## Energy Harvesting & Storage
## Room Naupaka Salon 5 - Session EH-WeM

### Efficient Power Conversion/Cells

**Moderator:** Paul Braun, University of Illinois at Urbana-Champaign, USA

8:00am **EH-WeM-1 Linear and Multi-photon Fluorescence of Thiophene based Copolymer as Novel Potential Material for Photovoltaics***, L Slusna,* Comenius University, Bratislava, Slovakia*; L Haizer,* International Laser Center, Bratislava, Slovakia*; E Jane,* Institute of Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia*; D Bondarev,* Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia*; V Szocs, M Drzik,* International Laser Center, Bratislava, Slovakia*; E Noskovicova,* Comenius University, Bratislava, Slovakia*; D Lorenc,* International Laser Center, Bratislava, Slovakia*; M Jerigova,* ***Dusan Velic,*** Comenius University, Bratislava, Slovakia

Currently, the most important applications for polythiophenes are in the area of solar cells, thin-film transistors, light-emitting diodes, sensors and nonlinear optics with low-cost and low-temperature processing [1]. On the other hand, polythiophenes show a great promise also in the area of nonlinear optics and photonics [2] with enhanced second and third order nonlinearities. Hence, dynamics of polythiophenes gained an increased interest, because it is providing detailed understanding of the complex processes occurring in π-conjugated polymers.

A novel copolymer (poly(thiophene-2,5-diyl-2,5-di-n-octyloxycarbonyl-1,4-phenylene)) denoted as P33 is introduced as a potential material for photovoltaics. P33 dissolved in chloroform was investigated by steady-state absorption, linear/non-linear fluorescence spectroscopies and time-resolved fluorescence spectroscopy.

Molar extinction coefficient of P33 was determined as 18315 $cm^{-1}.M^{-1}$. The P33 fluorescence quantum yield and P33 singlet fluorescence lifetime were determined as 0.4 and 810 ps, respectively. The P33 fluorescence fast decay component shows decay times of 1.2 ps, 2.0 ps, and 0.5 ps for increasing wavelengths of 480 nm, 500 nm, and 520 nm, respectively. The fast component has been previously attributed to transport of nearly instantaneously formed excitons to localized states known as downhill energy transfer. Multi-photon excited fluorescence has been observed for the P33 solutions in chloroform and for 800 nm and 1200 nm pumping. The P33 TPA cross-section was evaluated as 6.9 GM. This spectroscopic study provides basic fluorescence characteristics of the novel thiophene copolymer P33.

This work was supported by VEGA 1/0400/16 .

**References**

[1] I. Etxebarria, J. Ajuria, R. Pacios, Solution-processable polymeric solar cells: A review on materials, strategies and cell architectures to overcome 10%. Org. Electron. 19 (2015) 34–60.

[2] P. N. Prasad and D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, John Wiley & Sons, New York, 1991, ISBN 0-471-51 562-0

8:20am **EH-WeM-2 Novel Semi-Transparent Inorganic $Sb_2S_3$ Thin Film Solar Cells***,* ***Shi-Joon Sung****, S Lee, K Yang, J Kang, D Kim,* DGIST, Republic of Korea

In recent years, researches on transparent photovoltaics has been attracting immerse interests as a key component of multifunctional window applications. Until now, there were enormous researches on transparent photovoltaics were based on organic materials, such as dye sensitized solar cell (DSSC) or organic solar cell (OSC), because of wide bandgap of the organic materials. However, these organic-based transparent solar cells are still suffering from the stability problem, which is one of critical obstacles for the commercialization of organic-based solar cells. In order to overcome this problem, some researchers are nowadays interested in the inorganic-based transparent solar cell technologies, such as ultra-thin film solar cells, patterned aperture solar cells, and so on. However, in these cases, device fabrication process is complicated and the device performance is limited because of restricted physical dimensions.

Because inorganic $Sb_2S_3$ has wide bandgap (1.6 ~ 1.8 eV) and higher absorption coefficient ($10^5$ cm) compared with other inorganic materials, $Sb_2S_3$ might be a good candidate for inorganic semi-transparent absorber materials. In our work, we adopted ultra-thin and high quality $Sb_2S_3$ thin films as a semi-transparent absorber layer. The high quality $Sb_2S_3$ thin films with different thickness were deposited using atomic layer deposition (ALD) technique, which showed bandgap of 1.78 eV, absorption coefficient of $1\times10^5$ cm, and light transmittance up to 30 %. In order to fabricate semi-transparent solar cell devices, ALD $Sb_2S_3$ thin film with 80 nm thick were firstly deposited on transparent TiO/ITO substrates. Transparent P3HT and ultra-thin transparent Au electrode were also deposited onto the ALD $Sb_2S_3$ thin film. This semi-transparent $Sb_2S_3$ solar cell device showed power conversion efficiency of 3.44% and average light transmittance (from 400 to 800 nm) of 13%. The semi-transparent $Sb_2S_3$ solar cell device also showed excellent device stability over 180 days, which might be attributed to the inorganic $Sb_2S_3$ absorber material. Semi-transparent inorganic thin film solar cells based on $Sb_2S_3$ has a great potential to be a novel robust and stable transparent solar cell technology.

