

EERA AMPEA meeting
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Talk 1: The in-gap band concept in photocatalysis: mimicking the photosynthesis Z scheme with a single material

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Abstract

Recent work of ours has proposed, based on DFT results, several formulations of single-phase materials which, due to an electronic structure having a narrow, partially filled band inside the gap (in-gap band, IGB), may couple two low energy photons to achieve a higher energy electronic excitation (like in the Z-scheme used by nature in photosynthesis), allowing use of a wider spectral range of solar energy and therefore 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 adding V to In_2S_3 (with $\text{gap}=2.0$ eV) extends to <1.6 eV both photon absorption and spectral response in aqueous HCOOH photocatalytic oxidation. This is not due to bandgap narrowing: the material displays photo-luminescence (PL) emitting 2.0 eV photons not only if irradiated with photons having $E>2.0$ eV (as happens with pure In_2S_3), but also with those in the said <1.6 eV range, i.e. upconversion occurs [1].

The observed PL intensity grows linearly, not quadratically, with the intensity of the exciting photons in the $E<2.0$ eV range; it is also not seen when these have energies 1.55 eV $>E>1.0$ eV. Both things discard that it is due to frequency doubling, being explained instead by partial filling of a properly placed IGB, confirmed by advanced GW quantum calculations. Furthermore, both PL and photocatalytic activity with exciting photons having energy >2.0 eV are not degraded by adding V, i.e. the latter does not lead to higher recombination, explained by the delocalization of the IGB.

Same principle should be utilizable in H_2 photogeneration. Work to allow the latter process by coupling the sulphide photocatalyst to a hydrogenase enzyme is under way, and promising results are being obtained.

[1] R. Lucena et al., J. Mater. Chem. A 2 (2014) 8236.

Talk 2: Electrochemical Reduction of CO₂ by N-Doped Graphene – Highly effective binding sites and pathways to chemicals

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Abstract

CO₂ storage and conversion are important steps towards cost-effective low-carbon energy supply. Electrochemical or photochemical production of CO₂ can provide useful chemicals, such as hydrocarbons, alcohols, organic acids and carbon monoxide. However, challenges remain in highly efficient CO₂ conversion at least on two aspects: CO₂ activation is rather difficult; and high overpotential and low selectivity for conversion products. Therefore, catalysts are investigated with a strong focus on efficiency of CO₂ conversion in recent years, most of which are noble metals, metal oxides and metal-organic complexes. Current emphasis focuses on cost-effective metal-free catalysts to substitute noble metals.

Here, we employ a first-principles simulation strategy to identify mechanistic insights of oxygen reduction catalysts by combining electronic structure, formation energy of intermediates and kinetic activation barriers in our calculations.¹ Different reaction pathways were studied and possible active sites were screened on N-doped graphene/CNT catalysts for CO₂ conversion. The results show that the interplay of N-doping and curvature can effectively tune the intermediate binding energy and hence selectivity and overpotential of different products.² The graphene catalysts without curvature show strong selectivity for CO/HCOOH production, whereas the (6, 0) CNT with a high degree of curvature is effective for both CH₃OH and HCHO production. Curvature is also very influential to tune the overpotential for a given product, e.g. from 1.5 to 0.02 V for CO production and from 1.29 to 0.49 V for CH₃OH production.

References

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Talk 3: MAGNESIUM BASED MATERIALS FOR INNOVATIVE HYDROGEN STORAGE TANK

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Abstract

Magnesium hydride (MgH_2) is a suitable material for hydrogen storage applications because of its rather high hydrogen storage capacity (7.6 wt%). Reaction of magnesium with hydrogen is reversible but high temperatures are required (over 300°C) for desorption of hydrogen. Mechanical treatment of MgH_2 and in particular ball milling demonstrated to enhance hydrogen mobility and is suitable to add a catalyst resulting in faster kinetics of hydrogen absorption and desorption reactions. Application of solid compounds in tank for hydrogen storage requires suitable systems for heat management. It has been demonstrated that filling cylindrical tank with powders is detrimental for its continuous operation. The powder packs and sinters with increasing number of cycles and gas could not flow through it causing a reduction of mass of material which reacts with hydrogen. Consequently the storage capacity of the system decreases and kinetics become slower. In order to enhance heat management and gas contact the powder could be compressed in the form of pellets. Other agents, in particular carbon-based materials, for enhancing thermal conductivity, can be compacted with mixtures of magnesium hydride and catalyst. The pellets show improved properties in terms of heat exchange and better stability to cycling but a continuous increase of their dimensions took place upon repeated cycling. A new procedure of preparation has been studied in order to reduce the effects of cycling and to obtain a more stable system to be applied in tank for hydrogen storage. Light and Electron Microscopy, X-Ray diffraction have been used for the analysis of samples prepared before and after cycling, performed in a Sievert's type apparatus.

