



# PEC HOUSE

## A COMPETENCE CENTER DEVOTED TO THE PHOTOELECTROCHEMICAL SPLITTING OF WATER AND PRODUCTION OF HYDROGEN

### Midyear Report 2008

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#### ABSTRACT

PECHouse, the photoelectrochemistry centre of competence at the Swiss Federal Institute of Technology of Lausanne (EPFL), has been established to advance the technology of semiconductor-based photoelectrochemical (PEC) water splitting to produce  $H_2$  and  $O_2$  using sunlight as the energy input. The overall objective of the research is to design and develop novel semiconductor-based materials capable of harvesting and converting solar energy into chemical energy by oxidation of water into oxygen and hydrogen. Since its inception nine months ago PECHouse research activities have centered on assembling tools and techniques for the development of the next generation of photoelectrochemical technology, alongside furthering the development of the state-of-the-art  $\alpha-Fe_2O_3$  photoanodes conceived by EPFL. Here we present the midterm 2008 results on the centre's development as well as describe current research efforts with iron oxide photoanodes. Three specific project deliverables are also satisfied by presenting results with our new deposition equipment, identifying the most promising underlayer materials for iron oxide photoanodes, and reporting on the progress of new materials and techniques under development for the second phase of the research activities.

## Goals of the Project

As the world's supply of fossil fuels declines, hydrogen has become the most promising alternative fuel for the new energy economy. Hydrogen can be produced from various sources; however, hydrogen production from renewable sources is highly attractive. The most important renewable source of energy is the sun, which shines in 10 minutes on planet Earth an amount of energy equal to the total yearly human consumption, yet we harness less than 2% of the world's energy demand due to a lack of suitable materials. PECHouse has been established as a centre of competence based at the Swiss Federal Institute of Technology of Lausanne (EPFL), in order to foster world-class research activities for semiconductor-based photoelectrochemical (PEC) water splitting into  $H_2$  and  $O_2$  using sunlight as the energy input.

PECHouse was established in September 2007 with three separate but related workplans (WPs). The overall objective of the research is to design and develop novel semiconductor based materials capable of harvesting and converting solar energy into chemical energy by oxidation of water into oxygen and hydrogen. The first work plan (WP-1) extends continuing efforts on nanostructured iron oxide ( $Fe_2O_3$ ) photoanodes developed at EPFL's Laboratory of Photonics and Interfaces (LPI). [1] The specific goals for WP-1 in first half of 2008 concerned the **development and optimization of deposition techniques for the  $Fe_2O_3$  film, analyzing the effects of the silicon doping and the investigation of different interfacial thin film layers for the  $Fe_2O_3$ /transparent conducting oxide contact**. The second work plan (WP-2) represents a new direction of research in PEC water splitting at LPI and concerns the fabrication of ordered mesoporous oxides as precursors or hosts for new semiconductor photoanodes, and the investigation of new ternary and multinary oxide. The goals of WP-2 for the first half of 2008 were to **begin the development of materials and nanostructuring deposition techniques for the overall workplan goals and the recruitment of an outstanding Ph.D. student**, who will perform research with the PECHouse team mainly within WP-2. The final workplan (WP-3) is related to project management and dissemination. The **organization of a national meeting on PEC water splitting (SwissPEC), the hosting of the last IEA-HIA Task 20 expert meeting and the creation of a PECHouse website** highlight the activities performed within this workplan in the first half of 2008.

This report describes the research activities related to the PECHouse scientific area until June 30th, 2008. Subsequent reports will describe incremental progress, using the present report as baseline.

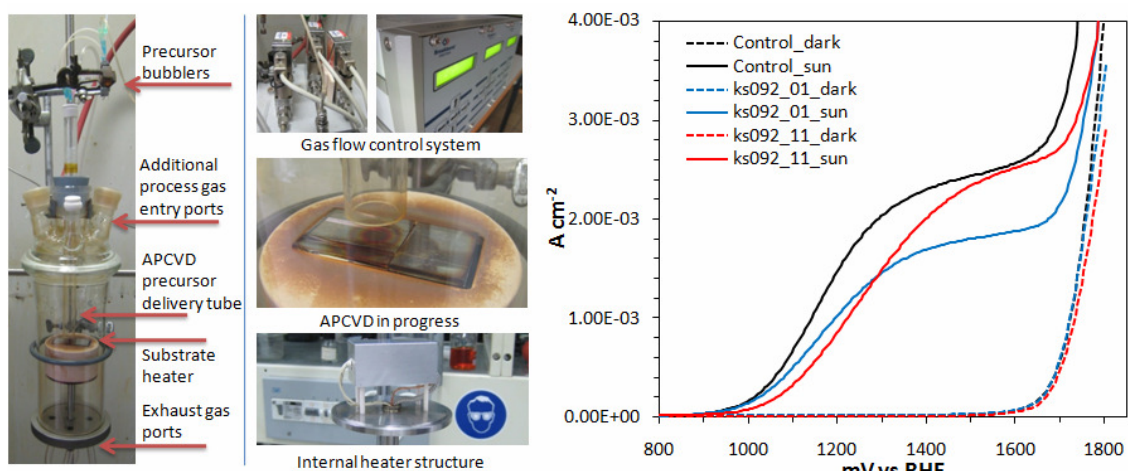
## Work accomplished and results achieved

### *WP-1: $\alpha$ - $Fe_2O_3$ photoanodes*

#### New deposition equipment

The first task for WP-1 was to update the somewhat artisanal thin film deposition system used in the previous research with iron oxide (atmospheric pressure metal-organic chemical vapor deposition). [2] In the PECHouse 2007 annual report we described the design and fabrication of a custom start-of-the-art deposition system capable of atmospheric pressure metal-organic chemical vapor deposition from both gaseous and solution-based precursors. The completed system consists of a cold-wall vertical process chamber with a height-adjustable titanium substrate heater capable of temperatures up to 600 °C (see Figure 1, left). The introduction of precursors to the process chamber is accomplished by volatilizing liquids in bubblers controlled by precise mass flow controllers (Bronkhorst Hi-Tech), or by entraining solution-based precursors which have been

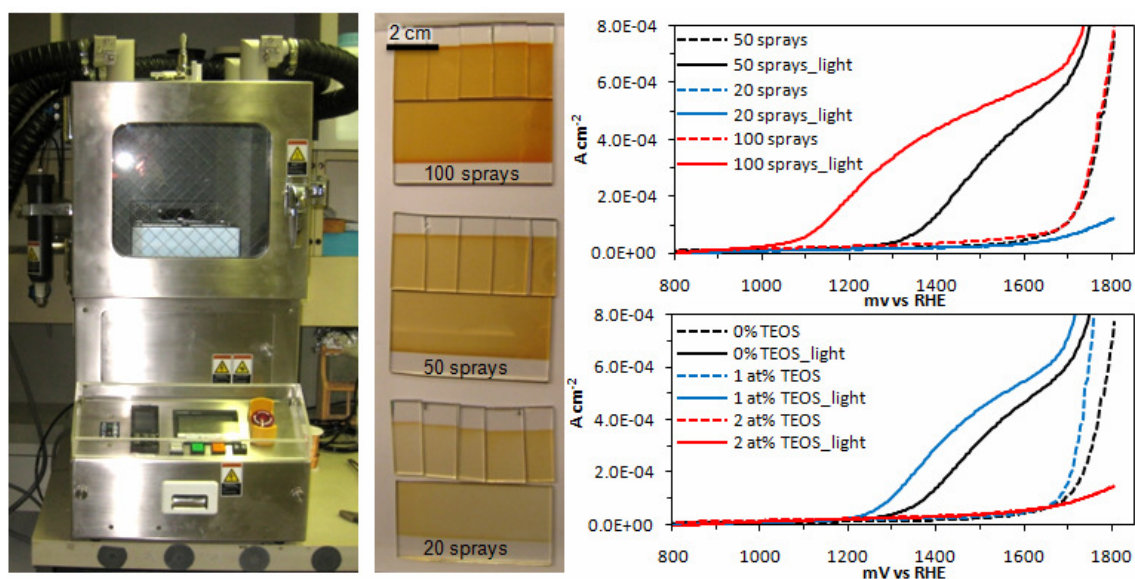
ultrasonically-dispersed into a gas flow by an advanced 120 kHz ultrasonic spray head (Sono-Tek) modified to be capable of pulsed operation mode.