8:40am **EH-WeM-3 In situ Scanning Tunneling Microscopy of the Electrocatalytic Reactions***,* ***Dong Wang,*** ICCAS, China

The electrocatalytic reactions at the electrode/electrolyte interface play a critical role in the performance of electrochemical energy storage and conversion devices. Understanding the structure and reaction processes at solid/liquid interface is of great importance in surface science and electrochemistry. In view of the dynamic and complex nature of the interface, in situ research approaches can provide valuable information of interfacial phenomena. In situ scanning tunneling microscopy (STM) is a powerful technique used for the interfacial investigation of electrochemical energy devices.

In this presentation, we employed high resolution electrochemical STM to investigate the typical electrochemical catalytic reactions, such as oxygen reduction reactions, oxygen evolution reactions, using the model molecular catalysts. The self-assembled metal porphyrin and phthalocyanine compounds show notable electrocatalytic activity. The real-time STM imaging provides direct evidence to study the interfacial electrochemical reactions at molecular level.

1. Gu, JY; Cai, ZF; Wang, D; Wan, LJ. ACS Nano. 2016, 10, 8746-8750.

2. Cai, ZF; Wang, X; Wang, D; Wan, LJ. ChemElectroChem, 2016, 3, 2048-2051.

9:00am **EH-WeM-4 Fabrication of Free-standing Thin Film by Injecting Polymer into Porous Substrate for Thin Film Solid Oxide Fuel Cells***,* ***Yusung Kim****, S Cha, W Yu, W Jeong, J So,* Seoul National Univeristy, Republic of Korea

Free standing thin films were fabricated by injecting polymer into porous substrate for thin film solid oxide fuel cells(TF-SOFCs). To apply thin film on porous substrate with pores of more than 1 micrometer, anode functional layer(AFL) is needed to reduce pore size. However, it is difficult to supply gas when the AFL is thickened due to the reduced pore size and porosity. To solve this problem, free standing under 1 micrometer thin film AFL was fabricated on a porous support. Based on the Si-based free standing thin film sofc, which is a field of TF-SOFCs, the pores of the porous NiO-YSZ support were blocked through injecting polystyrene, the NiO-YSZ thin film was deposited thereon, and the polystyrene was removed to make the free-standing thin film by pyrolysis. The pore blocking through the polymer was obviously a major influence on the thin film covering the pore. On the other hand, since the pore size of the support is about 10 µm, the pore size is not reduced when the thin film is deposited without pore blocking. In the process of melting and solidifying into a liquid to insert the polymer, a nanoscale gap was created due to the volume change due to the phase change, and the thin film deposited thereon also has this shape. Also it is verified that the NiO-YSZ thin film was successfully fabricated on the porous NiO-YSZ substrate by FIB-SEM analysis.

9:20am **EH-WeM-5 First-Principles Study on Influence of Metal Oxide on $H_2S$ Poisoning Tolerance of Pt Nano-Particle Catalyst in Polymer Electrolyte Fuel Cell***,* ***Kota Kuranari****, N Miyazaki, Y Ootani, N Ozawa,* Tohoku University, Japan*; M Kubo,* Institute for Materials Research, Tohoku University, Japan

Pt catalysts are used as anode catalysts for polymer electrolyte fuel cell (PEFC). The fuel in PEFC contains a small amount of impurities such as CO and $H_2S$. These impurities adsorb on active sites of Pt surfaces and degrade the hydrogen oxidation reaction activity of the anode catalyst. This loss of catalytic activity caused by impurities is known as impurity poisoning. Therefore, the development of the anode catalyst with the high impurity tolerance is strongly required. Takeguchi et al. experimentally found that adding $SnO_2$ as support material improves the CO tolerance of the Pt-based catalyst[1]. Furthermore, it is known that adsorbed impurities on the Pt catalyst can be removed by oxidation reaction. Kakati et al. reported that oxidation reaction by O and OH can recover from the $H_2S$ poisoning[2]. In order to develop the high impurity tolerant catalyst, it is necessary to reveal the effect of $SnO_2$ nano-particles on $H_2S$ tolerance and the recovery mechanism from $H_2S$ poisoning by oxidation reaction. In this study, we analyzed the adsorption states of $H_2S$ on $Pt/SnO_2(110)$ model and the recovery process from $H_2S$ poisoning by oxidation with OH using first-principles calculation.

