostructures on the atomic level, and how we can benefit from information on the structure-properties relationship for the future design of an efficient photocatalyst for solar-to-fuel energy conversion.

**I-3:L06 A New Strategy for Solar Water Splitting Materials Design**

**L. VAYSSIERES**, IRCRE, Xian Jiaotong University, Xi'an, China

With global climate change seriously compromising our environment, security, and health, and a concomitant exponential increase in energy demand from emerging countries, a significant renewed interest in the field of photocatalysis has occurred worldwide within the last decade. Large bandgap transition metal oxide semiconductors offer a wide range of applications for renewable energy systems and solar energy conversion. Most are stable, non toxic, earth-abundant, easy to prepare on a large scale as powders, thin films, dense ceramics and ordered anisotropic arrays at various dimensional scales, i.e. from nano- to micro- to macro-scales. They exhibit the widest range of electrical, optical, and electronic properties suitable for low cost solar water splitting and photovoltaic applications. A new design strategy to fabricate highly ordered hybrid heteronanostructures combining molecular co-catalysts and inorganic semiconductors will be demonstrated along with the latest advances in dimensional, interfacial, and morphological engineering for visible light active devices for low cost water splitting.

**I-3:IL07 Bioinspired Photoelectrode Designs for Solar Fuel Generation**

**K. RAJESHWAR**, University of Texas, Dept of Chemistry & Biochemistry, Arlington, TX, USA

In this talk, the synergies between electrocatalysis, photocatalysis, and photoelectrosynthesis will be underlined with the dioxygen reduction, hydrocarbon oxidation, and dinitrogen reduction as representative examples. Approaches based on the use of electrodes and photoelectrodes as well as those based on the use of colloidal suspensions will be compared and contrasted. Ideas on how we can learn from the intricate self-assembled architectures that Nature has evolved over millions of years, will be discussed with specific examples. The talk will then turn toward a discussion of work in the author's laboratory on the use of carbon and oxide semiconductor nanocomposites for driving catalytic processes of interest both in the dark and under irradiation of the oxide semiconductor component. Incorporation of bioinspired components such as flavins in these assemblies will be described. The reactions of interest here include dioxygen reduction and the reduction of carbon dioxide to fuels such as methanol. The role of the nanocomposite components and their complementary functionality within the material architecture will be discussed within the context of systems that Nature has evolved.



**I-3:IL08 Reduction of Small Molecules in Photocatalytic Systems****W. MACYK**, Faculty of Chemistry, Jagiellonian University, Kraków, Poland

Photocatalytic reduction of small molecules is very often a key step of a photocatalytic reaction. Reduction of water or carbon dioxide can be used to convert solar energy into fuels, however, also in processes of pollutants photodegradation reduction of a small molecule (O<sub>2</sub>) influences the overall efficiency of photocatalysis. During the presentation selected examples of photocatalytic reduction of small molecules will be presented. Factors influencing these reactions will be discussed. Among them redox properties of photocatalysts are particularly important. Recently, a new method of determination of the density of states was developed in our group. Its application enabled understanding the differences between rutile-TiO<sub>2</sub> and anatase-TiO<sub>2</sub>. The results revealed significantly better reduction properties of rutile than anatase. Therefore the reduction of oxygen is more efficient at rutile than at anatase. On the other hand, holes generated within anatase particles are stronger oxidants than holes from the valence band of rutile, so oxidation of water to hydroxyl radicals proceeds efficiently at anatase-TiO<sub>2</sub>, but not at rutile-TiO<sub>2</sub>. These properties explain the differences in photocatalytic activities of both crystalline forms of titanium dioxide.