**Figure 1: Second generation deposition equipment. Overview (left) of the completed atmospheric pressure cold-wall deposition tool. Configuration is shown for atmospheric pressure chemical vapor deposition of iron oxide. Photocurrent density plot (right) as a function of potential for the first silicon doped  $\text{Fe}_2\text{O}_3$  photoanodes to be fabricated from this equipment (blue and red curves) as compared to the state-of-the-art with the first generation deposition equipment (black curves). Electrodes were tested at AM 1.5 G  $100\text{ mW cm}^{-2}$  illumination with 1 M NaOH (ph 13.6) electrolyte.**

The initial optimization trials of this new equipment for the growth of nanostructured iron oxide photoanodes are very promising. The right portion of Figure 1 shows potentiostatic photocurrent measurements from the initial optimization trial with the second generation tool. Here, the photocurrent behavior for two representative  $\text{Fe}_2\text{O}_3$  photoanodes is shown against a control sample from the first generation system. It is important to note that this control sample (black curves, Figure 1) represents the top performance of iron oxide photoanodes without cobalt treatment. Remarkably, the new deposition system created iron oxide electrodes with good performance quite readily using only published process parameters. This was surprising given the artisanal assembly and empirical optimization approach used in the first generation system. In addition, with a plateau photocurrent over  $2.5\text{ mA cm}^{-2}$ , the iron oxide electrode coded ks092\_11 (red curves) demonstrates that the state of the art photocurrent is achievable with the new system. The photocurrent onset potential of ks092\_11 is shifted slightly anodically, and a higher ohmic resistance is observed, but slightly different process conditions gave an electrode (ks092\_01, blue curves) with a photocurrent onset that matches the old deposition system. In fact, by scaling the current density of ks092\_01 by a factor of 1.4 we note that it directly overlaps the control curve. The combination of these two electrodes from the second generation tool shows that the performance benchmarks from the old system are attainable on a new system, and given the increased ease with which parameters can be systematically and precisely varied using the new system, the further optimization will no doubt lead to a better understanding of the APCVD growth of nanostructured iron oxide photoanodes.

In addition the second generation cold wall atmospheric pressure deposition tool PECHouse and LPI have acquired a laboratory-scale commercial spray pyrolysis deposition system. The KM-25 apparatus from SPD labs, Inc (Japan) is designed for the automatic and consistent preparation of oxide thin films by the spray pyrolysis of soluble metal-based precursors. This system (shown in Figure 2, left) has already proved invaluable for the controlled and reproducible formation of oxide thin films for underlayer and fundamental host-guest studies. Since the simple spray pyrolysis deposition (SPD) of iron oxide films from  $\text{Fe}^{\text{III}}$ acetylacetonate in ethanol has already been investigated by LPI [3] an initial test of this tool was performed to reproduce those results and verify the performance of the new deposition tool. The results are shown in Figure 2.



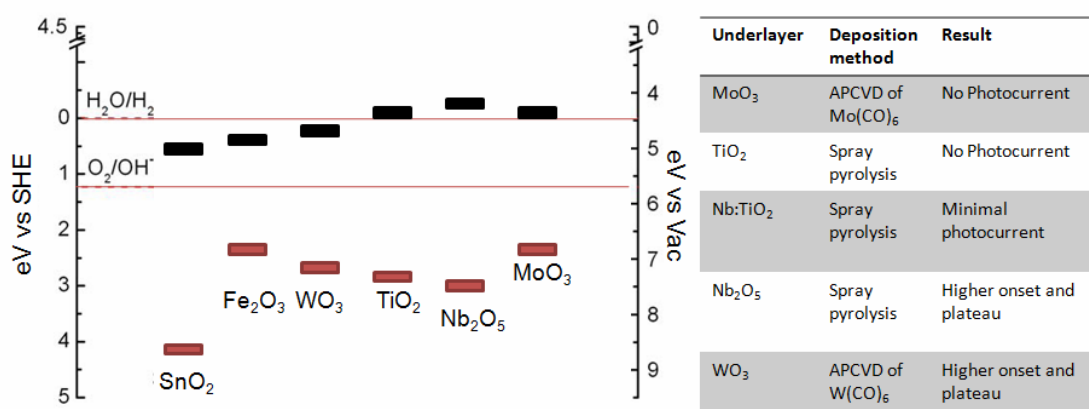
**Figure 2: Spray pyrolysis thin film deposition.** The KM-25 SPD apparatus (left) is the only turn-key bench-top laboratory spray pyrolysis deposition available commercially. Its automatic operation allows a substrate heating dwell time prior to the timed pulsed-spray of the precursor solution to the hot substrate, and a subsequent annealing step. Large-area, edge-masked films of  $\text{Fe}_2\text{O}_3$  from varying numbers of one second sprays of a 10 mM solution of  $\text{Fe}(\text{AcAc})_3$  in EtOH are shown in the center panel. Current-voltage behavior for these thin films are shown with varying number of sprays, corresponding to film thickness (top right) and varying amounts of silicon dopant in the form of TEOS (bottom right).

Our KM-25 SPD apparatus was fitted with a custom substrate holder to allow the preparation of large area  $60 \times 60 \text{ mm}^2$  thin films on FTO glass or other substrate. Each large substrate is equivalent in size to 12 electrodes prepared by the APCVD method, and uniformity and reproducibility is easily achieved with this automatic system. Typical thin films are shown in the center panel of Figure 2, with varying film thickness. By visible light absorption analysis a linear relation between the number of spray seconds to the thickness of the film was found for the standard iron oxide system:  $t = 1.23 s$ , where  $t$  is the thickness in nm and  $s$  is the number of spray seconds in one second sprays. Unlike the APCVD no growth lag time was observed. The performance of these iron oxide thin films closely matched the results previously reported by LPI. In addition, we also note that undoped films of iron oxide prepared this way also exhibit higher photocurrent than undoped films prepared by APCVD. This is most likely due to residual carbon atoms from the decomposition of the metal organic precursor. However, similar to electrodes prepared by APCVD we observe an increase in photocurrent with thickness until saturation, presumably where resistances to electron transport become too large. For undoped SPD films this point occurs approximately at 100 sprays of one second. Interestingly, thin films less than 40 sprays do not exhibit any photocurrent despite having an appreciable amount of light absorption. This is particularly illustrated by the film of 20 sprays shown in Figure 2. The center panel clearly shows the optical density of the film; however the dark current and the photocurrent overlap in the voltammetry measurement (top right graph). This is another example of the photoinactive dead layer also observed in the APCVD films and ultrasonic SPD films [4]. Another similarity of the SPD films to the other reported systems is the effects of doping. The plot at the bottom right of Figure 2 shows the photocurrent vs. potential behavior of thin SPD iron oxide films (50 sprays) with the addition of a small amount of TEOS as a dopant. Like electrodes prepared by APCVD and USPD a small amount of dopant ( $\sim 1$  at%) increases the photocurrent plateau and onset, but with the addition of excessive dopant ( $> 2$  at%) we see complete disappearance of photoactivity. The overall similarity of the behavior of SPD thin films under film thickness and dopant concentration variation as compared to the state of the art APCVD films indicates that the SPD thin film preparation method is not only useful to create underlayer films for the iron oxide system, but also as a rapid

and reproducible model system for the state of the art APCVD iron oxide photoanodes. If the solution to the dead layer problem can be found with the SPD method it will certainly be solved for the APCVD system.

### Underlayer investigations

The pan-deposition-method photoinactive deadlayer observed in iron oxide photoanodes leads to a decrease in performance, particularly in the thinnest layers. This manifests as a decrease in quantum (absorbed photon to current) efficiency, APCE, of thin films with decreasing thickness. It is therefore of great interest to solve the deadlayer problem to not only increase the performance of the nanostructured iron oxide electrodes made by APCVD, but to realize the WP-2 goal of the host-guest system with iron oxide as a thin absorber guest on a mesoscopic host material. In view of the latter goal, candidate materials with appropriate conduction band energies were screened for their use as underlayers by depositing them through various methods on the transparent conducting oxide substrate. Then silicon-doped iron oxide was grown on top by the APCVD technique. The materials chosen and a table summarizing the results are presented as Figure 3.

