

**Tuesday, December 10<sup>th</sup>**

**Session: SOLAR ENERGY: PHOTOCATALYSIS &  
PHOTOVOLTAICS**

*Givry-Savigny room*  
**14h15 - 17h30**

**Keynote speakers:**

**14h15: Hynd REMITA**

*Conjugated Polymer Nanostructures for Photocatalysis under Visible-Light*

**16h00: Philip SCHULZ**

*Interfaces and stability of halide perovskite semiconductors*

## Abstracts



**Thematic Session:** Solar energy

**Keywords:** gold, plasmon, CH<sub>4</sub> vs. H<sub>2</sub> selectivity, CO<sub>2</sub>, artificial photosynthesis

## Highly selective plasmonic CO<sub>2</sub> photoreduction with water over gold-containing photocatalysts

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The direct conversion of solar energy into valuable chemical fuels is a great challenge for clean energy production. In this context, the photocatalytic upgrade of carbon dioxide into methane via photoreduction with water appears as a sustainable way of turning a human emission waste into valuable synthetic natural gas [1]. The mechanism involves oxidation of water into protons and the transfer of 8 electrons and 8 protons to CO<sub>2</sub>. The reduction of the proton however severely competes with the reduction of CO<sub>2</sub>, as only 2 electrons are needed to produce H<sub>2</sub>. A maximum selectivity to methane of 90% (based on electron utilization) is observed in processes driven by titania semi-conductors, which involve photoinduced electron-hole pairs generated within the bulk crystalline structure. We have recently identified key structural features for Au/TiO<sub>2</sub> nanocomposites to achieve 100% selectivity to methane under pure visible irradiation ( $\lambda > 420$  nm) [2]. This unprecedented selectivity was clearly induced by the excited plasmonic gold nanoparticles (Au NPs). Au NPs indeed exhibit a localized surface plasmon resonance (LSPR) at about 550 nm. This unique selectivity was however associated with low methane production rates (few nanomoles per square meter per hour). Here we will present new gold-based nanostructures, including Au/graphene composites, which can achieve methane vs. hydrogen full selectivity under solar illumination at much higher methane production rates. The key features of the LSPR-driven mechanism, such as e.g. facilitation of CO<sub>2</sub> vs. H<sub>2</sub>O adsorption [3], will be highlighted.

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**Thematic Session:** (Nanophotonics & nano-optics)

**Keywords:** (sol-gel, one-pot synthesis, biotemplate, cellulose, hydrogen energy)

## One-pot Sol-Gel Self-biotemplating Assembly of Metal Oxides: Original approach for Photocatalyst Design

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Solar energy conversion using photocatalysis becomes a subject of great interest with important potential applications in environment, such as chemical fuel production (H<sub>2</sub>).<sup>[1] [2] [3]</sup> Titanium dioxide (TiO<sub>2</sub>) is the most popular semiconductor used in photocatalysis. However, TiO<sub>2</sub> has a large band gap and can only be excited by UV light. Furthermore, the fast recombination of electron-hole pairs lowers the solar energy conversion efficiency. Design of photocatalysts with 3D structure appears as a promising strategy to increase the production of electron/hole.<sup>[4] [5]</sup> In this aim, sol-gel chemistry and biotemplate nanomaterial (cellulose nanocrystals CNC) were combined for one-pot generation of chiral photocatalysts. This approach enables the improvement of light harvesting ability of the material. Evaporation-induced self-assembly (EISA) method produces iridescent hybrid films in which the chiral nematic arrangement of CNC is preserved. The morphological, textural and structural properties of the final photocatalysts were characterized by coupling SEM, BET, POM, WAXS, XPS and TRMC measurements. The effect of the CNC/TiO<sub>2</sub> ratio as well as the coupling with nanoparticles based on abundant metals (Cu, Ni, Bi) were evaluated for hydrogen generation. We found that structuration of the photocatalyst and its modification with non-nobel metal nanoparticles enhance light harvesting, charge carriers density and separation reaching higher photon to energy conversion compared to other morphologies of TiO<sub>2</sub>.