Talk 4-1: Plasma-assisted synthesis of metallic oxide nanostructures for water splitting applications

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Abstract

The direct conversion of solar energy into hydrogen represents an attractive but challenging alternative for photovoltaic solar cells. Several metal oxide semiconductors are able to split water into hydrogen and oxygen upon illumination, but the efficiencies are still low. An efficient photocatalyst is expected to have the following features: a narrow band gap to absorb a broad part of the solar spectrum, small dimensions and high crystallinity to reduce the loss of charge carriers by recombination and a band gap slightly larger than 1.23 eV with band edges pinned correctly for overall water splitting.

As photocatalyst, iron oxide and cupric oxide are promising candidates. These Earth abundant elements have narrow band gap (2.2 eV) but the positions of their conduction bands are not suitable to produce hydrogen. A solution would be to use quantum confinement effects to shift the conduction band to a suitable position for hydrogen production. However, quantum confinement effects occur only in very thin nanowires, typically with diameters smaller than 10 nm.

In this work, we show how to control the morphology of metallic oxide nanostructures synthesized from different substrates (pure metals, bi-layers, alloys or perovskites) by using a flowing microwave plasma afterglow oxidation process. The aspect ratio can be precisely controlled by the experimental parameters. For instance, by adjusting these parameters, we succeed in decreasing the average diameter of nanowires down to 5 nm in the case of copper oxide, with a fairly high surface number density for very short treatments, typically less than 1 minute.

Talk 4-2: Hydrogen storage in nanoporous solids

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Abstract

Hydrogen is an energy vector that should be extensively used in the future. Hydrogen storage at high pressure or in liquid state is controversial due to security issues that also imply social acceptability. Hydride-based technologies are progressively optimised for mobile and stationary applications. Nevertheless, hydrides are still challenging as far as desorption kinetics, durability and cycling are concerned.

Hydrogen adsorption on a solid surface allows reducing the storage pressure but requires low temperatures to enhance adsorption capacity. The theoretical upper limit for hydrogen storage in carbon materials is around 6.9 wt.% at 77K, and such value was already experimentally attained with some activated carbons. However, hydrogen storage at moderate pressures, lower than 4MPa, and at room temperature remains a challenge.

In stationary applications, for which volume and weight are not limiting factors, the challenge is to find materials able to store hydrogen at room temperature. One strategy for enhancing hydrogen adsorption on ACs consists in doping them with heteroatoms, to increase electrostatic interactions, or metal nanoparticles, to induce chemisorption and spill-over.

We will present different strategies to prepare activated carbons to be used at cryogenic conditions and room temperature. The effect of the carbon precursor, the eventual use of a pre-treatment as hydrothermal carbonisation, the utility of metal particle doping or heteroatoms presence will be analysed. The performances of these activated carbons will be discussed and compared to those of metallic organic frameworks and hydrides.

Talk 5: Novel Photoelectrodes and Noble metal-free Catalysts for Light-driven Water Electrolysis

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Abstract

The generation of fuels from sunlight and water is considered as a task of paramount importance for a sustainable energy supply in the future. Decomposition of water by a photoelectrochemical process is a possibility to harvest solar energy in the form of hydrogen in a large scale. For this purpose, a membrane can be used which, when immersed in an aqueous electrolyte and illuminated by sunlight, will be able to split water into hydrogen and oxygen. Such a device is frequently addressed as artificial leaf. From an economic and environmental point of view this device should comprise of cheap, abundant and non-toxic elements featuring a Solar-to-Hydrogen (STH) efficiency > 10% and generating hydrogen at a price of ~3 €/kg H₂.

In our lab two approaches have been pursued to realize artificial leaf type structures:

- triple junction thin film a-Si/μc-Si solar cells in superstrate geometry with integrated catalysts [1],
- tandem junction solar cells combined with novel semiconducting ternary metal oxide anodes [2].