For the calculation model, we put a $Pt_{29}$ cluster on $SnO_2(110)$. The $Pt_{29}$ cluster exposes Pt(111) on the top (See supplementary document Fig. 1). We calculated the adsorption energy of $H_2S$ on $Pt/SnO_2(110)$ and compared with the one on Pt(111) to reveal the effect of $SnO_2$ on $H_2S$ poisoning process. The adsorption energies of $H_2S$ were -18.38 and -24.73 kcal/mol on the Pt cluster of $Pt/SnO_2(110)$ and Pt(111), respectively. Thus, it was found that the adsorption of $H_2S$ on Pt is suppressed by addition of $SnO_2$. Next, we analyzed the recovery process from $H_2S$ poisoning by OH generated from dissociation of $H_2O$. It is known that $H_2S$ adsorption on Pt is dissociative and adsorbed sulfur atom is generated. The sulfur atom adsorbed on the surface decreases the activity of the Pt catalyst. In this study, we considered the reaction process (See supplementary document Fig. 2) based on the intermediate stable species during the $H_2S$ oxidation cascade in the gas phase[3] and calculated the activation energies of each elementary process. We found that the water dissociation is the rate-determining step on both $Pt/SnO_2(110)$ and Pt(111) and the activation energies were 18.78 and 23.70 kcal/mol, respectively. Therefore, we demonstrated that an addition of $SnO_2$ promotes an oxidation reaction of adsorbed sulfur on the Pt catalyst.

1) T. Takeguchi, et. al., Catal. Sci. Technol. 6, 3214 (2016).

2) B. K. Kakati, et al., J. Power Sources 252, 317 (2014).

3) F. Tureček, et al., J. Am. Chem. Soc. 118, 11321 (1996).

### 9:40am **EH-WeM-6 Impurity Tolerance of Pt/ Metal-Oxide Anode Catalyst for Polymer Electrolyte Fuel Cell: First-Principles Calculation***, Nobuki Ozawa, K Kuranari, M Kubo,* Tohoku University, Japan

Polymer electrolyte fuel cell (PEFC) needs anode materials with high tolerance to poisoning by impurities such as CO, $NH_3$, and $H_2S$ in the fuel, which degrades performance of the PEFC. Recently, a composite of Pt and $WO_3$ ($Pt/WO_3$) is used as a catalyst in the anode, and this catalyst is effective for CO removal by oxidation [1]. For theoretical design of anode materials with high tolerance to impurity poisoning, the mechanism of high tolerance of $Pt/WO_3$ to CO should be revealed. In this study, we investigated CO oxidation processes on $Pt/WO_3(001)$ by first-principles calculation. At first, we calculated the adsorption energies of CO on $Pt/WO_3(001)$ and an isolated Pt cluster, to discuss an effect of $WO_3$ on CO tolerance of Pt. For a $Pt/WO_3(001)$ model, a $Pt_{20}$ cluster is put on a $WO_3(001)$ surface. The adsorption energy of CO on the $Pt_{20}$ cluster is 36.40 kcal/mol, while that on an isolated $Pt_{20}$ cluster is 45.65 kcal/mol. These results indicate that the combination of the $WO_3$ surface and Pt cluster decreases the adsorption energy of CO on the Pt cluster. To investigate the reason why the adsorption energy of CO decreases by the $WO_3$ surface, we calculated d-band center [2] of the Pt atom on $Pt/WO_3(001)$ and Pt cluster. In general, downward shift of the d-band center increases the adsorption energy of CO. Here, the d-band center values of the Pt atom on $Pt/WO_3(001)$ and isolated Pt cluster are -2.28 and -2.15 eV, respectively. This means that $WO_3$ modifies the electronic states of the Pt cluster and leads to the downward shift of the d-band center, which decreases the adsorption energy of CO. Next, we discuss CO oxidation on $Pt/WO_3(001)$. The CO oxidation by $H_2O$ proceeds as follows; (i) $H_2O \rightarrow OH^- + H^+$ and (ii) $CO + OH^- \rightarrow CO_2 + H^+ + 2e^-$. Here, we firstly investigated $H_2O$ dissociation on $Pt/WO_3(001)$. In this calculation, the $H_2O$ molecule adsorbs on the interface between the Pt cluster and $WO_3(001)$ surface, and dissociates to $H^+$ on the Pt atom and $OH^-$ at the interface. The activation energy for the $H_2O$ dissociation is 19.87 kcal/mol, which is lower than that on a pure Pt(111) surface (23.70 kcal/mol). Thus, we suggest that $WO_3(001)$ can decrease an adsorption energy of CO and activation energy for $H_2O$ dissociation on Pt catalyst during CO oxidation process.