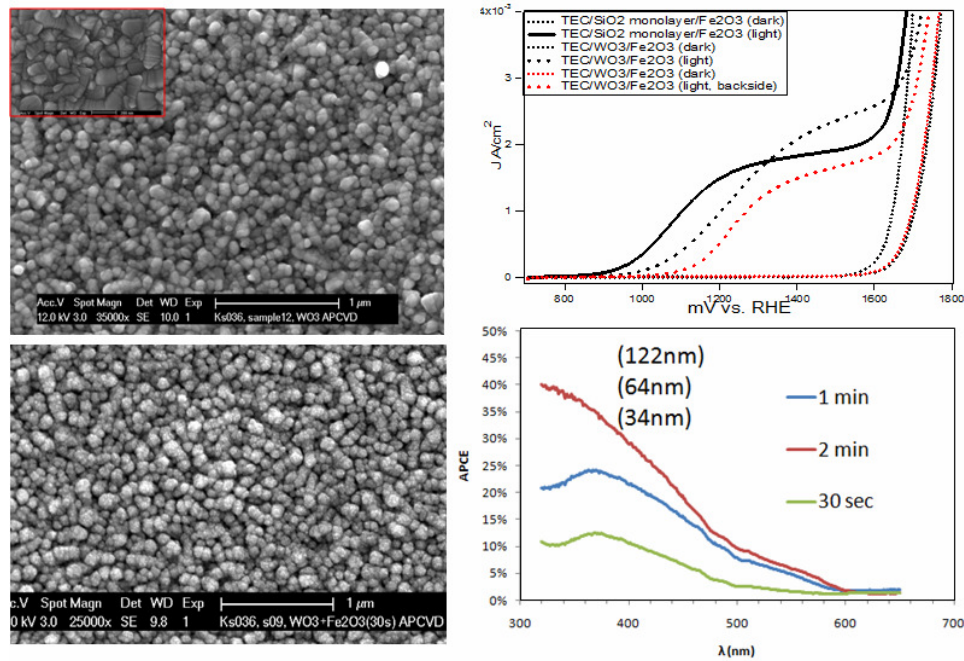


**Figure 3: Thick (~100 nm) underlayers for APCVD of iron oxide. Oxide materials were chosen for their stability and an appropriate conduction band energy (indicated by a black line on the energy diagram) to facilitate the transport of electrons from the iron oxide to the FTO. A summary of the deposition method and the performance result for each material is given in the table.**

The performance of the iron oxide with the various underlayers was generally poor; this suggests that the other factors, like surface roughness could be important to the ADCVD growth. However, two materials WO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> showed to be promising as underlayers for APCVD iron oxide. Here the composite underlayer/Fe<sub>2</sub>O<sub>3</sub> electrode exhibited increased plateau photocurrent over the control electrode (see Figure 4). To investigate this effect further electron microscopy and an iron oxide thickness series were performed on substrates with a WO<sub>3</sub> underlayer. The results of this investigation are also presented in Figure 4.

The decreased onset of the photocurrent (Figure 4, top right) is not surprising with this system as the conduction band of WO<sub>3</sub> is slightly higher in energy than iron oxide (see Figure 3). However, the increase of the plateau photocurrent is unexpected. An investigation of the morphology of the layers (Figure 4, left) shows that the WO<sub>3</sub> underlayer completely covers but has roughly the feature size as the underlying FTO, however the surface appears to have a higher roughness factor (actual/geometric surface area) given the spherical features of the WO<sub>3</sub> underlayer. After depositing a thin layer of iron oxide (~30 nm) by APCVD the SEM image appears bright due to the charging of the iron oxide. The iron oxide does not form a conformal layer on the WO<sub>3</sub> underlayer, but the uniform distribution of iron oxide nanoparticles are seen (upon visualization at higher magnification, not shown) attached to the WO<sub>3</sub> surface. The important question to answer about this system is whether or not the improved photocurrent is a result of an improved interface and a

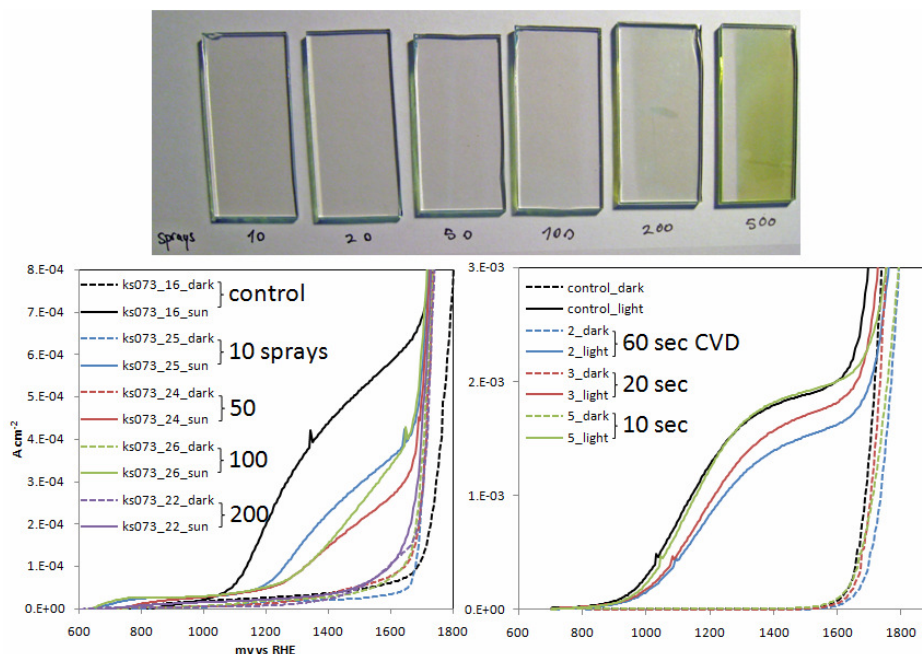
reduction of the photoinactive layer. To address this question, iron oxide films of different thicknesses were deposited on the  $\text{WO}_3$  underlayer and the APCE was measured. The quantum efficiency results are shown in the bottom right of Figure 4. Similar to the  $\text{FTO}/\text{Fe}_2\text{O}_3$  system we observe a decrease in quantum efficiency with decreased film thickness, and the deadlayer is still present. Thus, while the  $\text{WO}_3$ (or  $\text{Nb}_2\text{O}_5$ )/ $\text{Fe}_2\text{O}_3$  system remains quite promising as the photocurrent was effectively transmitted through the underlayer (as compared to the other underlayer materials tested) and as larger photocurrents were observed for the same deposition time, which could be a result of a faster deposition rate from the rougher surface, it does not solve the important deadlayer problem.



**Figure 4:** Results are shown of a detailed investigation of  $\text{WO}_3$  as an underlayer for iron oxide photoanodes. The top right graph shows the current voltage behavior for the composite  $\text{WO}_3/\text{Fe}_2\text{O}_3$  photoanodes as compared to the control sample with the standard  $\text{SiO}_2$  monolayer treatment. All iron layers were grown for 2 min. SEM pictures are presented on the left side. The top-down morphology of the as-deposited  $\text{WO}_3$  by APCVD (top) is compared directly to the FTO substrate at the same length scale (inset). The bottom left image shows the  $\text{WO}_3$  layer after depositing a  $\sim 30$  nm layer of  $\text{Fe}_2\text{O}_3$ . Finally the APCE results for the iron oxide on tungsten oxide underlayers is presented as a function of incident wavelength for three different thicknesses of iron oxide (as calculated by optical density, and shown in parenthesis) made by varying the deposition time.

These  $\text{WO}_3$  deadlayer results, when combined with the observation of the deadlayer on FTO and gold (as reported in December 2007) and with multiple deposition methods, suggests that factors other than electrostatics might be important to the activity of the first 10-50 nm of iron oxide. One possible explanation is the increase of recombination pathways due to crystalline disorder at the interface. To direct the crystallinity of the iron oxide at the interface with the substrate a templating layer with similar lattice parameters as iron oxide could be used. Hematite ( $\alpha$  -  $\text{Fe}_2\text{O}_3$ ) crystallizes in the rhombohedral system (space group  $R\bar{3}c$ ), and it has the same crystal structure and similar lattice parameters as corundum ( $\text{Al}_2\text{O}_3$ ), eskolaite ( $\text{Cr}_2\text{O}_3$ ) and karelianite ( $\text{V}_2\text{O}_3$ ). Since the most thermodynamically stable form of vanadium oxide is  $\text{V}_2\text{O}_5$  —making karelianite hard to synthesize under atmospheric conditions — and corundum layers will not crystallize at temperatures below 700  $^\circ\text{C}$  — too hot for our float glass substrate —  $\alpha$  -  $\text{Cr}_2\text{O}_3$  was chosen as a material for templating studies. Procedures were found for both the spray pyrolysis [5] and APCVD [6] of crystalline  $\alpha$  -  $\text{Cr}_2\text{O}_3$  thin films. These procedures were followed to produce  $\text{Cr}_2\text{O}_3$  thin films with varying

thicknesses, the films were annealed for 4 hours at 550 °C to ensure crystallinity, and iron oxide was deposited on top of the underlayer. The results of the templating study are shown in Figure 5.