As photoanode materials Fe₂WO₆, CuBi₂O₄ and BiVO₄, but also other oxides and oxynitrides are under investigation. Their performances have shown considerable improvement with respect to their photovoltage and their photocurrent densities when synthesized using reactive sputtering, sol-gel and spray pyrolysis, respectively. To lower the costs of the device, platinum can be replaced by molybdenum sulfides as hydrogen evolving catalyst. RuO₂ was replaced by manganese [3] and cobalt oxide thin films.

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Talk 6: Production of methane at low temperature under adiabatic conditions using plasma-catalysis

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Abstract

Mesoporous Ni-Ce_{1-x}Zr_xO₂ based catalyst is assessed for the methanation of CO₂ in plasma activated reactor as these materials exhibit large surface area with outstanding long-term stability and taking into account that this kind of ordered structures favor mass transport and accessibility of the reactants to the active sites. Due to the overall process, coalescence of particles is prevented and nickel dispersion into the catalyst structure is improved. These characteristics facilitate the catalyst activated by the generated plasma defining two working region. In the first one, the reactor does not need extra heating supply and it is working under adiabatic conditions. On the base of the plasma interaction, it starts at room temperature and as the discharge increases the temperature, the process is carried out until a new steady state is reached, stabilizing the working point of the reactor at this isothermal condition in the range of 130-160°C depending of the thermal conductivity of overall system including specially the catalyst. Here the catalyst composition plays a basic role in the catalytic functionality. Under isothermal conditions, in the range 200°C-420°C, the reactor must be externally heated for achieving these thermal values independently if plasma is or not used. Nevertheless, better selectivity and conversion are achieved always with plasma.

Under adiabatic conditions, at low temperatures, selectivity of 100% is achieved for the production of synthetic methane using 20% of CO₂ and 80% of H₂ with a conversion percentage around 85%. Under conventional conditions, selectivity is maintained and conversion stays above 80% up to 300°C. For higher temperature conversion decreases a little bite although the selectivity and conversion percentages are always much better than without plasma.

These performances allow the production of synthetic methane with an interesting energy balance and catalyst life time to facilitate better cost of the methane. It can easily scale up for a large production volume of synthetic methane from reusing CO₂ with a high throughput.

Talk 7: Solid Oxide Electrolyte Based Technologies for Power to Chemicals Applications

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Abstract

The storage of the surplus of renewable energy can be carried out by co-conversion of renewable H₂ and anthropic CO₂ to fuels and chemicals (methane, methanol, dimethyl ether, ethanol, etc.) in solid oxide electrolyte membrane reactors (SOEMRs), with a series of advantages over conventional catalytic technologies. A SOEMR consists of a ceramic ion-conducting (O²⁻, H⁺, K⁺, etc.) membrane, in which two porous metal or metal oxide electrodes are deposited on both sides of the membrane. Whenever a small external potential or current is imposed, a controlled flux of ionic species are supplied or removed to or from the working/catalyst electrode, providing an electrochemical modification of relative chemisorption between reactants which allows: increasing the catalytic activity towards higher reaction rate, and therefore, the operation of the catalyst under milder conditions (with subsequent energy savings), altering the selectivity to the desired product (increasing energy efficiency in product formation), improving catalyst tolerance to feed poisons (electrochemically retarding its chemisorption) and extending catalyst life time by in situ electrochemical regeneration, while monitoring and controlling the process (by an external electrochemical sensor). Electrochemically enhanced CO₂ hydrogenation is carried out in a single chamber SOEMR, where both electrodes are exposed to the same reaction mixture (CO₂ and H₂), being one them inert to the reaction (counter electrode). CO₂ hydrogenation and in-situ hydrogen production (by steam electrolysis, steam or dry reforming, etc.) can be simultaneously carried out in a double-chamber (each electrode exposed to different ambient reaction, being both catalytically actives) SOEMR, where protons produced by the different reactions over one of the electrodes are transferred through the solid electrolyte to the other electrode where react with CO₂ to form fuels and chemicals, making direct renewable energy storage possible.

Talk 8: Characterizing working heterogeneities in cation exchange membrane electrochemical systems: applications to fuel cells, electrolysers, redox-flow batteries and hydrogen electrochemical compression

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Abstract

Electrochemical open reactors as fuel cells, electrolysers, or redox flow batteries usually do not produce a uniform reaction rate (current density) between the reagent inlet and outlet. This is explained by the fact that the reagents and products concentrations are varying down the flow direction. These working heterogeneities, if not well managed, can lead to malfunctions and local degradations [1]. Since now ten years, our team has developed experimental and modeling tools that allow characterizing these working heterogeneities. The measurements are performed in situ using segmented cells as shown in figure 1 with local reference electrodes positioned on the cationic exchange membrane along the active area. The classical electrochemical characterization methods (polarization, impedance, voltammetry) are performed locally what yield useful information to accurately understand the mechanisms responsible for the system degradation.