**I-3:L09 TiO<sub>2</sub>/Pt/SnO<sub>2</sub> Multilayer Photo Catalytic Film****G.O. TESTONI, M.A. ZAGHETE, M.V. NOGUEIRA, J.P.C. COSTA, E.C. AGUIAR, J.A. VARELA, L. PERAZOLLI**, Araraquara, SP, BRAZIL; UNESP-Chemical Institute - DBTQ

In this work we obtained photoactive TiO<sub>2</sub>\*Pt\*SnO<sub>2</sub> multilayer films to be used in fixed bed reactors for advanced oxidation processes applications. The film consists of a metallic titanium substrate, 1.5 cm<sup>2</sup> area, a SnO<sub>2</sub> film deposited by electrophoresis (7 μm), a Pt film deposited by sputtering (90 nm) and a TiO<sub>2</sub> film exposed to germicidal UV light with a wavelength of 254 nm, also deposited by electrophoresis (25 μm). The multilayer film photoactivity was measured by discoloration studies of the Blue Methylene using UV – Vis, and the film was characterized by techniques of FEG- SEM, XRD, B.E.T. and XPS. The photoactivity results indicated a discoloration, after 120 min of exposure, of 60 % and 75 % using reactor with 1 and 2 films, i.e., 1.5 cm<sup>2</sup> and 3.0 cm<sup>2</sup>, respectively, of the exposed area to light.

**I-3:L10 Superhydrophilic and Photocatalytic Active Ceramic Glazes for Sanitary Ware****F. KNIES<sup>1,2</sup>, K. SCHRANTZ<sup>1</sup>, C. ANEZIRIS<sup>1,2</sup>, T. GRAULE<sup>1,2</sup>**, EMPA-Swiss Federal Labs for Materials Science and Technology, Laboratory for High Performance Ceramics, Duebendorf, Switzerland; <sup>2</sup>TU Bergakademie Freiberg, Institute for Ceramics, Glass and Building Materials, Freiberg, Germany

Self-cleaning, superhydrophilic surfaces are of high relevance both for public places like hospitals and as well for households applications. In the present work the aim is to transfer the knowledge for photocatalytic active, but little mechanically utilised surfaces to more mechanically utilised surfaces. By everyday use sanitary ceramics in households get confronted with strong cleaning agents, abrasive brushes and sponges. Due to this sol-gel-coatings are not stable for longer time periods. To avoid this problem of surface degradation, we incorporate photocatalytic active oxides in the bulk of the glaze. The properties are now not influenced by scratches originating from extensive cleaning procedures. To generate both photocatalytically active as well as superhydrophilic surfaces we were incorporating TiO<sub>2</sub>, ZnO and CeO<sub>2</sub> in an industrial standard glaze. The glazes were analysed for optical appearance, surface roughness, wetting and cleaning behaviour and results compared with a standard ZrSiO<sub>4</sub>-whitened glaze with a medium roughness of 60 nm and a water wetting angle of 45°. Samples are irradiated with 365 nm UV light and tested for Methylene Blue degradation and wetting angle. Promising results were achieved with both zinc oxide and rare earth metal oxide incorporation.

**I-3:IL11 VOCs Removal in Semiconductor Clean Lab Using Fiber-illuminated Honeycomb Reactor****YI-TING WU, KUNG-TE LU, JEFFREY C.S. WU**, Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan

The circuit feature sizes of the wafer in the semiconductor factory shrink from 28 nanometers to 14 nm in recent years. Under such precise manufacturing process, the control and the detection of low concentration volatile organic compounds (VOCs) are very important because VOCs will affect the quality of production process in the high-tech clean room. In this study, fiber-illuminated honeycomb reactor (FIHR) is developed for the removal of VOCs. The design and efficiency of fiber-illuminated honeycomb reactor was investigated. The photocatalyst, TiO<sub>2</sub>, was prepared by thermal-hydrolysis method. Products of VOCs photoreaction were detected by gas chromatography–mass spectrometry (GC-MS). By using FIHR, we found removal efficiency of m-xylene is significantly enhanced to 96.5 % as compared to 22.0 % for UV irradiation only. Using the FIHR with Mn-TiO<sub>2</sub> photocatalyst not only increased the m-xylene removal efficiency, but also increased the CO<sub>2</sub> selectivity. Mn-TiO<sub>2</sub> in FIHR also showed a very good reusability, 82 % of removal efficiency was still achieved after 72 hours. The FIHR gave very high removal efficiency for VOCs at ppb level under room temperature. The FIHR has great potential for the application in the clean room air purification system.