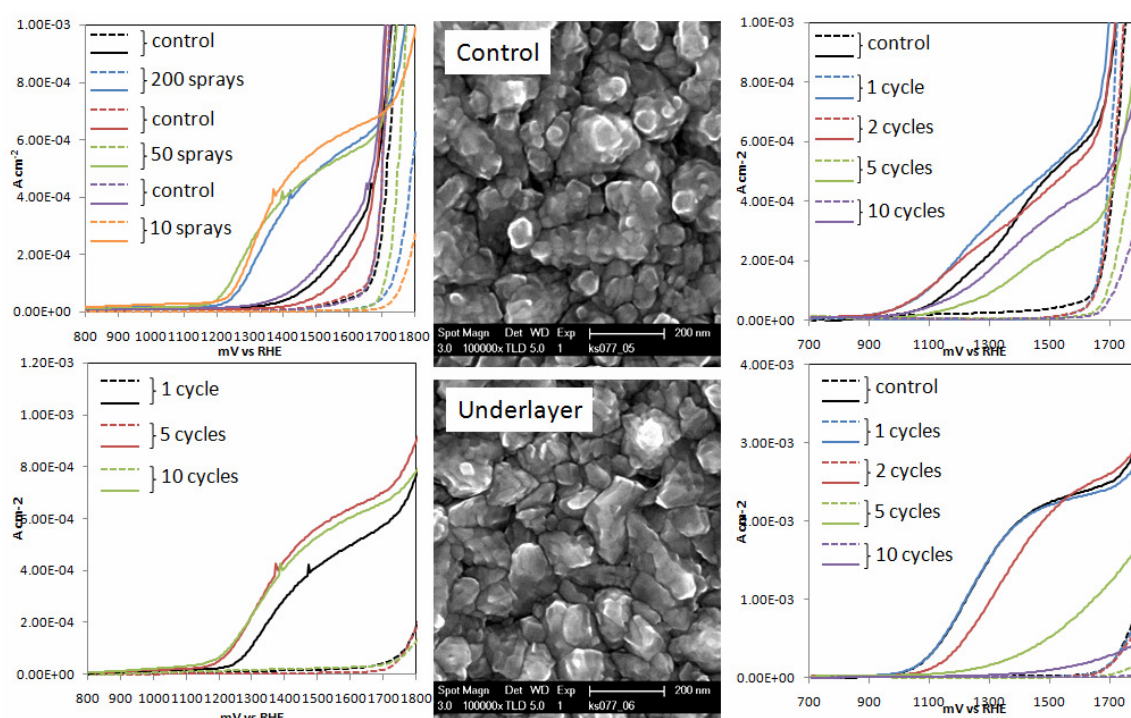


**Figure 5: Chromium oxide templating layer for iron oxide photoanodes.** Films prepared by the spray pyrolysis technique are shown with increasing number of sprays (top). The photoanode performance of thin films of iron oxide (120 nm, undoped spray pyrolysis) are shown with the chromium oxide templating layers in the plot on the left. The performance of APCVD iron oxide films are also shown with different thicknesses (varied by deposition time) of APCVD chromium oxide (right plot).

First a series of films was prepared using SPD with varying the number of sprays (Figure 5, top). Even the thinnest layer (10 sprays, undetectable by UV/vis absorption spectroscopy) reduced the photocurrent of iron oxide deposited on top (Figure 5, left). This is consistent with expectations of electron blocking due to the reported band offset of the  $\text{Cr}_2\text{O}_3/\text{Fe}_2\text{O}_3$  system. The conduction band is 3 eV higher in  $\text{Cr}_2\text{O}_3$  [7]. However, the templating approach could still work if the underlayer was thin enough to allow electron tunneling to the FTO. Additional control of the  $\text{Cr}_2\text{O}_3$  underlayer thickness was offered by the APCVD approach. Here the FTO substrate could be exposed to the precursor vapors for a short amount leading to ultra thin films. A ten second exposure led to an underlayer that did not affect the photocurrent of a  $\text{Fe}_2\text{O}_3$  film deposited on top via APCVD (Figure 5, right), but a twenty second exposure was thick enough to block electrons and reduce photocurrent. This trend continues with underlayers deposited for longer times. So while the crystalline templating approach still may be a viable way to reduce the recombination at the interface and increase the performance of thin films of iron oxide, these results with a  $\text{Cr}_2\text{O}_3$  underlayer suggest that with this material the thickness needed to achieve crystallinity and thus have a directing effect is too thick to allow the conduction of electrons to the FTO. This problem may be overcome by heavily doping the  $\text{Cr}_2\text{O}_3$  underlayer with deep donor states allowing a dopant band of vacant electron states to facilitate the transport of electrons. We are currently investigating the feasibility of this approach.

The above approaches to address the deadlayer have been similar in their use of an underlayer, as the interface between the FTO and the iron oxide is the source of the problem. Even before the establishment of PECHouse research at LPI serendipitously found that a TEOS vapor treatment prior to the deposition of iron oxide by APCVD enhanced the performance of the photoanodes. The TEOS treatment was found to deposit an ultrathin (~ monolayer) of Si (presumably as silica). This treatment was also found to be self limiting—extending the time of the treatment had no effect. Since this treatment has been shown to have a positive effect we embarked on an investigation of

this effect on both SPD and APCVD films of iron oxide, and by varying the thickness of the silica layer, in hopes of learning more about this successful underlayer and determining its effects on the deadlayer. First, we treated standard FTO with a TEOS:ethanol solution by spraying it on the heated substrate various numbers of times. The subsequent SPD of a thin film (50 nm) of iron oxide gives an appropriate model system to examine the consequences of the silica treatment. The results of this model study are presented in Figure 6. The photoelectrochemical performance of the electrodes are shown in the top left plot. Here the effects of the TEOS treatment are clear. Electrodes not treated with TEOS had very limited photocurrents, while each film that had been treated with TEOS showed a remarkable photocurrent. No morphological differences can be noted between the treated and untreated films as illustrated by the scanning electron micrographs presented in Figure 6. This certainly demonstrates the silica underlayer has a powerful effect on the deadlayer, as it greatly enhances the performance of these SPD thin films. However, it should be noted that these enhanced films still only had an APCE maximum of 13% — too low for use in a host/guest system. Interestingly, the dark currents (dashed curves, top left plot, Figure 6) show different behavior between silica treated and control as well. The silica treated electrodes have dark currents which onset at a more anodic voltage as compared to the untreated electrodes. This is consistent with the ultra-thin silica layer acting as a blocking layer — as in a MIS junction diode — here, recombination between holes in the iron oxide and electron in the FTO is suppressed due to the blocking layer, but electron conduction is still accomplished through tunneling. Finally, we note that there was little difference in the performance of the photoanodes when varying the number of treatments further suggesting that the treatment is self limiting even when the TEOS is applied by spraying. As we do not have control over the thickness of the silica underlayer the question as to which thickness of silica underlayer is optimal for this system becomes conspicuous.



**Figure 6: Results from silica underlayer studies** are shown with photoanode performance from Iron oxide films deposited with the SPD approach on the left side, and APCVD on the right. The top SPD plot shows the I-V characteristics of 50 nm iron oxide films with and without a TEOS (1:5 v/v in EtOH, sprayed on 400° C FTO) treatment. The center shows scanning electron micrographs of a SPD iron oxide film (50 nm) without (top) and with (bottom) a silica underlayer. The bottom SPD plot shows the same 50 nm iron oxide films with the varying silica underlayer thickness by the MALD technique (see text). The MALD technique was also used to prepare silica underlayers for the APCVD iron oxide films (30 sec APCVD Fe<sub>2</sub>O<sub>3</sub>, top, 4 min, bottom).

The CVD of silica thin films using TEOS is a common procedure at temperatures greater than 700 °C. At the temperatures accessible to us (< 550 °C) the TEOS treatment is self-limiting because it cannot completely decompose. However, the low temperature CVD of silica using TEOS is possible using ozone as a reactive process gas [8]. This reactivity to ozone was easily exploited in our labs using a UV/ozone cleaner. A manual atomic layer deposition (MALD) technique was developed to create thickness controlled ultra-thin films of silica on the FTO. First a TEOS:EtOH solution was sprayed on a FTO at 500 °C the substrate was cooled before the application of 20 min of UV/ozone. This process was repeated with varying numbers of cycles and the resulting substrates were used for the deposition of iron oxide by SPD and APCVD. Iron oxide (50 nm) from SPD showed a promising response to the MALD silica layers (Figure 6, bottom left). A more cathodic onset and a higher plateau photocurrent were observed on substrates treated five and ten times, as compared to just one cycle. However, a different trend was observed with thin films deposited by APCVD (30 sec, ~ 20 nm). While substrates treated with one or two cycles of the silica deposition showed a slight increase in photocurrent and onset higher numbers of cycles decreased the performance of the these thin films (Figure 6, top right). This effect is more pronounced on thick films grown by APCVD (Figure 6, bottom right). Here even the film treated twice showed a decrease in performance. While these initial results with the APCVD films are not impressive, here is this first instance we see a qualitative difference in the behaviors of the SPD and the APCVD iron oxide films, and as such further investigation is necessary to determine the cause for this difference. Currently thin films with and without silica underlayers are being examined by impedance spectroscopy to electronically characterize the interface.

