1st TYAN International Thematic Workshop report
by
Dr. Mahesh Kumar

Within the framework of the United Nations Sustainable Development Goals (UN's SDGs) in terms of Equality Education, Affordable and Clean Energy, Climate Actions and Partnerships for the Goals, the TWAS Young Affiliate Network (TYAN), for the first time, organizes 1st TYAN International Thematic Workshop on "**Fundamentals of Photoelectrochemistry: From Materials Chemistry to Energy Conversion**" on 23-27th April, 2018, in Chascomus, Argentina.

Goal

A thematic workshop in photoelectrochemistry is assembled because this research area combines photochemical and electrochemical concepts for the study of the photo-induced oxidation-reduction reactions between appropriate materials interfaces. In general, it is the chemistry resulting from the interaction of light with electrochemical systems, and involves the energy conversion from the light into other energy forms. Then, photoelectrochemistry plays a pivotal role in developing renewable energy conversion and storage technology, the main goals of this international workshop are:

- to update the concepts and to share the recent success in solar energy conversion.
- to initiate joint research projects among TYAN members from different continents and local colleagues.
- to establish a network of interactions with synergistic research relationships.
- to build capacity on renewable energy in developing countries.

Topics

- Basic Electrochemistry (an introductory approach)
- Photochemistry
- Introduction to Photoelectrochemistry
- Spectroscopy
- Optical and Electrical Properties of the Interfaces
- Bioinspiration and Key Processes
- Advanced Materials to Energy Conversion
- Renewable Energy Production
- Artificial Photosynthesis, Solar Hydrogen Generation, etc.

Outcomes

As young scientists, we are worried about the future of our planet. We believe that a better future is possible through education, which wiill allow the more conscious use of our precious resources. But, at the same time, we recognize the need for more sustainable ways of producing and harvesting energy. We want to contribute to the development of new, sustainable technologies, to improve the quality of life for people around the world, specially in remote areas, where difficulties are enhanced. In that sense, we propose to work with three main topics: WATER, SOLAR CELLS, HYDROGEN. These three topics belong to a major

challenge that is called SMART VILLAGE. This big project has the aim of planning and developing ways of living which are completely sustainable, clean, with no waist.

The energy crisis is another broad and complex topic. Most people do not feel connected to its reality unless the price of gas goes up. The energy crisis is something that is on-going and getting worse, despite many efforts. The greenhouse effect is another major issue and accounts for global climate change. Carbon dioxide is one of the chief greens house gases responsible and it is prompted, not only uses the green energy sources but also reduce the power consumption. The session was focus on development of clean energy sources and energy efficient devices sensors for environmental gas monitoring.

Presentations:

Oral presentation, session 1: Chairman Dr. Hojamberdiev

[1] Dr. Franco Cabrerizo

Photophysical and photochemical properties of natural dyes for DSSC

Dye-sensitized solar cell (DSSC) is low-cost photovoltaic cell belonging to the group of thin film solar cells. DSSC constitutes an alternative to those based on the use of silicon. These cells are composed of a porous layer of a semiconductor (typically, TiO2 nanoparticles), covered with a molecular dye, and immersed under an electrolyte solution, above which is a platinum-based catalyst (cathode). Although the current devices show a number of attractive features (competitive cost/efficiency ratio, relative low cost of production, among others), there is still plenty of room for improvement. In particular, we are focused on the search of efficient naturally occurring dyes as well as on the evaluation of different strategies to further improve the stability of DSSC when subject to UV radiation. The present talk is aimed to summarize how several highly available spectroscopic techniques such as UV-visible absorption and fluorescence emission spectroscopy can be used to understand/explain the behavior and/or to further optimize the construction of DSSC. Briefly, thermodynamic parameter of the photoelectron transfer processes involved, as well as information regarding the stability and dye's environment under different working conditions can be obtained. In addition, the role and effects of UV-absorbing species represented by a family of naturally occurring alkaloids called β-carbolines is shown and discussed in detail.