**I-3:IL12 Mechanistic Studies of Charge Carriers in Materials for Artificial Photosynthesis****A.J. COWAN**, University of Liverpool, Department of Chemistry, Liverpool, UK

The utilization of solar energy conversion technologies on a TW scale will require the development of storage technologies to overcome the intermittent nature of sunlight at ground level. An extremely attractive approach is to develop “artificial leaf” materials that use solar energy for either water splitting to produce hydrogen or combined water oxidation and carbon dioxide reduction to potentially produce a range of fuels including, CH<sub>3</sub>OH, CO, CH<sub>4</sub>. To enable the rational development and design of new more efficient artificial leaf materials we carry out a range of transient spectroscopic measurements on state of the art photoelectrodes to identify the key design rules to be fed into both our own and collaborators synthetic research programmes. Here I will present an overview of our recent synthetic and mechanistic work including studies on both (i) semiconductor materials for water oxidation, concentrating on the study of mechanism of activity of oxygen deficient metal oxides (ii) the development of novel semiconductor/molecular catalyst photoelectrodes for the reduction of protons and/or CO<sub>2</sub> to fuels.

**I-3:L13 Artificial Photosynthesis Device Development for CO<sub>2</sub> Photoelectrocatalytic Conversion****J.F. THOMPSON, BIN CHEN, J. MINUZZO, N. LONDONO**, NASA Ames Research Centre, Mountain View, CA, USA; **G. WHITING**, Palo Alto Research Center (PARC)

We present development of a 3D photocatalytic device with a nanostructured photoelectrocatalyst. Containing TiO<sub>2</sub> and transition metal co-catalysts allowing the reaction of CO<sub>2</sub> and H<sub>2</sub>O to produce oxygen and hydrocarbons at a rate of at least 622μL per hour for every gram of catalyst. The novel composite catalyst significantly improves upon current published literature. In addition to the high rate of methane production, the composition can also be tuned to produce other hydrocarbons. Operating at ambient pressure and concentration and using sunlight as an energy source, the device enables placement of devices in environments where electrical power is limited. The device has broad applications in heavy CO<sub>2</sub> emitters, from power plants to vehicles, as well as in life support for space travel. The catalyst is processed through thin film deposition onto the device and uses acrylic waveguide material with origami structures to deliver solar radiation to the available surface area of the catalyst, allowing maximized catalyst efficiency. Furthermore, 3D printing techniques accomplish a catalytic ink coating upon the waveguide substrate. The printing

strategies enable a high tortuosity design for efficient mass transport of CO<sub>2</sub>, as well as high reaction surface areas.

### I-3:L14 Photocatalytic Ag/AgCl Polymer Composites

**E.W. TATE, J.H. JOHNSTON**, School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand

In our recent work, photocatalytic Ag/AgCl composite materials were produced using the support materials of polyurethane paint and nylon. This was achieved through the development of a simple aqueous synthesis method, utilising the substrate to control the formation of the AgCl nanoparticles and their stabilisation. These were then exposed to UV light to generate Ag nanodomains and hence form plasmonic Ag/AgCl photocatalysts, successfully incorporating the plasmonic photocatalyst nanoparticles within the support. UV Vis, XRD, SEM and EDS were used to characterise the Ag/AgCl nanoparticles and their distribution within the composites. The photocatalytic activity of the Ag/AgCl composites was evaluated by the photodegradation of methylene blue, showing them to be effective photocatalysts. Due to the inherent antimicrobial properties of the Ag/AgCl nanoparticles, the composites were also seen to display significant antimicrobial action against E. Coli. These novel composite materials have promising applications in water treatment, where the photocatalytic mechanism is effective in the reduction of organic contaminants, whilst the Ag<sup>+</sup> simultaneously imparts antimicrobial action. This then lead to the design and incorporation of these composites into a laboratory scale reactor system.

### Poster Presentations

#### I:P01 Enhancement of Photocatalytic Reaction by Coupling TiO<sub>2</sub> with Graphene Oxide

**H.M. YADAVEM, JUNG-SIK KIM**, Department of Materials Science and Engineering, University of Seoul, Republic of Korea

Anatase TiO<sub>2</sub>-graphene oxide (GO) nanocomposites with different GO loadings were prepared by a solvothermal method. The prepared photocatalysts were characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infra-red spectroscopy (FTIR), and photoluminescence spectroscopy (PL). The XRD results confirmed the anatase phase of TiO<sub>2</sub> in the composites and Raman analysis revealed the presence of GO in the nanocomposites. TEM studies indicated the uniform dispersion of TiO<sub>2</sub> nanoparticles on the GO surface with slight aggregation. The photocatalytic performance of the prepared nanocomposites was evaluated by the degradation of gaseous benzene under UV light irradiation. Anatase TiO<sub>2</sub>-GO nanocomposites exhibits better photocatalytic performance than pure TiO<sub>2</sub> nanoparticles.