In conclusion, the considerable amount of effort placed into underlayer research has led to some interesting discoveries. Namely, thick underlayers of  $\text{WO}_3$  and  $\text{Nb}_2\text{O}_5$  are suitable for scaffold materials, but do not solve the dead layer problem, and the deadlayer is greatly reduced by the silica underlayer for SPD films. In addition, we found that a crystal templating approach with  $\text{Cr}_2\text{O}_3$  was not effective due to the conduction band offset. In view of these results the most promising underlayer materials for future research in the second half of 2008 are 1) the ultrathin blocking layers like silica—layers of alumina and other high-k dielectric at different thicknesses will be further investigated—and 2) optimized hematite thin films using SPD—the templating approach and the ultra-thin blocking layer approach will be combined to optimize the structural and electrical aspects of the  $\text{Fe}_2\text{O}_3$ /FTO interface. These thin films will be used as underlayers for APCVD iron oxide.

#### Scrutinizing the doping effect

While the silicon doping amount has been optimized in the past, the specific role the silicon plays in the state of the art iron oxide photoanodes has not been systematically scrutinized. Specifically, the individual contributions to the refinement of the morphology and the increase of the conductivity should first be understood, before these separate factors can be optimized. To this end, post-film-growth doping by silicon ion implantation has been investigated with the collaboration of Prof. Schoenes from the Technische Universitaet Braunschweig. Silicon ion implantation was carried out both on an undoped APCVD sample (400-nm thick) and on an oxidized film by thermal evaporation of iron (100-nm thick), and a homogenous doping profile at a level of 6 at% was found by calculation using a SRIM code. Both the samples were not photoactive according to the I-V measurement, even after the thermal activation at 550 °C for 5 minutes first and 5 hours after. Only a small photocurrent has been achieved from the APCVD sample after the second annealing. Because the silicon doping was much higher than the optimum found with the silicon doped APCVD samples, a further trial is necessary. This will be performed in the second half of 2008. In addition, the SPD of hematite thin films provides a simple and effective way to screen dopants for hematite. Research to this effect is a top priority for scrutinizing the doping effect in the second half of 2008.

## *WP-2: Ordered mesoporous oxides*

### PhD student recruitment

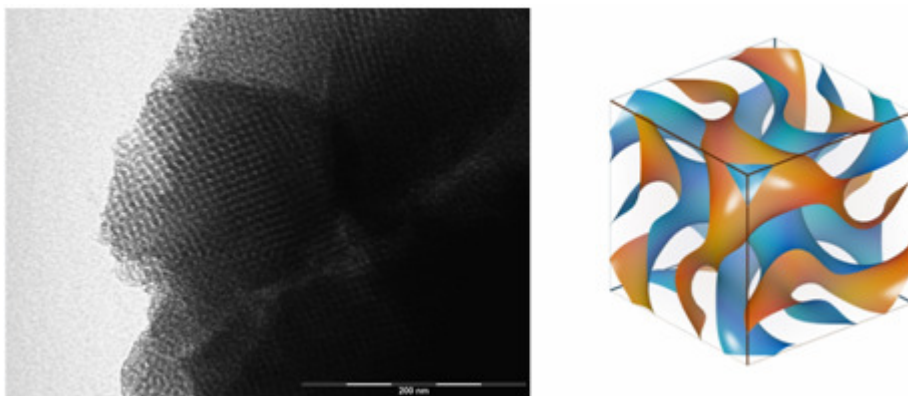
A primary task to workplan 2 was to recruit an outstanding PhD student who will research mainly on the specific tasks related to this work plan. This was achieved by the appointment of Adriana Paracchino (Masters of Materials Science, University of Torino). Adriana has previously conducted research on materials for solar energy conversion. This, with her broad background in materials science and her high level of motivation make her an excellent fit to the PECHouse team.

### Materials and techniques developed

The mesostructured host-guest approach for PEC watersplitting is a very attractive route to boost many aspects of a photoelectrode's performance by combining selective attributes from multiple materials. To realize these nanostructures at this next level of sophistication, our first goal is to develop the necessary tools and techniques. Here we present a progress report on the techniques and materials developed for workplan 2. First we describe progress made on two novel approaches for the synthesis of ordered mesoporous oxides. Each route provides unique advantages in the design of photoanodes, which we detail below. Then we describe a technique developed for the deposition of the host semiconductor onto a mesoporous oxide. Finally, we present a description of a new ternary oxide being investigated for this workplan.

### *Hard templating of ordered mesoporous metal oxides*

In this approach, a silica- or carbon-based mesoporous solid serves as a template for the synthesis of the desired ceramic. We have used a mesoporous silica known as KIT-6, which is a bicontinuous structure, meaning that there is a continuous network of pores and a continuous network of silica. The silica forms a cubic mesostructure known as the double gyroid, which can be seen in Figure 7

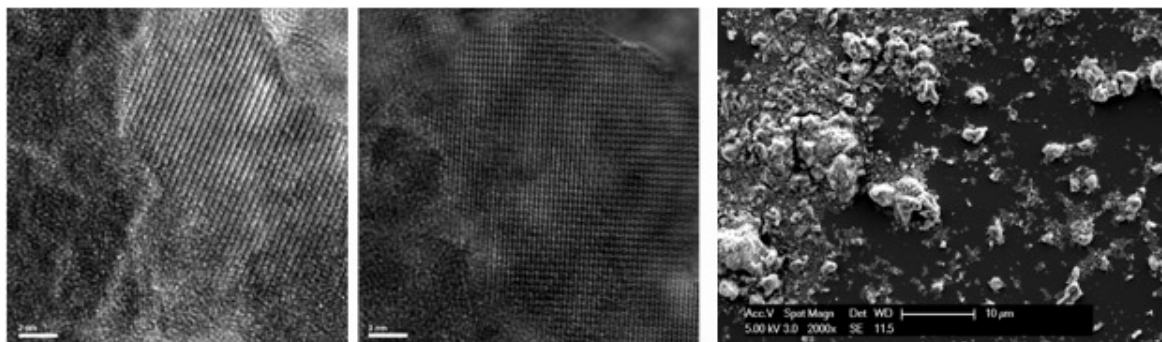


**Figure 7: TEM image of KIT-6 mesoporous silica (left). An illustration (right) shows the two silica networks (tubes with blue exterior and orange interior) and the resulting network of pores (white regions between tubes).**

In the hard templating approach, molecular precursors of a ceramic are infiltrated into the silica's pores. Heating the silica decomposes the molecular precursor, producing a silica-metal oxide nanocomposite. The silica is etched away, leaving a mesoporous metal oxide in the form of the silica's pores, and having a network of mesopores in the form of the silica.

As a first experiment, we infiltrated  $\text{Fe}(\text{NO})_3$  into the KIT-6 and calcined the material to 600 °C, following a recently developed protocol (JACS, 128, 5468 (2006)). Silica was etched under basic

conditions to produce ordered mesoporous hematite. High-resolution TEM images of the hematite lattice fringes are shown in Figure 8 (left and center), revealing the highly crystalline mesoporous structure.



**Figure 8: High resolution TEM images of mesoporous hematite lattice fringes (left and center), and SEM image of a mesoporous hematite powder.**

A challenge facing this approach involves the integration of the mesoporous hematite into a photoanode device architecture. Figure 8 also shows an SEM image of the particles of mesoporous hematite fabricated in this approach. Particle size ranges from 100 nm to several microns. We will improve the homogeneity of particle size by ball milling, which will enable us to doctor blade the particles onto a substrate. Annealing will sinter the particles to the substrate, and allow us to test this preliminary device architecture and assess the potential of this synthetic methodology.