[2] Dr. Mahesh Kumar

Self-aligned ZnO nanorods for energy efficient hydrogen sensor

The energy crisis is a broad and complex topic. Most people do not feel connected to its reality unless the price of gas goes up. The energy crisis is something that is on-going and getting worse, despite many efforts. Due to the increase in demand for energy over the past few decades, the resources required to meet these demands are being drastically depleted. There have been several developments in the field of energy conservation. Hydrogen gas sensors are important for utilization of hydrogen as a clean and renewable alternative to carbon-based fuels. Though, there is broad range of hydrogen sensors designed on the basis

of optical and electrical properties of materials, but these sensors are either working at very high temperature (> 150 °C) or incompatible with integrated circuits for sensing device fabrication and reproducibility. The proposed ZnO nanorods based sensor is able to detect hydrogen gas at lower temperature with fast response and recovery times and can be integrated with existing Si based technology. The lower working temperature is necessary for power saving and reduction of risk associated with hydrogen gas. The sensing performance was improved by decorated with optimum concentration of reduced graphene oxide (rGO). The talk will focus on various types of energy efficient gas nano-sensors based on 2D materials and metal oxides.

Oral presentation, session 2: Chairman Dr. de Camargo

[1] Dr. Raquel Giuliam

Semiconductor foams: giant surfaces with tunable properties at nanoscale dimensions

A sponge, or foam, has a significantly larger surface area than a solid piece with same mass, thus favoring surface reactions. Semiconductor nanofoams offer new possibilities for the development of more efficient devices, by exploring the potentiality of semiconductors together with the efficiency of porous materials whose properties are governed by quantum effects. Ternary semiconductor compounds containing In, Ga, Al and Sb exhibit structural parameters that vary as a function of stoichiometry. When antimonide films are irradiated by swift heavy ions, dramatic morphological changes take place, giving rise to semiconductor foams with giant surface area. This presentation is about the development and characterization of semiconductor nanofoams formed by ion irradiation of thin films deposited by magnetron sputtering.

[2] Beatriz Barja

Spectral conversion for solar cells : The potential uses of lanthanide ions

The efficiency of solar cells is limited to 35%, mainly due to spectral mismatch losses. These losses can be reduced by up- and down conversion lanthanides based materials. A brief discussion of the potential uses of these materials.

Oral presentation, session 3: Chairman Dr. Adewuyi

[1] Dr. Ronald Vargas

Kinetic studies in photocatalysis and oxygen transfer reaction.

After introducing the general aspects of the photoelectrochemical oxygen transfer reaction of organic compounds in aqueous solutions, the fundamental and mechanistic theory of these reactions are discussed. Commonly used photocatalytic materials and its characteristics are described considering their performance during the oxidation of some organic compounds. Additionally, kinetic models described in the literature are compared with the proposed formalism, were both mass transport and kinetics of Langmuir-Hinshelwood surface reactions are considered. The Langmuir equilibrium constants and kinetic reaction rate

constants obtained with the rotating disk electrode and the mathematical model developed compare well with the corresponding values determined from independent adsorption isotherm and photolysis studies, respectively, demonstrating that the approach presented appropriately describes the kinetic couplings between mass transport, adsorption-desorption equilibrium, and surface reactions, occurring in processes following the Langmuir-Hinshelwood mechanism. Experimental systems based on wastewater treatment of phenolic effluents are presented as examples, the UV light photocatalytic oxidation on phosphorus modified TiO2 nanoparticles implies a very high efficiency. Finally, the importance of predicting reaction rates, and the physicochemical parameters that describe the chemical interactions during the photocatalytic oxidation of organic compounds in the understanding, design, operation and control of these reactive systems have been envisage.

[2] Dr. Wardemar Marmisollé

Soft Matter Nanoarchitectonics for Electrochemical Applications

The performance of many electrochemical systems critically depends on the electrode surface characteristics. The conjugation of a great variety of soft matter building blocks (polymers, nanomaterials, surfactants) into hybrid electrode coatings has promoted the development of electrochemical devices in several fields from sensors to energy storage and conversion. One of the major challenges of the construction of hybrid coatings is to achieve the appropriate integration of the different building blocks. This issue becomes more critical when dealing with electrochemical applications as the electroactivity of the whole film is a necessary condition, demanding the formation of nanoscale uniform blends. The rational design and construction of nanostructures into functional materials with control at the nanoscale is commonly referred as nanoarchitectonics. In this presentation, we will present some examples of nanoarchitectonics including strategies for the integration of conducting polymers, nanoparticles and other building blocks into functional coated electrodes for some electrochemical applications.