[1] P.-Y. Olu, et al., *Electrochem. Commun.*, 71, 69 (2016).

[2] B. Hammer, et al., Catal. Lett., 46, 31 (1997).

### 10:20am **EH-WeM-8 Harvesting Sunlight for Photoelectric and Photothermal Conversions with Titanium Nitride Nanostructures***, Satoshi Ishii,* National Institute for Materials Science, Japan*; S Shinde, R Sugavaneshwar, M Kaur, T Nagao,* National Institute for Materials Science **INVITED**

Harvesting sunlight enables conversion of photon energy to electronic energy and thermal energy. Among different classes of materials, metals have unique properties in light harvesting. Since metals are highly conductive and do not have bandgaps, metals can generate hot carriers even with low energy photons to be injected into an adjacent semiconductor. The excited hot carriers eventually become heat and heat the metals themselves and their surroundings. These photoelectric and photothermal effects can be enhanced by the optical resonances i.e. surface plasmon resonances. Hence, number of researches have taken advantage of plasmon resonances in photoelectric and photothermal conversions. As gold and silver are known to be excellent plasmonic materials, nanostructures made of these noble metals have been widely used in the recent studies.

In contrast, we have been working with titanium nitride (TiN) nanostructure to show that it can also be used in photoelectric and photothermal conversions. Titanium nitride is chemically stable and much cost-effective than gold or silver, making it a practical choice of material. In addition, TiN is plasmonic in visible and near infrared and superior to gold and silver in absorbing broad spectrum. In the first part, we present that TiN nanostructures can generate photocurrent by the irradiation of visible light, and can enhance the visible photocatalytic activities of carbon nitride which is a UV-active metal-free photocatalyst. In the second part, we show that TiN nanoparticles are efficient sunlight absorbers to generate solar heat. Since each TiN nanoparticle act as a nanoscale heater, solar heated TiN nanoparticles offer efficient water distillation and chemical reactions such as oxidation of carbon monoxide. Our results demonstrate that TiN nanostructures have the potential to replace gold and silver nanostructures in sunlight harvesting applications with better efficiencies.

### 11:00am **EH-WeM-10 Solar Printing: From Benchtop to Rooftop***, Paul Dastoor,* University of Newcastle, Australia **INVITED**

Organic photovoltaics (OPV) are poised to play a major role in the global energy portfolio driven by their capability to be printed at high speeds across large areas using roll-to-roll (R2R) processing techniques; creating the tantalising vision of coating every roof and other suitable building surface with photovoltaic materials at extremely low cost. Indeed, recent full economic modelling of the balance of materials (BOM) and balance of system (BOS) costs, have highlighted the long-term commercial viability of OPV-based technology in today's energy marketplace.

However, the chlorinated solvents that are used in current OPV technology are under continual regulatory pressure due to their hazardous and toxic nature. Indeed, increasingly harsh technical requirements for using these solvents means that their implementation in high speed printing lines will be highly problematic if not economically impractical. In addition, tailoring device morphology across large areas is fraught with difficulty due to the challenge of controlling phase segregation of polymer mixtures using conventional printing. Water-based polymer nanoparticle dispersions (solar paint) offer the prospect of simultaneously controlling the nanoscale architecture of the active layer whilst eliminating the need for hazardous organic solvents during device fabrication. However, the behaviour of these nanoparticulate devices is complex and thus understanding their structure-function relationships requires characterisation techniques that can probe chemical structure on the nanoscale. In this paper we review our progress in understanding the structure-function relationships of organic electronic nanoparticulate thin films. In particular, I will discuss how scanning transmission X-ray microscopy is an invaluable tool for characterising these materials.

Finally, I will explore the future prospects and economics for large scale manufacture of solar cells based on printing. I will discuss our recent achievements in the development of a fully operating R2R printing line and the installation of several large scale (> 100 $m^2$) demonstrations of printed solar modules.

# Author Index

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