#### *Surface structuring as a route to ordered mesostructured oxides*

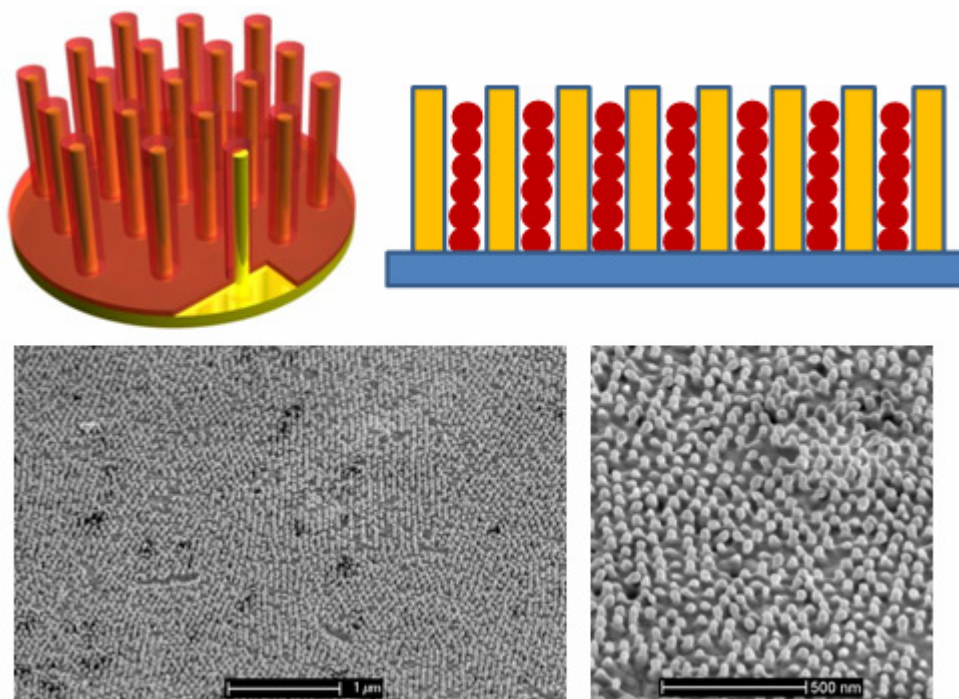
Perhaps one of the most direct routes to ordered mesoporous oxides is based on an ordered mesoporous collector electrode (i.e., a metal or fluorine-doped tin oxide that collects electrons or holes from the photoelectrode). A possible architecture — which also represents a guest-host architecture — is illustrated in Figure 9. The advantages of this architecture are several-fold. First, the metallic nanostructure provides a natural template for semiconductor deposition, allowing a high surface area metal oxide to be deposited. Second, the metal serves as an electrical conduit, carrying electrons or holes to or from the semiconductor. This may increase the range of semiconductors that can be considered as a photoelectrode, as problems arising from the low inherent conductivity of some semiconductors are minimized. Third, the nanostructured metal surface provides a potential route for enhanced light absorption through plasmon-mediated energy transfer from the metal to the semiconductor. Alternatively, if the metal is etched away, a vertically oriented network of pores forms, enabling a high degree of accessibility to the semiconductor.

We have developed an approach based on the thermal evaporation of a metal onto an ordered mesostructured aluminum surface. The aluminum has a conical array of pits into which the metal is deposited. The metal is transferred to a glass substrate and the aluminum is removed, yielding an ordered, quasi-conical array of metal (in this case, gold). Preliminary results are presented in Figure 9. We are beginning to develop approaches for depositing semiconductors on these metal collector electrodes.

#### *Electrophoretic Deposition*

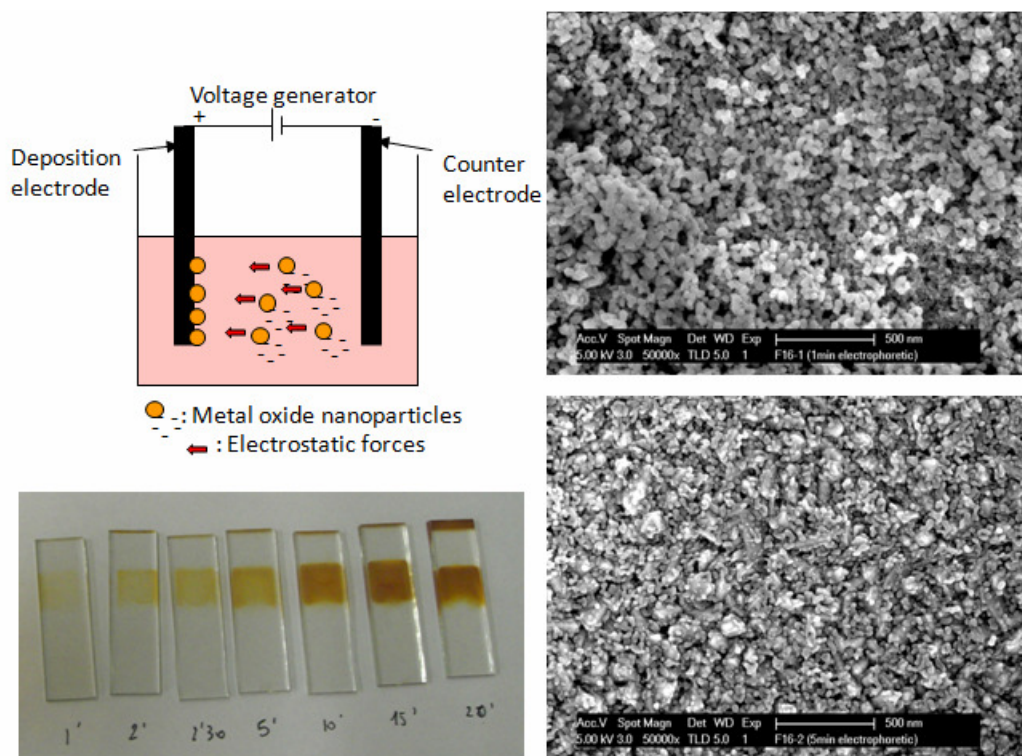
The deposition of a guest material onto a mesoscopic host presents new challenges as opposed to conventional oxide semiconductor deposition on compact films. To address this challenge, a deposition method has been developed for a guest material in the host-guest approach: electrophoretic deposition. This technique consists of applying a potential difference between two electrodes through an electrolyte comprising dispersed nanoparticles of the desired materials

(Figure 10, upper left). With the effect of the electric field, the nanoparticles (which have an overall surface charge depending on the electrolyte species and concentration) will migrate to the electrode of the opposite charge and bind weakly to the surface. An annealing or sintering step is then required to strongly bind the particles to the substrate. This method has two main advantages. First, it allows conformal deposition on a mesoporous electrode as the charged nanoparticles try to reach the oppositely-charged surface. Second it is indefinitely scalable and therefore easily adaptable to industry.



**Figure 9:** (Top, left) Illustration of a metallic nanowire array (yellow) with a semiconductor (red) supported on it. (Top, right) Illustration of a semiconductor deposited between metal nanowires. The metal can then be etched away, yielding a mesoporous oxide with pores ordered normal to the electrode surface. Also, low magnification (bottom, left) and high magnification (bottom, right) SEM images of an ordered mesostructured gold surface formed by our new synthetic process. The sample is viewed at a 40 degree angle from the surface normal.

A first experiment with electrophoretic deposition was realized with conductive glass TEC15 as the deposition electrode and stainless steel as the counter electrode.  $\alpha$ - $\text{Fe}_2\text{O}_3$  nanoparticles with an average diameter of 10-20 nanometers, purchased from BASF (Ludwigshaven, Germany), were ground in a mortar with a minimum of acetylacetone in order to have a good dispersion. 8 mg ( $5 \cdot 10^{-5}$  mol) of this iron oxide were then mixed with 13 mg of magnesium nitrate ( $5 \cdot 10^{-5}$  mol) in 40 ml of isopropanol to form the electrolyte. An electric field of 50 V/cm had been applied between these electrodes, placed 2 centimeters apart from each other, for different times from 1 up to 20 minutes (see Figure 10). The samples showed a good homogeneity and the possibility of depositing films of different thickness. Thus, it seems possible to deposit a monolayer of iron oxide particles on a mesoporous scaffold with this technique. Moreover, the scanning electron microscopy (SEM) pictures (see Figure 10), demonstrate that the coverage of the substrate by the nanoparticles is relatively conformal. Electrophoresis seems to be an interesting technique for the deposition of iron oxide as a guest in a host-guest structure because of the deposition properties: conformality and thickness control. Many parameters, such as the concentration and the pH of the electrolyte, the applied voltage and the deposition time, are adjustable and shall allow the desired morphology to be obtained, i.e. a monolayer of iron oxide particles on a mesoporous host material.



**Figure 10: Electrophoretic deposition principle (upper left)** Surface-charged nanoparticles are driven to an electrode with an electric field imposed by a voltage generator. Electrophoretic deposition samples on conductive glass TEC 15 (lower left). A difference of potential of 50 V/cm was applied for different lengths of time between a conductive glass TEC 15 and a stainless steel foil electrode. Scanning Electron Microscopy pictures (right) of 1min (top) and 5 min (bottom) electrophoretic deposition films, annealed for one hour at 500°C, showing a good coverage of the substrate surface.