Oral presentation, session 4: Chairman Dr. Adewuyi

[1] Dr. Andrea de Camargo

New approaches to energy efficient light emitting device applications

Global warming concerns, along with the need for energy matrix diversification, have motivated research and development of efficient, sustainable and environmentally friendly technologies for the production and consumption of energy. In the fields of illumination and displays, efficient electroluminescent devices (as light-emitting diodes LEDs and light emitting electrochemical cells LECs) have emerged as alternatives to conventional incandescent and fluorescent lamps. Their low voltage, operational current and power-consumption, in addition to long device lifetimes, high performance, and low cost maintenance, suggest environmental and economic advantages. The heart of the matter is at the development of highly efficient multi-color emitters and effective techniques for device fabrication. New materials based on metal coordination compounds such as Ir(III), Pt(II) and

Cu(I) can play an important role in this field due to their unique features including thermal and photochemical stabilities, a variety of emission colors through judicious molecular design, and high emission quantum yields. Particularly, iridium and platinum complexes, subjected to strong spin-orbit coupling, can harvest generated excitons of both singlet and triplet multiplicity (in opposition to purely organic device layers that can harvest only singlet excitons), yielding enhanced global efficiency. On a further step, modern host guest materials based on the loading of the luminescent guest complexes into versatile, inorganic or hybrid host matrices provide a more flexible platform of application in the bulk, particulate or thin film forms. The solid host provides protection of the molecular active species against exposition to potentialy quenching agents such as O2 and OH-, and it also prevents toxic leakage. For the past five years, the research at LEMAF - Laboratory of Spectroscopy of Functional Materials at IFSC/USP in Brazil, has included the design, synthesis, structural and photophysical characterization of materials based on sol-gel derived mesoporous silicates, alumino- and organosilicates, as well as the nanoclays laponite and bentonite, loaded with complexes. The loading strategies take advantage of host-guest synergies such: i) topotactic modification by ion-exchange of the host with cationic guest species, ii) in situ assembly of MCM-41 structure using CTAB micelles containing metallo-surfactants as structuring agents; iii) ship-in-a-bottle approach for the assembly of complexes in the pores of silicate hosts. An overview of improved emission efficiency results, towards the potential development of lighting devices, will be given.

[2] Dr. Mathías Rafti

Synthesis, characterization and prospect applications of Metal Organic Frameworks

Metal Organic Frameworks (MOFs) are porous materials with high surface areas offering a great deal of flexibility regarding the chemistry of pore walls. In the last few decades successful examples of its use in many important applications such as catalysis, separation, drug delivery or removal of environmental hazardous materials have been presented in the mainstream scientific literature. After a brief introduction summarizing the above discussed points, some selected examples developed in our lab will be presented, the assembly of both films and colloidal suspensions of MOFs, together with possible applications.

Oral presentation, session 5: Chairman Dr. Kumar

[1] Dr. Amal Ibrahim

Functional polymeric materials and nanocomposites for future energy production

Nowadays, saving clean energy production is considered as real challenge as one of the sustainable development goals (i.e. SDGS goals; goal. 7; affordable and clean energy). Accordingly, renewable energy term including solar energy appeared to express about important natural energy resources as the best durable energy resources. However, designing efficient and innovative solar cells to obtain highest capacity and energy production becomes another challenge where finding suitable functional materials is a critical issue. On that way, our research group prepared functional polymeric materials with electric activity. Our

research started by using functional polymeric materials as hyperbranched, dendritic polymers and some polymeric nanocomposites as dielectric and semiconducting materials. Our current and future plans are extending to prepare new polymeric materials as functional conductive materials for solar cells and renewable energy production. Nano-particles are involved in such solar cells to enhance its activity.

