CHAPTER VI : Conclusions and perspectives

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CONCLUSIONS AND PERSPECTIVES

VI.1 Conclusions

Hydrogen is a good alternative to fossil fuels in order to reduce the CO_2 emissions. The H_2 production can be achieved by different methods and we have decided to work on a low carbon footprint technique: the photoelectrolysis of water.

As said by Nick Nigro, senior manager of transportation initiatives at the Center for Climate and Energy Solutions: "Going to low-emissions vehicles is necessary, but not sufficient. To effectively address climate change, you have to look all the ways upstream and produce the fuel in a low-carbon way."

Specifically, we tuned the fabrication of a doped mesoporous hematite film used as photoanode in water splitting.
We had two targets:

1) To reduce the distance between the holes generation point and the electrolyte by optimizing the mesostructure.
2) To improve the electronic conductivity by doping.

We successfully implemented the fabrication of a crystallized, Ti-doped mesoporous hematite film by spin coating and subsequent heat treatment. The porous mesostructure increases the active surface of the film and we have deduced that it allows a deeper penetration of the electrolyte into the film, reducing the holes path distance from the generation area to the electrolyte. The consequence is a higher photocurrent for mesoporous films compared to collapsed and dense films, and this under front and under back illumination.

Moreover, preserving the mesostructure up to 850°C was very challenging, and we managed to do so thanks to the use of a SiO_2 scaffold. Indeed, a heat treatment at such a high temperature is required to activate the dopant, which results in an increase of the majority charge carrier (e^-) concentration in mesoporous films. This can also explain the higher photocurrent obtained with the sample M850 compared to the M800 and the M470.

For dense films, an annealing at 800°C compared to 470°C increases the majority charge carrier concentration but an annealing at 850°C decreases it. The hypothesis envisaged to explain this decrease is the formation of TiO_2 clusters localized at grain boundaries. However, those clusters seem to assist the conductivity of electrons into the film because the performances are slightly improved despite the reduction of majority charge carrier.

In order to compare the three different nanostructures, we have analyzed the surface and the crystallinity by different methods: XRD, TEM and AFM. The performances are also strongly influenced by the recombinations that can occur at each interface.

The analysis of each interface is therefore essential for the diagnosis. In this work, we have used the electrochemical impedance spectroscopy (EIS) and determined the equivalent circuit corresponding to our film by combining admittance and impedance data.

Increasing the electronic conductivity is not enough to suppress recombination because hematite anodes also suffer from kinetics issues for the oxidation of water into oxygen.

In this work, a holes scavenger (H_2O_2) was used to simulate the action of a catalyst on the surface of the film. The photocurrent was higher and the onset potential lower than in NaOH. This is due to the reduction of the holes injection barrier at the interface between the film and the electrolyte.

Finally, on a more applied point of view, we have tested a promising deposition method as an alternative to spin coating: Ultrasonic Spray Pyrolysis (USP). This technique is easier to implement at industrial scale for larger substrate area.

Films prepared by USP were less adherent than films prepared by spin coating. However, the first tests were promising because the crystalline orientation of USP deposited films was more favorable for the electronic conductivity (higher (110):(104) ratio) than the crystalline orientation of spin coated films.

A summary of the main results of this thesis work is represented in Figure IV-1.