#### I:P02 Effect of Annealing on the PL and Photocatalytic Properties of Solution Combusted ZnO Nanopowders

**SUNG PARK, JI HYUNG RYU, JUNG EUN PARK, MIN JAE HAN, JAE CHUN LEE**, Dept. of Materials Science and Engineering, Myongji University, Yongin, Korea

Nano-sized ZnO powders were prepared by Solution Combustion Method (SCM). The ZnO powder using Zn(OH)<sub>2</sub> and glycine as an oxidant and a fuel (fuel/oxidant=0.8), showed good powder characteristics such as average grain size of 30nm and the specific surface area of 120m<sup>2</sup>/g. PL spectra from SCM ZnO powders showed a single sharp peak at near 390nm. Furthermore, the blue light intensity was doubled when the synthesized ZnO powders was annealed at 400 °C. Also, to confirm photocatalytic activities of the annealed ZnO powder, the Ag ions from a used photo-film developer were completely removed within 10min. The Ag ions removal rate of the annealed ZnO nanopowder was more than 2 orders of magnitude faster than that of the SCM ZnO nanopowder. These results might be very useful for the high efficient photocatalyst application.

#### I:P03 Alkali Metal-doped TiO<sub>2</sub> Nanotube Array Films with Enhanced Open Circuit Voltage for Photocatalytic Solar Fuel Generation

**S. ABD EL-NASSER, A. ESAWI**, Department of Mechanical Engineering and the Yousef Jameel Science and Technology Research Center, The American University in Cairo, New Cairo, Egypt

Photo-electrochemical water splitting represents a favorable approach that can be used to convert and store solar energy in the form of Hydrogen which has recently gained a great attention as an energy carrier as it possesses the highest energy density (120MJ/kg) known for any fuel and no carbon footprint. To this end, Titanium (II) oxide is considered a very promising semiconductor material for water splitting due to its abundance, stability and vectorial charge transfer. However, TiO<sub>2</sub> possesses an onset potential between -0.7 and -0.8 V vs NHE, which requires large amount of external bias to be applied in order to perform the reaction. Any modification in the band edges of TiO<sub>2</sub> will have a decisive impact on the open-circuit potential and hence improve its phot-electrochemical performance. In this regard, doping with alkali-metals was proposed as an effective approach to improve the photoactive performance of TiO<sub>2</sub> due to their remarkable low work function considering their low first ionization potential. In this work we intend to combine the enhanced charge transport properties of TiO<sub>2</sub> with the low work function capabilities of alkali-metals in order to build new-concept hybrid photo-electrochemical system for hydrogen production.

#### I:P04 Hybrid DFT Study of the Fe:NiOOH OER Catalyst and its Interface to BiVO<sub>4</sub>

**J.C. CONESA**, Inst. de Catálisis y Petroleoquímica, CSIC, Madrid, Spain

Fe-doped NiOOH is one of the best inexpensive catalysts for O<sub>2</sub> evolution in photo/electrocatalytic water splitting, but its atomic and electronic features are not well understood, as its structure, made of H bond-linked sheets, is normally highly disordered. Here its bulk electronic structure, Fe-doped or not, is modeled with a hybrid DFT method able to give accurate bandgaps. Different sheet stackings and proton orderings are studied. Several of them having different stackings and Ni coordinations and redox states have close lowest energies, explaining the said disorder. Bandgaps, with edges made of Ni 3d levels, are in the -1.0-1.4 eV range. Substituting Ni by Fe gives filled Fe 3d levels near the valence band edge; in some cases a Ni(3+) + Fe(3+) → Ni(2+) + Fe(4+) process occurs, eventually with proton jump from Fe to Ni coordination spheres. This suggests a high electronic and protonic conductivity, which probably helps the electrocatalytic activity of the material. The band alignment of NiOOH with photocatalyst BiVO<sub>4</sub> is modeled also using hybrid DFT and a method taking electrostatic potential as reference; the results imply that the NiOOH valence band lies closely above that of BiVO<sub>4</sub>, facilitating the transfer of photo-holes to the former as desired to drive O<sub>2</sub> evolution.