#### *Ternary oxide investigation*

$\text{CuAlO}_2$  is a p-type semiconductor crystallizing in the delafossite structure with interesting properties as to solar induced water splitting: it is stable over the whole pH range, affording a long utilization in aqueous electrolytes without undergoing photocorrosion, it has a small indirect band gap of about 1.6 eV, and even thin films (500 nm) show good conductivity (up to 1 S/cm) and low transparency (15% at 300 nm and 50% at 700 nm) [9,10]. The problem in obtaining p-type behavior has to do with the strong localization of holes to oxygen ions at the VB edge, due to the large electronegativity of O. But in  $\text{CuAlO}_2$  the valence and conduction bands arise from d-orbitals, owing to the linear coordination of Cu in the delafossite structure. Research efforts with this material have been focused on its synthesis in the form of submicrometric particles suitable for spin coating or doctor blading on FTO glass.

We observed that conventional solid-state synthesis of  $\text{CuAlO}_2$  affords particles with a 5-10 micron diameter. To reduce the particle size, planetary wet ball milling was performed for varying amounts of time. A 24-hour ball milling leads to a significant fraction of amorphous material whereas a 2-4 hours milling leads to platelets that are below 1 micron. Unfortunately the process caused considerable contamination from the steel container and the particles were still too large to doctor blade for photoelectrode assembly.

Hard template synthesis constitutes a possible route to obtain ordered crystalline oxides. The crystalline oxide growth proceeds inside the previously synthesized silica scaffold starting from an aqueous solution of the metal nitrates. The pore and wall sizes of the silica scaffold and therefore of the oxide replica can be easily tailored. This method has been successfully employed for several binary oxides [11,12]. After calcination and silica removal the crystalline product can be

collected. Our first attempts at its synthesis starting from Cu and Al nitrates and following calcination at 1000°C led mainly to amorphous alumina and copper oxide, accompanied by a loss of the silica mesostructure as a result of the high synthesis temperature. To lower the synthesis temperature, metal chlorides will be employed, which, under the flow of humidified air, will generate HCl in situ and favor the formation of CuAlO<sub>2</sub>.

The synthesis of a thin film of CuAlO<sub>2</sub> directly on a glass substrate has been performed by spray-pyrolysis [13,14]. We attempted to reproduce these results using FTO glass. Different spray setups have been investigated in order to understand the role of the substrate temperature, solution pH and solvent. The deposition of a thin brownish film of copper aluminate only occurred at low temperature (380°C), at pH 2, and with water as the solvent. Unfortunately in these conditions the FTO glass breaks due to a combination of thermal stress and acid-induced attack of the FTO substrate. Since the deposition upon ordinary glass without FTO was successful, alternate collector electrodes or acid-stable buffer layers need to be explored.

Another possible route is the hydrothermal synthesis of delafosites, developed by Poeppelmeier and coworkers [15,16]. This synthesis from copper and aluminum oxides may proceed in relatively mild conditions of temperature (210°C) and pressure (<10 atm) thanks to the use of NaOH as mineralizer. The experiment will be performed in the next weeks with a new hydrothermal bomb.

In conclusion, PECHouse is developing several unique and promising approaches for the synthesis of ordered mesostructured photoelectrodes of complex oxides with guest-host type morphologies. Several distinct steps are currently underway: the synthesis of new semiconducting oxides, such as CuAlO<sub>2</sub> and the development of suitable mesostructuring approaches. Future work will focus on the integration of these new materials into devices. The general challenge in device integration will be to make good electronic contact between the ordered mesostructured particles and the FTO substrate. To address this problem, an alternative device production methodology will be developed. First, the mesostructured powder will be doctor bladed onto a temporary substrate but the powder will not be sintered at this stage. Next, FTO will be deposited via an in-house flash chemical vapor deposition system to make a conformal electronic contact to the powder. In the final steps, the FTO will be attached via a ceramic glue to a permanent glass substrate and the film will be removed from the temporary substrate. In this way, the randomly shaped mesostructured particles may be efficiently integrated into advanced device morphologies. It should also be noted that the fundamental knowledge being gained through WP-1 is benefiting the types of mesostructured architectures and synthetic routes that are targeted in WP-2. Similarly, the new methods developed in WP-2 will improve the APCVD of hematite by providing unique mesostructured substrates that may influence device performance.

### *WP-3: Project management and dissemination*

#### Financial

The SFOE total financial support to PECHouse for 2008 will amount to Frs. 355'808, with a first payment of Frs. 177'904 upon acceptance of the present mid-year report. Frs. 355'808 are intended to cover :

- the salaries of two post-doctoral researchers and one new Ph.D. student working 100 % on PECHouse research activities;
- 25 % of the salary of a senior scientist active within PECHouse;
- the project management provided by the EPFL Energy Center;
- consumables and other expenses (travel, etc.).

At the end of the year, we will provide a comprehensive financial report of all the expenses.

As a result of the augmented Steering Committee meeting held on March 12<sup>th</sup> 2008, it was decided to reduce the resource allocation for the senior scientist to 25 % for 2009 and following years, thereby freeing additional financial resources for collaborations with Swiss and/or international organization.

#### Human resources

Mr. Florian Le Formal benefits from a Marie Curie Network grant as a Ph.D. student. As a result, an additional person, Ms. Adriana Paracchino, who holds a M.Sc. in Materials science from the University of Torino, has joined PECHouse as a new Ph.D. student starting in February 2008 : her salary is entirely covered through SFOE financial support.

Dr. Monica Barroso has left LPI on February 1<sup>st</sup>, 2008, after having accepted a position as a Post-Doc in the Photochemistry and Molecular Spectroscopy Group at the University of Coimbra, in Portugal.

Prof. Michael Grätzel and Dr. Md. Khaja Nazeeruddin both provided proactive, as well as constant overview and inputs to the various research activities and directions. The project has also benefited from useful inputs and feedbacks from Drs. Andreas Kay and Paul Liska..

Prof. Hans Björn Püttgen and Dr. Massimiliano Capezzali provided management support to PECHouse. They have closely worked with the scientific team, in particular as far as the search for additional funding and the organization of various meetings were concerned (see below).

#### Steering Committee

The first semi-annual augmented meeting of the Steering Committee with SFOE – as foreseen in the contract - took place on March 12<sup>th</sup>, with Dr. Stefan Oberholzer (SFOE) , Prof. Andreas Luzzi (SPF Rapperswil), Dr. Michael Spirig (SPF Rapperswil), Prof. Michael Grätzel, Prof. Hans Björn Püttgen and Dr. Massimiliano Capezzali – Prof. Hubert Girault could not attend. It was notably decided to hold a Swiss meeting on PEC-based hydrogen production (SwissPEC, see below), to host at EPFL the IEA-HIA Annex 20 European expert meeting (see below). Moreover, it was agreed upon that the contribution of Dr. Md. Khaja Nazeeruddin to PECHouse will be fixed at 25 % of his worktime from 2009 on. Official minutes of this meeting have been made available.

The second meeting of the PECHouse Steering Committee took place on April 3<sup>rd</sup>, 2008 and was attended by its three members, namely Profs. Püttgen, Grätzel and Girault. The overall setting of PECHouse was discussed, with a particular emphasis on needed actions to extend its reach to a broader scientific community and to additional industrial partners, such as the Swatch group. It was decided to explore the possibility to submit one or more CTI projects, as well as to organize an international event around the hydrogen production by PEC technologies in 2009.

#### Internal EPFL meeting

On April 17<sup>th</sup>, 2008, PECHouse activities were presented to some of the faculty members of the EPFL Institute of Chemical Sciences and Engineering (ISIC) and to two professors of the School of Engineering (STI), in order to investigate possible internal collaborations. As a result of this meeting, fruitful contacts have been established with Prof. Heinrich Hofmann and Dr. Patrik Hoffmann, with concrete collaborative ideas on issues such as nanopowder and nanodeposition technologies. The latter shall be concretized during the second half of 2008.

#### Liaison with relevant national and international research groups

In order to gather the major representatives of the national scientific community in the broad domain of hydrogen research, the PECHouse team has organized a Swiss meeting, named

SwissPEC and held at the EPFL on April 22<sup>nd</sup>, 2008. The research activities and the structure of PECHouse were presented to the approximately twenty attendees. Other presentations included Prof. Edwin Constable of the University of Basel, Prof. Andreas Züttel of EMPA, Profs. Xile Hu and Jacques-Edouard Moser of EPFL, as well as Drs. Laetitia Philippe and Anke Weidenkaff from EMPA. Fruitful discussions have taken place among the scientists, with various collaborative ideas taking shape, in particular with EMPA laboratories.

On May 16<sup>th</sup>, 2008, the IEA-HIA Annex 20 European expert meeting was hosted at EPFL and co-organized between the PECHouse team and the operating agent Prof. Andreas Luzzi. A dozen external scientists participated in this meeting, all presenting their research activities in PEC technologies for hydrogen production. A tentative Program-of-Work for a new Annex (26) on “New Material for PEC hydrogen production”, prepared by Prof. Eric Miller, has been basically accepted by the attendees and will thus be forwarded to IEA later in the year.

