Campagne 2020 Contrats Doctoraux Instituts/Initiatives

Proposition de Projet de Recherche Doctoral (PRD)

Appel à projet IMat - Institut des Matériaux 2020

Intitulé du Projet de Recherche Doctoral : Design of heterostructurated photoelectrodes for water splitting

Directeur de Thèse porteur du projet (titulaire d'une HDR) :

NOM : **Durupthy** Prénom : **Olivier**
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Unité de Recherche :
Intitulé : Laboratoire de Chimie de la Matière Condensée de Paris
Code *(ex. UMR xxxx)* : UMR 7574

ED397-Physique Chimie des Matériaux

Ecole Doctorale de rattachement de l'équipe & d'inscription du doctorant :

Doctorants actuellement encadrés par le directeur de thèse (préciser le nombre de doctorants, leur année de 1ere inscription et la quotité d'encadrement) : Antoine Deswazière débuté en 2017 encadré à 50%, Mélissa Richard débuté en 2019 endacré à 50%

Co-encadrant :

NOM : **Laberty-Robert** Prénom : **Christel**
Titre : Professeur des Universités ou HDR ☒
e-mail : christel.laberty@sorbonne-universite.fr

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ED397-Physique Chimie des Matériaux

Ecole Doctorale de rattachement : Ou si ED non Alliance SU :

Doctorants actuellement encadrés par le co-directeur de thèse (préciser le nombre de doctorants, leur année de 1ere inscription et la quotité d'encadrement) : 1,5 en 1ère année, 0,75 en 3ieme année.

Cotutelle internationale : ☒ Non ☐ Oui, précisez Pays et Université :

Description du projet de recherche doctoral *(en français ou en anglais)*

3 pages maximum – interligne simple – Ce texte sera diffusé en ligne

Détailler le contexte, l'objectif scientifique, la justification de l'approche scientifique ainsi que l'adéquation à l'initiative/l'Institut.
Le cas échéant, préciser le rôle de chaque encadrant ainsi que les compétences scientifiques apportées. Indiquer les publications/productions des encadrants en lien avec le projet.
Préciser le profil d'étudiant(e) recherché.

1. Objective, Context, Rationale for the science approach, Risks

The aim of this project is to design multilayered heterostructuring photoelectrodes for OER in acidic conditions to optimize light absorption and then charge carrier generation and separation for making efficient photoelectrodes for tandem solar-driven water splitting electrochemical devices.

Hydrogen will play a key role in any future fossil fuel-free energy infrastructure that relies on chemical fuels as energy carriers. Since water is the only abundant source of hydrogen on the planet and sunlight is the most abundant energy source, developing the technology for solar-driven water splitting on a multi-GW scale is and will become a central challenge. Photovoltaics and wind-powered electrolysis are likely to be the technology of choice to produce renewable hydrogen for the next few decades. However, the integration of light absorption and catalysis in 'direct' photoelectrolysis routes offers several advantages, such as lower current densities and better heat management, and may become technologically relevant in the second half of this century. To do so and breakthroughs are needed to accomplish this goal.

The key active components in a water splitting device are the light absorber(s) and the electrocatalysts. Many research efforts are currently being devoted to the latter, and several efficient and earth-abundant candidates for the hydrogen evolution reaction (HER) over a range of acidic and alkaline conditions are now available. Earth-abundant candidates for the more difficult oxygen evolution reaction (OER) in alkaline conditions and near-neutral pH have also been identified. What is still missing are earth-abundant candidates for the OER in acidic conditions. More precisely, the main bottleneck for a true photoelectrochemical device is not the catalyst but a chemically stable light absorber with a bandf gap between 1.5 and 2 eV and long carrier lifetimes.