### References

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**Thematic Session:** Solar Energy

**Keywords:** Water photooxidation, solar fuel, ALD

## Surface Nanostructuring and Functionalization for Efficient Water Photooxidation

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Water photosplitting is a promising way to transform the solar irradiation into a storable and transportable fuel (e.g.  $H_2$ ). Si can be used as photoanode because it absorbs in the visible range and its electronic structure is suitable to drive water photooxidation. Though, Si suffers from a strong corrosion in KOH and a high reflectivity. The strategy is to combine Si microstructuring with ALD of a protective layer.  $TiO_2$  is combined to Si due to its absorption in the UV range and its stability at high pH.  $TiO_2$  is grown using TTIP and TDMAT at various temperatures (70-250°C) and annealed at 450°C. Numerous surfaces analyses have been employed to compare the physico-chemical properties. The influence of precursor nature and the temperature has been correlated to the Si/ $TiO_2$  photoelectrochemical performances. The best layers (stability and efficiency) are achieved when  $TiO_2$  is grown from TDMAT at 150°C. To further increase the efficiency a co-catalyst must be added. Ni is often associated to Si/ $TiO_2$  due to its low cost and high activity. Usually, metallic Ni is deposited by PVD or electrodeposition but the quality of the films is not fully satisfying on tortuous substrates. Here a two-steps process has been developed: (i) conformal ALD of NiO on the nanostructured Si/ $TiO_2$  photoanode and (ii) reduction to Ni by an annealing under  $H_2$ . In this case the efficiency of the multilayered photoelectrode is drastically improved ( $\times 300$ ). This approach has been extended to another microstructured heterojunction Si/ $Fe_2O_3$ . Higher photoelectrochemical performances have been evidenced on hematite.



**Thematic Session:** Solar energy

**Keywords:** photoelectrochemistry, water splitting, electrodeposition, bismuth vanadate

## BiVO<sub>4</sub> photoanodes prepared by alkaline electrodeposition, enhanced with Fe co-catalysts for solar water splitting

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Water electrolysis can be used for producing H<sub>2</sub> with a high degree of purity, which is a promising approach for the long-term storage and transport of solar energy (1,2). To make an efficient photoelectrochemical cell, it is important to have a photoanode (performing oxidation of water in O<sub>2</sub>) having a high conversion efficiency and based on abundant and inexpensive materials. Among the semiconductors, *n*-type bismuth vanadate (BiVO<sub>4</sub>) has attracted a considerable attention thanks to its absorption in the visible spectrum (E<sub>g</sub> = 2.4 eV) and its sufficiently low valence band (3-5). BiVO<sub>4</sub> is based on relatively abundant materials and can be manufactured by inexpensive processes. On the other hand, BiVO<sub>4</sub> suffers from a poor electron-hole separation (6,7) and low kinetics for water oxidation. In this work, we have developed a new technique for depositing Bi<sup>0</sup> on a transparent conductive oxide in alkaline solution, and the bismuth deposit was converted into BiVO<sub>4</sub>. After the demonstration that such BiVO<sub>4</sub> electrodes can be effectively used as photoanodes, we have studied the effect of an amorphous FeO<sub>x</sub> catalyst layer, deposited by a simple and general method and we have demonstrated its effectiveness on our BiVO<sub>4</sub>. After coating the photoanode the activity considerably increased, as demonstrated by the decreased onset potential and the improved fill factor (8).

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**Thematic Session:** Solar energy

**Keywords:** Kesterite, semi-transparent, solar cells, alloying

## Alloying of pure sulphide Kesterite in semi-transparent solar cells: towards the tandem integration with crystallin silicon

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**Abstract:**

The kesterite compound called  $\text{Cu}_2\text{ZnSnS}_4$  or CZTS, derived from abundant and non-toxic raw materials, is a promising candidate using as an absorbent layer in thin-film solar cells. Its high band gap energy, make it one of the best absorbent materials for use in the top cell for the tandem configuration. However, Kesterite solar cells still suffers from a low conversion efficiency due to the large defect of the open-circuit voltage  $V_{oc}$ , result from the easy formation of anti-site defects, the disorder in Cu/Zn plane and the non-ideal bands alignment at the heterojunction.