#### Additional funding

One of the tasks attributed to PECHouse concerns the quest for additional funding, which will ultimately allow the structure to get financially self-sustained. As a first step, we have initiated an internal EPFL procedure aimed at obtaining funding for an ulterior and critical scientific equipment, namely a small-angle X-ray diffractometer for the analysis of thin films. The procedure is presently on the way and we are optimistic about the outcome.

The second step was the submittal of a collaborative project to the FP7 Energy-NMP 2008-1 Call, centered on new materials for energy applications. The proposal was entitled “Nanostructured Photoelectrodes for Energy Conversion”, with NanoPEC as an acronym. The requested amount reaches 3 Mio. Euros and the coordination is assumed by Prof. Michael Grätzel. Although similar in many respects, this proposal goes further than the former FP7 PECHit proposal, in the sense that it shall concentrate on new concepts and methods, afforded by nanotechnology, in order to design innovative composite nanostructures in which each component performs specialized functions. The proposal consortium encompasses six academic institutions (EPFL, TU Delft, Technion, University of Warsaw, University of Porto and University of Oslo), as well as ENI S.p.A. as an industrial partner, thus ensuring a unique synergy of world-class competences and infrastructures aimed at reaching the ambitious goals. The latter are quantitatively the same as the ones agreed upon within PECHouse, thus strengthening our roadmap. EMPA will also be associated to this project, if accepted. NanoPEC has successfully passed the first stage of the procedure : 131 projects were initially submitted for this call and only 33 of them were retained for the second stage. 3 Swiss-led projects were among the 131 initial projects, but only NanoPEC was accepted at stage 2. We are presently waiting for the final decision from the EC.

Finally, the PECHouse team plans to submit a proposal for the 4th Call for proposals of the CCEM, with the deadline set on September 15th, 2008. EMPA will certainly be a natural partner for such a project, the details of which will be worked out during the second half of August 2008. The choice of an industrial partner shall represent a crucial decision for such a project.

#### PECHouse website

Since a few months, PECHouse has an Internet portal at the address <http://pechouse.epfl.ch>. Parts of it are still under construction, but the visitors can already obtain valuable information about the initiative, the collaborators and about related events. It is foreseen to add an intranet part, which would allow efficient document exchange among PECHouse co-workers and partners.

#### Other dissemination activities

In the first six months of 2008, PECHouse research activities have been presented by Prof. Michael Grätzel at the following scientific events :

- 6th Annual iNANO Meeting, Aarhus, Denmark, January 23<sup>rd</sup>, 2008
- 2nd Symposium Hydrogen & Energy, Braunwald, Switzerland, January 23<sup>rd</sup> to 25<sup>th</sup>, 2008
- ICONN International Conference on Nanoscience and Nanotechnology, Melbourne, Australia, February 24<sup>th</sup> to 28<sup>th</sup>, 2008
- Muetterties Lectures, University of California, Berkeley, USA, February 29<sup>th</sup> to March 7<sup>th</sup>, 2008

PECHouse research activities have been presented by Dr. Kevin Sivula at the following events :

- 235th meeting of the American Chemical Society, NanoPower symposium, April 6<sup>th</sup> to 10<sup>th</sup>, 2008, New Orleans, Louisiana, USA (on behalf of Prof. Michael Grätzel)
- Nanosystems Initiative Munich workshop "Interactions in Hybrid Nanosystems" May 1<sup>st</sup> to 4<sup>th</sup>, 2008, Frauenwörth, Chiemsee, Germany
- Invited EMPA seminar June 3<sup>rd</sup>, 2008, Dübendorf, Switzerland

The goals and the challenges of PECHouse have further been presented on a poster, displayed on the booth of the EPFL Energy Center at the Energissima renewable energy fair, which took place in Fribourg during the third week of April 2008. Such a fair attracted many thousand visitors from all over Switzerland, thus enabling us to reach out to a broader public.

On July 1<sup>st</sup>, 2008, at 11.10am, PECHouse was the subject of a live radio segment on World Radio Switzerland (88.4 FM in Geneva) during the "On the Beat" program, which typically features special guests, interviews with experts, lifestyle features and regular news updates. The show's host, Pete Forster, first introduced PECHouse research followed by a 10 minutes telephone interview with Dr. Kevin Sivula. The basics, goals, and timeline of the technology were discussed. Finally, listeners who wanted more information were instructed to visit the PECHouse website.

Finally, an article has been devoted to PEC-based production of hydrogen in the French-speaking Swiss newspaper "Le Temps", focusing in particular on PECHouse. It has been written by Mr. Pierre Veya, associate editor of "Le Temps", based on interviews with Profs. Michael Grätzel and Hans Björn Püttgen, as well as with Dr. Massimiliano Capezzali.

## Evaluation of the accomplishments through June 30<sup>th</sup>, 2008 and outlook

The first months of 2008 have seen the successful growth of the PECHouse center of competence at EPFL. Our dissemination activities have introduced the PEC community to the ambitious goals and to the personalities working within PECHouse. In addition, considerable amount of research was accomplished in the two scientific workplans. In order to specifically evaluate the progress of PECHouse the results obtained for each work package are examined in view of their respective approaching milestones.

### WP-1: $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanodes

The first milestone for this work package, projected for the end of 2009, is to obtain a reproducible photocurrent of 3 mA/cm<sup>2</sup> (at 1.23 V vs. RHE) under standard solar illumination conditions with small-scale iron oxide photoanodes. Since the iron oxide photoanode preparation via APCVD was rigorously optimized by the former generation of researchers at LPI, the current goal will most likely not be achieved by incremental optimization of deposition parameters, but rather by understanding and overcoming limitations of the current optimized system.

The FTO/iron oxide interface has been identified as a major limitation of the system and research progress performed this term has increased our understanding of it. Using WO<sub>3</sub> (and previously gold) underlayers we showed this was not a problem specific to the electronic nature of fluorine doped thin oxide, as previously believed. While initial experiments with a templating approach

designed to direct the crystallinity of the iron oxide at the interface thus reducing recombination, proved ineffective, a route has been designed for further investigations this approach. In addition, a step forward was taken in the understanding of the deadlayer through the investigation of the silica underlayer. We were able to significantly reduce the deadlayer in iron oxide thin films prepared by SPD. This suggests that the deadlayer is a result of a Schottky-type barrier at the iron oxide interface—a problem which can be solved by optimizing the blocking layer and the doping of the iron oxide at the interface.

The silicon doping of APCVD iron oxide photoanodes has been shown to both alter the feature size of the films nanostructured cauliflower components, and the conductivity of the films. Since a significant increase in the photocurrent is predicted if these two effects could be uncoupled and independently optimized, research on the dopant is important. The first fundamental steps are to understand how the current silicon doping affects the performance of the electrodes. Our collaboration with Prof. Schoenes will lead to a better understanding of the electronic effects of the dopant. This, coupled with doped thin film studies prepared with different dopants via SPD, will put the research on the dopant on track for the dopant-related deliverable at the end of the year.

Since, at this stage, the nature of the current research on iron oxide photoanodes concerns more the building of fundamental knowledge of the system, it is difficult to accurately quantify the progress to the upcoming milestone. However, our research this term has eliminated many candidate underlayer materials, identified promising experimental approaches for the continued optimization of the important FTO/Fe<sub>2</sub>O<sub>3</sub> interface, and has led to the further understanding of the limitations of this material while offering possible solutions. Further underlayer and dopant research is on track to allow the increase in material performance in the second half of 2008, and the completion of our first milestone in 2009. In addition, the successful acquisition and construction of new deposition equipment has provided PECHouse with a broad and stable platform which gives confidence to our future research endeavors.

#### WP-2: Ordered mesoporous oxide guest-host approach

As the second workplan represents a new concept for the structure of water-splitting photoelectrodes the first milestone is a proof-of-concept demonstration. By mid 2009 the potential of the host-guest approach will be confirmed by preparing an anode which has an enhanced quantum efficiency of long light wavelengths. This will be possible using not only the tools and techniques that are currently being developed for this work plan, but, since the host-guest approach magnifies interface issues, also the interface/underlayer examinations from WP-1. The first term of 2008 has proven to be very productive for research toward the first milestone of WP-2. In addition to the decrease of the iron oxides photoinactive dead layer previously mentioned, the nanostructuring techniques have been successfully demonstrated. The next half of this year will focus on the challenge of addressing these host-guest structures electronically, so as to integrate these materials and techniques into devices.

In conclusion, the development of materials, methods, tools and techniques for both of the PECHouse work plans has progressed rapidly with many promising avenues being currently investigated; the deliverables outlined for the three work packages this term have been successfully achieved and included in this report, and research plans are on track to accomplish the tasks and deliverables for the second half of 2008.

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