#### I:P05 Effect of Solvent Additives and P3HT on PDTSTTz/PCBM based Bulk Heterojunction Solar Cells

**A.E. DEJENE**, Ministry of Mines and Energy of Ethiopia, Addis Ababa, Bole-13, Ethiopia

In this investigation, photovoltaic (PV) parameters improvements in PDTSTTz:PCBM blend were made through solvent additives and secondary donor addition. Short carbon chain solvent additives such as iodomethane (IMe), iodoethane (IEt), iodobutane (IBu) and diiodomethane (DIMe) were used. The results have shown that, short circuit current density (J<sub>sc</sub>), as well as power conversion efficiency (PCE) of PDTSTTz:PCBM blend cell increased with the increase in length of carbon chains of the additives. IBu with relatively the longest carbon chain has better performance improving impact than IMe (with the shortest carbon chain). The same trend was observed for fill factor (FF). Other PV parameter, an open circuit voltages (V<sub>oc</sub>) did not show significant change following these solvent additives. The effect of secondary donor addition on PDTSTTz/PCBM system was done by adding different proportions of P3HT. As P3HT (secondary donor) and PDTSTTz (hosting donor) are complementing each other in light absorption, PDTSTTz/PCBM system

containing optimum proportion of P3HT could provide wider range of light absorption and as a result it exhibited higher short circuit current (11.08 mA/cm<sup>2</sup>) and then PCE of 2.42%.

#### I:P06 ZnO<sub>2</sub> Thin Films for Polymer Solar Cells

MYUNG-SEOK JEON, DO-HEYOUNG KIM, School of Chemical Engineering, Chonnam National University, Gwangju, Korea

Polymer solar cell (PSC) is considered as one of the promising candidates for the partial replacement of Si-based solar cell due to its advantages of low cost, easy fabrication, and moderate power conversion efficiency compared Si-based solar cells. However, poor stability of a conventional PSC in ambient condition should be resolved for commercialization. To improve the stability, there has been great attention in the alternative architecture, inverted structures where indium tin oxide (ITO) acts as electron collecting layer by lowering its work function with thin layer of inorganic metal oxides. ZnO<sub>2</sub> is considered as a promising material to improve charge extraction for electrons in PSC. Here, we compare two processes for the formation of the ZnO<sub>2</sub> films and sol-gel based ZnO<sub>2</sub> films. The effect on interface properties, surface morphology, and solar cell parameters with the films prepared by the sol-gel and CVD TiO<sub>2</sub> will be discussed.

#### I:P07 Flux Coating Fabrication of Nitride and Oxynitride Crystal Layers for Photoanode Applied to Solar Hydrogen Production

KATSUYA TESHIMA, SAYAKA SUZUKI, SHUJI OISHI, Shinshu University, Nagano, Japan; T. Ishizaki, Shibaura Institute of Technology, Japan

Photoelectrochemical cell composed of photoanode and photocathode is a device to split water efficiently. The advantage of photoelectrochemical cell is separate generation of oxygen and hydrogen from anode and cathode, water splitting without external bias, and easy operation compared to suspension systems. There, however, are still difficulties to improve energy conversion efficiency. For example, there are no clear synthesis route for high quality materials and difficulty in fabrication of good interface between photocatalyst and current collector which is a resistive layer for carrier transport. In this regards, we attempt to fabricate photocatalyst crystals and crystal layers (= films) by flux method. Flux method is a liquid phase crystal growth technique using molten metals and molten metal salts as solvents. Dissolution and recrystallization of target substance in the high temperature solution promote growth of the high-quality crystals without thermal strains. In particular, we have prepared oxynitride and nitride crystals for the photoelectrodes such as LaTiO<sub>2</sub>N, Ta<sub>3</sub>N<sub>5</sub>, SrTaO<sub>2</sub>N, BaTaO<sub>2</sub>N, and BaNbO<sub>2</sub>N by flux method.