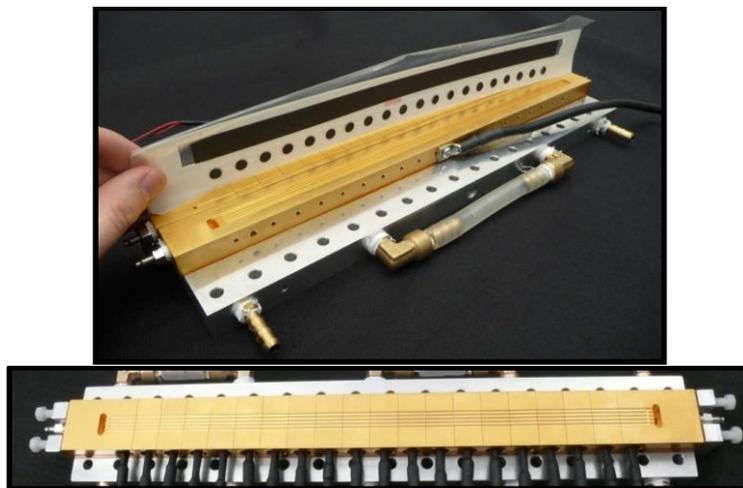


Figure 1: Instrumented cell with local reference electrodes on the membrane along the active area

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Talk 9: Solar Power to Chemicals Technologies

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Abstract

Thermochemical multistep processes are promising options to face future energy problems. Such reactions can be used to enhance the availability of solar energy in terms of energy transport, of energy demand/supply management and of potential energy related applications. Coupling concentrated sunlight to suitable sequences of thermochemical reaction enables the production of fuels like hydrogen or syngas and other fuels by water- and CO₂-splitting as well as the storage of solar energy by breaking and forming chemical bonds in suitable reversible reactions. These processes are sustainable and environmentally attractive since only water, CO₂ are used as the only raw materials and solar power and heat as the only energy source. All other materials involved are recycled within the process. The concentrated solar energy is converted into storable and transportable chemicals and fuels. One of the major barriers to technological success of many of those processes is the identification of suitable active materials like catalysts and redox materials exhibiting satisfactory durability, reactivity and efficiencies. Beyond this, materials play an important role in the construction of key components of the respective high-temperature processes and for the implementation in commercial solar plants. Besides materials aspects also process engineering issues needs to be overcome. One of the most striking challenges is to couple an intermittent energy source to a chemical process. The most promising processes and the main applications are being described and discussed with respect to further development and future potential. The main challenges of those processes are being analyzed. Technical approaches and development progress in terms of solving them are addressed and assessed.

Talk 10: Microstructured heat exchanger-reactors (HER) in energy sector. Illustration to hydrogen production via methane steam reforming

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Abstract

Today, the production of syngas by methane reforming (SMR) is the most widely used industrial process to synthesize hydrogen. It is based on a technology developed forty years ago in which the reactive gas (*water vapor/methane*) is supplied through a specific device consisting on metallic tubes supporting a fixed bed of catalyst.

Since the SMR reaction requires heat (*i.e. SMR is an endothermic reaction*), the tubes are arranged in a furnace in which heat is supplied by burners. The advantage of this process is that it is now mature and well controlled. One of its drawbacks is that its overall efficiency suffers heat transfer limitations, and notably heat losses.

In order to overcome these issues, the replacement of all tubes and furnace burners by a set of exchangers - microstructured reactors could constitute an innovative alternative for designing the next generation of gas-reforming plants. Indeed, these exchangers - reactors should lead to: (i) much more effective mass transfer and heat transfer due to their high surface-volume ratio, (ii) much lower pressure drops than the conventional reactors equipped with a fixed bed of catalyst, (iii) good thermal and structural stabilities and (iv) a finer control of the operating conditions of the processes leading to higher production efficiency.

Thus, the present talk will give a short overview of the physico-chemical concepts developed and actions carried out recently for optimizing the new generation of “hydrogen making-plant”, namely: (i) the production of metallic reactor-exchangers constituted with channels of millimeter size, (ii) the modeling of such devices to determine the most appropriate design, (iii) the development of methods of manufacture and assembly of these devices, (iv) the determination of the chemical composition of high temperature protective coatings and their deposition process.