In this context, instead of developing new materials which is a long way, we propose to engineer semiconductor electrode to manipulate and confine light in ultrathin film for improving the short intrinsic diffusion length of photoexcited charge carriers. This strategy has been applied to BiVO4 photoelectrode that was modified by Ag@SiO2 core-shell nanoparticles with an enhancement by a factor of 2.5 of the photocurrent. Other studies have shown that 65 nm Ag NPs on BiVO4 photoanodes facilitate hole injection to the electrolyte but also enhanced the absorption of the semiconductor (by 6%) through light scattering. More recently, the fabrication of light absorbers on well-defined surface-textured substrates has demonstrated an improvement in light water-splitting photocurrent through light confinement. Other strategies proposed more complex architecture that integrate conductive distributed Bragg reflector (cDBR). Different layered of TiO2 and SiO2 with different density have been stack on the back side of a transparent conductive substrate, that plays the role of an optical filter and a conductive counter electrode. This architecture allows producing high and stable photocurrent (5.75 mA.cm-2) without any additional bias and a conversion efficiency of 7.1%.

Such brief state of the art highlights the interest of architecturing the conductive substrate of the photoelectrode to enlarge the light absorption. Accordingly, this project proposes new approaches that would enable to enlarge light absorption with long carrier lifetime by engineering the architecture of the electrode by staking layers with different density and composition.

To enhance light absorption, different strategies will be explored using FTO and silicon substrates. For conductive FTO substrate, we plan to take the benefit of the assembly of well-defined metallic NPs though a well-controlled dip coating process of metallic NPs suspension to scatter light in the photo-electroactive layers. Alternatively, we plan to fabricate distributed Bragg reflector made of alternated of dense and porous SiO2/TiO2 layers onto FTO susbtrate by using the sol-gel chemistry coupled with dip-coating in well-controlled solution including template or not and controlled atmosphere and temperature. For silicon substrate, we plan to used chemically etched silicon.

The photoelectrochemical layer will be BiVO4 deposited ontop of the architectured substrates. Challenges are in the concentration, the mobility and photocharge recombination in this layer. Different strategies will be developed including doping, tuning porosity and nano-arhitecturing of the layer. However, those strategies have been proven to not be as efficient they should be as a lot of defect are often created during the fabrication of the electrode. To overcome those limitations, we plan to use our expertises in designing eco-friendly synthesis route for well-crystallized nanoparticles with tuned particle size. Doped Mo-, Nb- doped or un-doped BiVO4 nanoparticles will be considered. Finally, this NPs will be suspended and deposited by the dip-coating approach, well-mastered in the lab onto the nanostructured substrate. The photoelectrocatalytic properties of the prepared electrodes will be studied in standardized conditions in order to compare them to state of the art results. The results on electrodes efficiency will direct us in the selection of the best texturation of the electrode as well as the appropriate composition. A full cell set-up available in the laboratory will allow us to determine an efficiency of coupled electrode for both O2 and H2 production which is hardly reported in the literature.

Risks : i) One of the challenges is to achieve uniform layer with controlled thickness and with a "good" particle-particle BiVO4 contact in order to avoid photo-charge recombination and to reach good photoconductivity. To do so, we will be using non-traditional heat-treatments, such as rapid thermal processing (micro-wave approach) to favor sintering between BiVO4 nanoparticles keeping the sub-layer architecture identically. ii) As highly porous photoelectrodes with high specific surface area will be developped one should consider the stability of the electrode with time because of photo or/an chemical dissolution of BiVO4 in the acidic media. To avoid it, conformal dense, thin layer will be deposited by ALD or dip-coating.

2. Consistency and skills of the team

The synthesis control of single phase materials as well as heterostructurated nanomaterials is well mastered in the Nano group of the LCMCP using decades of knowledge on sol-gel chemistry. For instance, oxide-metal, oxide-oxide or oxide-graphene heterostructure were developed in the group. A large number of studies were devoted to the photocatalytic efficiency of several oxide materials including TiO2, Bi2WO6 and BiVO4. Additionally, heterostructures for optic (Au@SiO2), catalytic (Au@TiO2) and electrocatalytic (Co3O4@graphene) applications were developed by the project leader. Olivier Durupthy will steer the project and bring is input on the synthetic approach of tailored heterostructures.