#### I:P08 Grafting of TiO<sub>2</sub> on PMMA Film and Reusability in Photodegradation of Organic Dye under UV and Visible Light Irradiation

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Grafting TiO<sub>2</sub> on PMMA was studied by atom-transfer radical-polymerization (ATRP). Each step in grafting process was monitored by fourier transform infrared spectroscopy (FT-IR), <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra. The glass temperature of grafted-PMMA film was determined by using differential scanning calorimetry (DSC). The morphology and bulk composition were characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). The surface composition was characterized by X-ray photoelectron spectroscopy (XPS). As results, a novel method of grafting TiO<sub>2</sub> on PMMA was successfully grafted and confirmed in various techniques. The photocatalytic activity was evaluated under UV and visible light irradiation. The reusability of TiO<sub>2</sub>-g-PMMA films was studied in details.

#### I:P09 Step by Step toward a Transparent Photo-super-capacitor

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We have combined various nano-structures as nanorods, QDs, thin films of semiconductor materials using deposition techniques following the criterion of low-cost, easily up-scaling and friendly to ambient. We have obtained ZnO nanorods by electrochemical methods and we have combined with QDs of CdS obtained by Spin-Coating Assisted SILAR to study the interaction of n-ZnO and the QDs of CdS with a mean diameter about 5 nm. The interaction between ZnO and CdS QDs/ZnO NRs was evaluated in a photoelectrochemical solar cell configuration with a polysulfide electrolyte under white illumination. The decoration of ZnO NRs with CdS QDs leads to a cell performance of JSC = 2.67 mA/cm<sup>2</sup>, VOC = 0.74 V, FF = 0.30 and η = 1.48%. The next step was to design and to do a pseudo-capacitor with an hybrid nano-architecture obtained by growing hierarchical ZnO NRs@CuS@PEDOT@MnO<sub>2</sub> core@shell heterostructured nanorod arrays on ITO/glass substrates, this structure is shaping as a semi-transparent supercapacitor electrode. We have prepared a glass/ITO substrate of PVP, Poly (3,4 ethylenedioxythiophene) PEDOT, HEMIm[BF<sub>4</sub>], and ZnO hybrid nano- architectures with good electrochemical performance. These hybrid nano-structured electrode exhibits excellent electrochemical performance, with high specific areal capacitance, good rate capability, cyclic stability and diffused transparency.

#### I:HP10 Ni and Ni-M Nanoparticles Supported on Hierarchical Oxides for Methane Dry Reforming Catalysis

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Methane dry reforming (DRM) catalysts with hierarchical nanostructures based on non-precious metal/alloys have been prepared using conventional hydrothermal methods. The hierarchical catalysts are resulted from hydrothermal treatment of SiO<sub>2</sub> nanospheres or Al<sup>3+</sup> salt with the presence of Ni<sup>2+</sup> and the alloy precursor ions. The metal nanoparticles resulted from high temperature decomposition of hierarchical allosilicates or aluminates in hydrogen show a strong metal-support interaction, which corresponds to a superior catalytic performance and a high resistance to sintering and coking of the catalysts during high temperature DRM catalysis. The synthetic mechanisms for the synthetic routes are proposed and discussed.

#### I:HP11 Photocatalytic Semihydrogenation of Triple Bond of Organosilanes without Use of H<sub>2</sub>

Y. KOJIMA, K. HASHIMOTO, H. KOMINAMI, A. TANAKA, Department of Applied Chemistry, Kindai University, Higashiosaka, Japan

Photocatalysis of titanium(IV) oxide (TiO<sub>2</sub>) has been promised to apply to synthesis of organic compounds. Since photocatalysis of TiO<sub>2</sub> occurs at room temperature and atmosphere, photocatalytic reactions are environmentally friendly processes. We have shown various types of conversion of organic compounds over TiO<sub>2</sub> photocatalyst; for example, hydrogenation of nitrile group and deoxygenation of epoxide group. However, most of the papers report conversion of CHONS compounds whereas we focused on organosilanes in this study. Organosilanes having the C=C

bond are useful compounds as surface modification agents and they are synthesized by semihydrogenation of organosilanes having the C≡C triple bond. However, a reducing reagents such as hydrogen (H<sub>2</sub>) gas and undesirable chemicals are necessary for the semihydrogenation. In this study, we examined photocatalytic hydrogenation of organosilanes having the C≡C triple bond to explore the possibility of photocatalysis and found that photocatalytic semihydrogenation of organosilanes occurred without the use of H<sub>2</sub>.