Oral presentation, session 6: Chairman Dr. Giuliam

[1] Dr. Mahesh Kumar

UV-Activated MoS2 Based Fast and Reversible NO2 Sensor Working at Room Temperature

Continued growth of industrialization has led to the emission of various toxic and combustible gases. Among them, NO2 is one of the most poisonous gases which are mainly produced by the exhaust of automobiles and power plants. Exposure to even low concentration of NO2 results in several skin and respiratory diseases, so highly selective and sensitive gas sensors are required to detect the presence of ppm level of NO2.The emerged two-dimensional (2D) materials have gained considerable attention in chemical sensing owing to its naturally high surface–to-volume ratio. However, the poor response time and incomplete recovery at room temperature remain a challenge to develop high-performance practical gas sensor. Herein, we report ultrafast detection and reversible MoS2 gas sensor at room temperature. The sensor's performance was investigated to NO2 at room temperature and under thermal as well as photo energy. Incomplete recovery and high response time ~249 sec of sensor were observed at room temperature. Thermal energy was enough to complete recovery but it was at the expense of sensitivity. Further, under photo excitation, MoS2 exhibited an increment in response with ultrafast response time of ~29 sec and excellent recovery to NO2 (100ppm) at room temperature. Moreover, sensor showed reliable selectivity toward NO2 against various other gases. These unprecedented results are discussed based on the degree of charge perturbation on the surface of sensing layer in the context of NO2 /MoS2 interaction under optical-illumination.

[2] Dr. Mirabbos Hojamberdiev

Flux growth of transition metal oxynitride crystals for photocatalytic water splitting

Transition metal (oxy)nitride perovskites with narrow band gaps and suitable band structures are regarded as an emerging class of inorganic materials that can effectively utilize solar energy in the visible light region for photocatalytic water splitting and environmental remediation. We investigated three beneficial approaches for improving the photocatalytic efficiency of oxynitride perovskites: (i) to reduce the defect density and to improve visible-light-driven photocatalytic water oxidation activity by applying an NH3-assisted direct flux growth method, (ii) to enhance the visible-light-driven photocatalytic water oxidation activity by bandgap engineering (tungsten doping), and (iii) to explore tungsten-based oxynitride perovskites (AW(O,N)3, A = Sr, La, Pr, Nd, and Eu) as novel materials for visible-light-driven photocatalytic water oxidation. The findings evidenced that the direct flux growth method and tungsten doping improved the photocatalytic water oxidation activity.

Oral presentation, session 7: Chairman Dr. Ibrahim

[1] Dr. Adewale Adewuyi

Green Chemistry: A tool to sustainable development in Africa

With the increasing human population, industrialization, environmental concerns and depletion in supply of nonrenewable resources, Africa needs to develop new process routes, synthetic methods, analytical tools and policies that are more affordable, reliable and safer. Green chemistry can play a pivotal role in making this a reality with sustainable path that meets current scientific and technological development without compromising the progress and success of future generation. The fundamentally attractive concept of green chemistry is solvent free reactions. These are interesting alternative approach, mainly when this condition eliminates the use of a solid support or solvent from reaction. When less waste is generated, environmental compliance casts go down while treatment and disposal become unnecessary. In our studies, we have developed a route for biodiesel production from underutilized seed oils. The process was monitored with FTIR and NMR. Further evaluations with biomass in environmental studies were characterized using X-Ray difractometer, TG, SEM, Particle size analyzer, CHN and BET. This has shown interesting results in waste water treatment and corrosion control as the processes are green, cheap and sustainable. Our finding has revealed that green chemistry is the key to a less polluted and safer environment in Africa.

[2] Dr. Hernán Grecco

Sensors and actuators to understand 3D organization of living matter

Cellular function emerges from the concerted action of nanometer-sized molecules. From their mobility and interaction, micrometer-sized patterns are formed. In turn, these patterns modulate the same interactions that create them, connecting spatial and temporal scales. Understanding how cellular function emerges from such simultaneous upward and downward causation requires going beyond the phenotype to quantify cellular processes with molecular resolution. In this talk I will describe our efforts towards understanding spatial organization of living matter. Achieving this goal requires novel imaging and analysis techniques that are able to cope with the variance of biological systems.

Oral presentation, session 8: Chairman Dr. Cabrerizo

[1] Dr. María Mangione

Nanotechnology and nanochemistry: innovation and development of novel materials

In the present lecture will briefly describe the design and synthesis of dendrimeric pi-conjugated macromolecules containing electroactive terminal moieties such as triphenylamine and carbazole and the optoelectronic properties of the monomers and the electrogenerated films.