The RMES group of the LCMCP is particularly implicated in the design and test of single phase photoelectrodes as at least 3 PhD and 2 post-doc have worked on TiO2, Fe2O3, WO3 and BiVO4 materials and their integration, evaluation of their

performances in half and full cells. They can fully characterize the photo-electrochemical response of a defined electrode as well as its durability. Advanced characterizations such as Mott-Schottky and IPCE can also be performed with in-house equipment. Christel Laberty-Robert will bring its expertise on the material-performance relationship and will point out the technical requirements for the photo-electrode design.

The MHP group is specialist in film design and texturation of different oxides through bottom-up and top-down approaches. They have prepared multiscale porous films of crystalline TiO2 using for instance inverse opals replica or nanolithography imprinting. Such a texturation allows an improved collection of charge carriers and a better accessibility of electrolyte to the catalytic sites through optimized porosity. Finally, the texturation control will improve light harvesting and then, the total photoconversion yield. Cédric Boissière will bring its expertise to adapt the efficient experimental conditions for nanomaterials preparation with film preparation and texturation. Moreover he is the specialist of film characterization (thickness, composition, porosity) through ellipsometry.

3. Selected publications related to the project:

i) Saison, T.; Chemin, N.; Chanéac, C.; Durupthy, O.; Mariey, L.; Maugé, F.; Brezova, V.; Jolivet, J.-P., New Insights Into BiVO4 Properties as Visible Light Photocatalyst. J. Phys. Chem. C 2015, 119 (23), 12967-12977. ii) Petit, S.; Melissen, S. T. A. G.; Duclaux, L.; Sougrati, M. T.; Le Bahers, T.; Sautet, P.; Dambournet, D.; Borkiewicz, O.; Laberty-Robert, C.; Durupthy, O., How Should Iron and Titanium be Combined in Oxides to Improve Photoelectrochemical Properties? J. Phys. Chem. C 2016, 120 (43), 24521-24532. iii) Mesoporous Thin Film WO3 Photoanode for Photoelectrochemical Water Splitting: A Sol-Gel Dip Coating Approach, S. Hilliard, G. Baldinozzi, H. Stux, S. Kresmann, V. Artero, C. Laberty-Robert, Sustainable Energy and Fuels, 1, 145-153, 2017. iv) Engineering n-p junction for photo-electrochemical hydrogen production, J. Toupin, H. Strub, S. Kresmann , V. Artero, C. Laberty-Robert, Phys. Chem. Chem. Phys.,19, 30675-30682, 2017. v) Solar water splitting BiVO4 thin film photoanodes by sol-gel dip coating technique, S. Hilliard, D. Friedrich, S. Kressman, H. Strub, V. Artero, C. Laberty-Robert, ChemPhotoChem, 1 (6), 273-280, 2017. vi) Porosity and mechanical properties of mesoporous thin films assessed by environmental ellipsometric porosimetry, C Boissiere, D Grosso, S Lepoutre, L Nicole, A Bruneau, C Sanchez, Langmuir 2007, 21 (26) 12362-12371. vii) Engineering Functionality Gradients by Dip Coating Process in Acceleration Mode, M Faustini, DR Ceratti, B Louis, M Boudot, PA Albouy, C Boissiere, D Grosso ACS Appl. Mater. Interfaces 2014, 6 19 17102-17110

4. Searched student profile: The candidate must be attracted by the energy dommain, he must possess a background in materials chemistry and good knowledge in electrochemistry. He must be interested in both synthesis and characterization techniques. An additional competence in materials physics (optic and semic-conductors) is also appreciated. The candidate must be able to organize its work, report its activity both in french and english, interact with its supervisors and participate to the life of the laboratory

Merci de nommer votre fichier pdf :
«ACRONYME de l'institut/initiative_2_NOM Porteur Projet_2020 »

à envoyer simultanément par e-mail à l'ED de rattachement et au programme :
cd_instituts_et_initiatives@listes.upmc.fr avant le 30 mars.