**I:HP12 Chemoselective and Diastereoselective Hydrogenation of Alkynes to Alkenes in an Alcoholic Suspension of a Cu-TiO<sub>2</sub> Photocatalyst without Use of Additives and Reducing Gas**

**H. KOMINAMI, M. HIGA, T. NOJIMA, T. ITO, K. NAKANISHI, K. HASHIMOTO, K. IMAMURA**, Department of Applied Chemistry, Kindai University, Higashiosaka, Japan

Selective hydrogenation (semihydrogenation) of alkynes to corresponding alkenes is important and one of most difficult reactions. This reaction is regarded as a chemoselective reaction because, during the hydrogenation, only the C≡C triple bond should be hydrogenated in the presence of the C=C double bond formed thereof. Lindlar's catalyst, i.e., lead (Pb)-promoted palladium (Pd) supported on calcium carbonate, has been used for selective hydrogenation of alkynes to corresponding alkenes; however, this catalyst system requires undesirable additives, Pb salts and organic bases such as quinoline, to reduce the activity of Pd and increase the selectivity of alkenes and it gives a large amount of undesirable waste. In this study, we examined a new photocatalytic reaction system, i.e., hydrogenation of alkynes in alcoholic suspensions of metal-loaded TiO<sub>2</sub> photocatalysts at room temperature without the use of reducing gas. We found that alkynes were chemoselectively converted to corresponding alkenes over copper (Cu)-loaded TiO<sub>2</sub> without consecutive hydrogenation of the C=C double bond. Notably, internal alkynes were diastereoselectively hydrogenated to cis-alkenes, and alkynes with functional groups were converted to corresponding alkenes, the functional groups being preserved.

**I:HP13 Photocatalytic Chemoselective Reduction of Aromatic Aldehydes in an Ethanol Suspension of TiO<sub>2</sub>**

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When titanium(IV) oxide (TiO<sub>2</sub>) is irradiated by UV light, charge separation occurs and thus-formed electron in conduction band and holes in valence band causes reduction and oxidation, respectively. This redox reaction proceeds at room temperature and under atmospheric pressure. Therefore, photocatalytic reaction is a "green" redox system. We reported photocatalytic chemoselective reduction of nitro aromatics having other reducible groups over TiO<sub>2</sub> using organic acid or alcohol as a hole scavenger. Aromatic alcohols having other reducible groups are produced by chemoselective reduction of corresponding aromatic aldehydes using appropriate reducing agents. However, it is difficult to reduce only the aldehyde group without reducing other reducible groups. Moreover, a conventional reduction of aldehydes by metal hydrides produces waste liquid containing undesirable elements. In this study, we examined the photocatalytic reduction of aromatic aldehydes having other reducible groups using TiO<sub>2</sub> in the presence of ethanol as a hole scavenger under irradiation of UV light, and we found that only the aldehyde group was chemoselectively reduced to a hydroxyl group and that aromatic alcohols having other reducible groups were obtained in high yields without using metal hydrides.

**I:HP14 Synthesis and Evaluation of Plasmonic Photocatalyst Working under Irradiation of Red Light**

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Titanium(IV) oxide (TiO<sub>2</sub>) is a wide band gap photocatalyst (band gap = 3.2 eV) that can induce H<sub>2</sub> formation, decomposition of organic compounds and organic synthesis under ultraviolet (UV) light irradiation. However, UV light accounts for only ~5% of the total solar energy, whereas visible light accounts for ~50% of total solar energy. Therefore, the development of photocatalysts using visible light is an important topic from a practical point of view. In the previous studies, we found that colloidal gold (Au) nanoparticles loaded on TiO<sub>2</sub> (Au/TiO<sub>2</sub>) showed strong photoabsorption at around 550 nm due to surface plasmon resonance (SPR) of Au particles and induced various oxidation-reduction reactions under irradiation of visible light. The development of photocatalysts, which work under irradiation of light with wavelengths longer than λ = 550 nm is important in order to utilize solar energy efficiently. In this study, we examined post-calcination of Au/TiO<sub>2</sub> sample at 1023 K, and found that photoabsorption due to SPR was shifted to longer wavelength (λ = 620 nm). Herein, we report mineralization of oxalic acid to CO<sub>2</sub> under irradiation of red light.