Kesterite alloy is new strategy of partial cations substitution with other elements. This approach aims to improve the properties of this type of solar cell by reduce the anti-site defects and Cu/Zn disorder, improve the grain size and ameliorate the charge separations at the heterojunction.

In this work, thin films of silver alloy kesterite (CAZTS) were layered on glass substrates from sol-gel solution by spin coating followed by a heat treatment under sulphide. The heterojunctions were fabricated by chemical bath deposition (CBD) of CdS on the surface of CAZTS films. The microstructural, optical and electronic properties of obtained films and junctions were characterised by different techniques. The silver alloy kesterite films, were integrated for optical properties evaluation into semi-transparent solar cells.

This type of configuration, semi-transparent CAZTS solar cells, developed in this work, opens the way to the future integration with silicon for high performance CAZTS / Si tandem cells.



**Thematic Session:** (nanomaterials)

**Keywords:** (photovoltaic, thin film, nanomaterials, simulation)

## Study of Photovoltaic Cells based on Nanomaterials

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**Abstract:** In this study Gallium-Indium Nitride (InGaN) is used to obtain a high efficiency solar cell. So an optimization of the critical parameters of the cell was carried out using COMSOL-Multiphysics simulations. GaN/Grad  $\text{In}_x\text{Ga}_{1-x}\text{N}$ /  $\text{In}_x\text{Ga}_{1-x}\text{N}$ /Grad  $\text{In}_x\text{Ga}_{1-x}\text{N}$ /ZnO graded layer nanostructure with 40nm thicknesses for GaN and ZnO, 100nm for the InGaN active layer and 60nm for the graded layers, been used. N-doping of  $10^{15}$  in the InGaN layer and  $10^{18}$  in the GaN layer. Carrier mobility is calculated using the Caughy-Thomas model. The Maxwell-Boltzman statistic was used to define the diffusion of electrons in energy levels. Recombinations of Shockley-Read-Hall (SRH) to model losses in our structure were taken into account. The SRH lifetime of the electrons and holes is set at  $1.7 \cdot 10^{-9}$  s and  $0.65 \cdot 10^{-9}$  s respectively, the mobility coefficients at 1.5 and optical capture at  $1.1 \cdot 10^{-8} \text{ cm}^{-2}\text{s}^{-1}$  for both materials used (GaN, InGaN). The simulation results show that in this structure the potential wells no longer exist; expansion of the gap; possibility to adapt the energy gap of the material by adjusting the atomic ratio In/Ga. With the variation of the thickness of the active layer  $\text{In}_x\text{Ga}_{1-x}\text{N}$  between 25nm and 700nm, the efficiency of the structure for different concentrations x of indium was studied. The best yield was obtained for 400 nm and x = 55%.

**Thematic Session: Solar Energy, Surface & interface at the nanoscale, Nanomaterials**

**Keywords:** ferrocene, rectification, click chemistry, SAM

### Achieve rectification of current by ferrocenyl triazole derivates

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Rectenna solar cells are electronic devices which were described for the first time in the 70s and these devices allow transforming light into electricity, thanks to the association of a nano-antenna and a rectifying element. Due to the size of the device and the challenge of rectification of the terahertz frequencies, the realization of such devices remains difficult.

Rectification of current by molecules is a really active research field due to the possibility to drastically reduce the size of electronic devices. Theorized by Aviram and Ratner, the rectification can be achieved by an asymmetric molecule, enabling the electrons to be transferred in a preferential direction through the compound. The state of the art of the organic molecular rectifiers shows rectification ratios up to  $10^5$ . Such ratios were obtained with molecules composed of a ferrocene unit, which is the key for the rectification process, linked to an insulating alkyl chain. At present, only few studies have been devoted to control the orientation of the molecular rectifiers. More precisely, the possibility to anchor onto two different electrodes while controlling their orientation has only been scarcely investigated. In our case, such a control of the molecular orientation has been obtained by developing a two-step process based on Click Chemistry.

Here, we present unprecedented works on the synthesis of new ferrocene derivatives designed as molecular rectifiers. Especially, a special effort is devoted: firstly, to allow the molecule to be covalently linked to two metal electrodes (allowing implementation into future device) and secondly to definitely control the orientation of the molecular rectifier relative to both electrodes thanks to Click Chemistry.