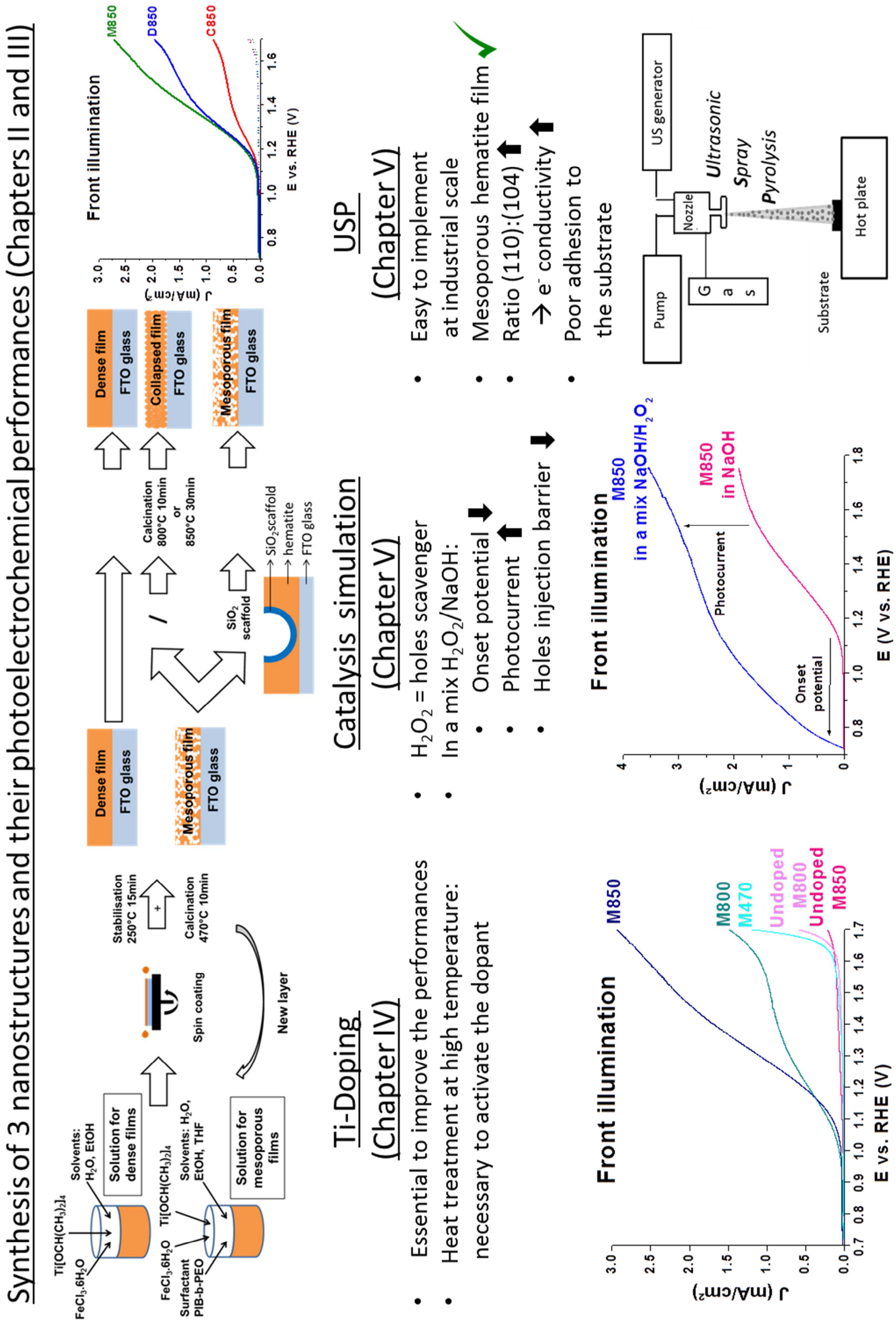

Figure VI-1: Summary of the main results of the thesis work.

VI.2 Perspectives

The performances of the hematite films used as photoanode depend on the recombinations phenomena, which are influenced by the oxidation reaction kinetic and the conductivity of electrons and holes.

Tests in a mix $NaOH/H_2O_2$ were promising: they result in a decrease of the onset potential and an increase of the photocurrent. Therefore, the deposition a catalyst on the surface of our Ti-doped films should increase their performances by improving the oxidation reaction kinetic[1-6].

The conductivity of the hematite film depends on a lot of parameters such as the crystallinity, the crystal preferential orientation, the doping and the heat treatment temperature and duration.

The specific causes of the improvements due to the Ti-doping are still unclear[1]. The insertion of Ti can also have an impact on the activation of the surface toward water oxidation[1]. The mechanism of the water oxidation is not completely understood and further studies and theoretical simulations must be done in order to improve the transfer of holes from the semiconductor to the electrolyte.

Contrary to mesoporous films, the heat treatment at 850°C reduces the charge carrier density in the dense film. An elemental analysis of thin layers by TEM would help verifying the hypothesis of TiO_2 cluster formation at high temperature for dense films and the possible diffusion of Sn from the substrate into the hematite films.

Other modifications due to the heat treatment at higher temperature can also be a cause of the performances improvement. An analysis of charge transport by AFM and an imaging of the crystalline structure by DF-TEM, as done by Scott C. Warren et al. to identify the champion nanostructures for solar water splitting[7], could complete the analysis of conductivity in our hematite films.

The interface between the hematite film and the FTO-glass is also studied in the literature. Metal oxide underlayers, such as TiO_2 and Ga_2O_3, have been reported to increase the water splitting performances by reducing recombination at the interface between the FTO-glass and the hematite film[8-10]. This underlayer can also modify the crystallinity and/or the crystal orientation of the hematite film[1].

Introducing a metal oxide layer between the FTO-glass and our mesoporous hematite film could improve the performances of the film by reducing recombinations at the interface between hematite and FTO and/or by changing the crystalline orientation (increasing the (110):(104) ratio).

Other studies are carried out on the nanostructuration of the transparent conductive oxide (TCO) layer of the substrate combined with the deposition of a thin film absorber (TFA) top layer such as hematite on this nanostructured TCO[11-13]. The nanostructure increases the specific surface and, because the thickness of the hematite film is very thin, the charge carrier transport is not an issue anymore. The electronic conductivity is then ensured by the TCO.

All these examples show the importance of the different interfaces in the performances of a hematite film deposited on a TCO-glass and used as photoanode in water splitting. Therefore, an analysis of these interfaces is essential to optimize the synthesis and the properties of photoanodes. For this purpose, Electrochemical Impedance Spectroscopy (EIS) is a powerful tool to obtain information about the interfaces.

Besides, the preparation method by combining spin coating and soft-templating used in this work is versatile. Other metal oxides used in water splitting or other applications such as photovoltaic or batteries can be prepared with the same technique. For example, the SiO_2 scaffold could be used in the synthesis of mesoporous metal oxides that have to be treated at high temperature in order to ensure the keeping of the mesostructure.