**I:HP15 Decoration of Ultra-long Carbon Nanotubes with Cu<sub>2</sub>O Nanocrystals: A Hybrid Platform for Enhanced Photoelectrochemical CO<sub>2</sub> Reduction**

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Photoelectrochemical (PEC) reduction of CO<sub>2</sub> to form useful chemicals is an increasingly studied avenue for harnessing and storing solar energy. In the quest for efficient and stable photocathodes, nanostructured hybrid assemblies are eminently attractive candidates, because they exhibit multiple favorable properties that cannot be expected from a single material alone. One possible direction is to combine p-type inorganic semiconductors with highly-conductive large surface area supporting electrodes. In this work the controlled synthesis and PEC behavior of carbon nanotube (CNT)/Cu<sub>2</sub>O films for CO<sub>2</sub> reduction is presented. A carefully designed, multiple-step electrodeposition protocol was developed that ensured homogeneous coating of the CNT film (created from mm high CNT forest) with the Cu<sub>2</sub>O nanocrystals. The hybrid films had five-times higher electrical conductivity compared to their pure Cu<sub>2</sub>O counterparts, which drastically increased the measured photocurrents for CO<sub>2</sub> reduction. Long term photoelectrolysis measurements proved that the hybrids were more stable than the oxide alone. The results presented in the poster, together with the established structure/property relationships, may contribute to the rational design of nanocarbon/inorganic semiconductor hybrids for PEC cells.

**I:HP16 Solution Combustion Synthesis of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Parallel Bandgap Engineering through Foreign Ion Incorporation**

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Bandgap engineering is an effective strategy to expand the light harvesting capability of different semiconductor photocatalysts. This can be achieved via either doping or stoichiometric metal ion incorporation. Solution Combustion Synthesis (SCS) is an attractive alternative avenue to prepare such complex materials, compared to other high-cost procedures. This method employs metal salts (mostly nitrates) as oxidants and organic compounds (urea, hexamethylenetetramine) as fuels. The combustion reaction occurring between the reactants is highly exothermic and involves the release of copious amount of gaseous products. Thus the inherent feature of this versatile synthesis technique is its ability to produce crystalline metal oxide nanomaterials in a few minutes of reaction time. Here we specifically present the SCS synthesis of ternary metal titanate (Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>) and the alloying of the parent structure with different foreign metal ions (Fe(III) and Mn(II)). The effect of increasing metal ion incorporation on the structure and optical properties of the resulting materials was studied. Overall, we found that SCS is indeed a lucrative method in terms of fine tuning the optical properties of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>-based semiconductor oxides.

I:HP17 **Solution Combustion Synthesis, Characterization, and Photoelectrochemistry of CuNb<sub>2</sub>O<sub>6</sub> and ZnNb<sub>2</sub>O<sub>6</sub> Nanoparticles**

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One of the most critical challenges of the 21st century is the shift in energy use from fossil fuels to renewable sources. Utilizing sunlight via solar fuels is unambiguously an effective strategy for attacking supply and environmental concerns. The use of photoelectrochemical (PEC) techniques can be suitable for this purpose. Currently, the most important examples of solar fuels are: H<sub>2</sub>, obtained via water-splitting, and high-energy chemicals, such as CO, CH<sub>4</sub>, HCOOH, CH<sub>3</sub>OH, etc., produced by the photochemical or PEC conversion of CO<sub>2</sub>. Thus, our main goal is to find n- and p-type semiconductor materials or assemble nanocomposites which can *efficiently* catalyze these processes. In my poster presentation I am showing the PEC behavior of copper-, and zinc niobate thin films, fabricated on ITO electrodes using spray coating technique. The nanoparticles were synthesized by the time-, and energy-efficient solution combustion technique. The nanoparticles and films were characterized by several techniques, such as: photovoltammetry, stationary measurements (chronoamperometry), TG/DSC, XRD, SEM, HR-TEM, DR-UV-vis and Raman spectroscopy. Along with these measurements, the applicability of the materials in water splitting-, and carbon dioxide reduction reactions was also investigated.

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