However, spin coating is difficult to implement at industrial scale. Therefore, the ultrasonic spray pyrolysis was tested as preparation method. But the synthesis must be improved.

Instead of using the same parameters as in spin coating, an optimization of the preparation method is required to improve the adherence of USP deposited films. The deposition of a thin dense layer before the mesoporous film can also improve the adherence of the mesoporous film. The first tests of deposition with USP were promising and we must go on with this preparation method.

This research is a drop in an ocean of research against the global warming. Climate change and the scientific predictions are subject to debate and I want to finish with a quote from Monika Kopacz, atmospheric scientist:

"It is no secret that a lot of climate-change research is subject to opinion, that climate models sometimes disagree even on the signs of the future changes (e.g. drier vs. wetter future climate). The problem is, only sensational exaggeration makes the kind of story that will get politicians' and readers' attention. So, yes, climate scientists might exaggerate, but in today's world, this is the only way to assure any political action and thus more federal financing to reduce the scientific uncertainty."

For the future generations, can we take the risk to not believe in the global warming and continue to pollute?

VI.3 References

(1) Zandi, O.; Hamann, T. W.: The potential versus current state of water splitting with hematite. *Physical Chemistry Chemical Physics* **2015**, *17*, 22485-22503.

(2) Zhong, D. K.; Cornuz, M.; Sivula, K.; Gratzel, M.; Gamelin, D. R.: Photo-assisted electrodeposition of cobalt-phosphate (Co-Pi) catalyst on hematite photoanodes for solar water oxidation. *Energy Environ. Sci.* **2011**, *4*, 1759-1764.

(3) Tilley, S. D.; Cornuz, M.; Sivula, K.; Graetzel, M.: Light-Induced Water Splitting with Hematite: Improved Nanostructure and Iridium Oxide Catalysis. *Angew. Chem., Int. Ed.* **2010**, *49*, 6405-6408, S6405/1-S6405/3.

(4) Gao, M.-R.; Xu, Y.-F.; Jiang, J.; Zheng, Y.-R.; Yu, S.-H.: Water Oxidation Electrocatalyzed by an Efficient $Mn_3O_4/CoSe_2$ Nanocomposite. *Journal of the American Chemical Society* **2012**, *134*, 2930-2933.

(5) Barroso, M.; Cowan, A. J.; Pendlebury, S. R.; Grätzel, M.; Klug, D. R.; Durrant, J. R.: The Role of Cobalt Phosphate in Enhancing the Photocatalytic Activity of α-Fe_2O_3 toward Water Oxidation. *J. Am. Chem. Soc.* **2011**, *133*, 14868-14871.

(6) Trotochaud, L.; Ranney, J. K.; Williams, K. N.; Boettcher, S. W.: Solution-Cast Metal Oxide Thin Film Electrocatalysts for Oxygen Evolution. *Journal of the American Chemical Society* **2012**, *134*, 17253-17261.

(7) Warren, S. C.; Voïtchovsky, K.; Dotan, H.; Leroy, C. M.; Cornuz, M.; Stellacci, F.; Hébert, C.; Rothschild, A.; Grätzel, M.: Identifying champion nanostructures for solar water-splitting. *Nat Mater* **2013**, *12*, 842-849.

(8) Hisatomi, T.; Dotan, H.; Stefik, M.; Sivula, K.; Rothschild, A.; Grätzel, M.; Mathews, N.: Enhancement in the Performance of Ultrathin Hematite Photoanode for Water Splitting by an Oxide Underlayer. *Advanced Materials* **2012**, *24*, 2699-2702.

(9) Wang, J.; Feng, B.; Su, J.; Guo, L.: Enhanced Bulk and Interfacial Charge Transfer Dynamics for Efficient Photoelectrochemical Water Splitting: The Case of Hematite Nanorod Arrays. *ACS Applied Materials & Interfaces* **2016**, *8*, 23143-23150.

(10) Zhang, C.; Wu, Q.; Ke, X.; Wang, J.; Jin, X.; Xue, S.: Ultrathin hematite films deposited layer-by-layer on a TiO_2 underlayer for efficient water splitting under visible light. *International Journal of Hydrogen Energy* **2014**, *39*, 14604-14612.

(11) Wang, D.; Zhang, Y.; Wang, J.; Peng, C.; Huang, Q.; Su, S.; Wang, L.; Huang, W.; Fan, C.: Template-Free Synthesis of Hematite Photoanodes with Nanostructured ATO Conductive Underlayer for PEC Water Splitting. *ACS Applied Materials & Interfaces* **2013**, *6*, 36-40.

(12) Zandi, O.; Beardslee, J. A.; Hamann, T.: Substrate Dependent Water Splitting with Ultrathin α-Fe_2O_3 Electrodes. *The Journal of Physical Chemistry C* **2014**, *118*, 16494-16503.

(13) Le Formal, F.; Grätzel, M.; Sivula, K.: Controlling Photoactivity in Ultrathin Hematite Films for Solar Water-Splitting. *Advanced Functional Materials* **2010**, *20*, 1099-1107.