Sorbonne Université/ China Scholarship Council program 2020

Thesis proposal

Title of the research project: **Development of hybrid 3D p-n junctions involving electronically conducting polymers and nanostructured titanium dioxide thin films**

Keywords: **Conducting polymers, oxides, nanostructured materials, electrochemistry, semiconductors, 3D p-n junctions, IMPS**

Joint supervision: no

Joint PhD (cotutelle): no

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Institution: **Sorbonne Université**

Doctoral school (N°+name): **ED 388, Ecole doctorale de Chimie Physique et de Chimie Analytique de Paris Centre**

Research laboratory: **Labo. Interfaces et Systèmes Electrochimiques (LISE, UMR CNRS/SU 8235)**

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Subject description (2 pages max):

1) Study context

Hybrid materials resulting from the combination of electronically conducting polymers (ECPs) with metal oxides constitute undoubtedly an exciting family of innovative and promising materials in view of numerous applications in the field of energy conversion and storage in particular. Hybrid solar cells are based on p-n junctions involving such hybrid materials. Like organic solar cells, they often suffer from a fast degradation of their components and their light conversion efficiency is often too low. In order to reduce these weaknesses, the concept of bulk heterojunction (or 3D p-n junction) has been raised because it allows simultaneously and advantageously the production of large contact areas between the p and n components of the junction as well as the conservation of continuous domains in view of the evacuation of charge carriers in the absence of photo-induced charge recombinations.

The objective of this research subject is to develop hybrid solar cells (HSCs) based on three-dimension (3D) p-n junctions [1]. At this stage of our investigations, it is difficult for us to anticipate the performances of the hybrid solar cells that will be elaborated and tested in this research project but a 8-10 % value seems to be a reasonable objective for the light conversion efficiency in the limits of this Ph.D. work, knowing that this value would be higher than the 4,5 % value reported for commercial solar cells involving Dyesol DSL-30 type titanium dioxide.

2) Details of the proposal

In order to reach our objectives, the research plan suggested in this project is therefore divided into four parts described below.

I / Elaboration of 3D p-n junctions

In a first step, two types of organic/inorganic hybrid layers will be synthesized according to two different synthesis methods (A and B). In method A, vertically aligned TiO_2 nanotube arrays (TiO_2 VANTAs) will be first prepared by using the anodization technique on a titanium foil in an ethylene glycol/water mixture, and then annealed so as to obtain the anatase type cristallinity. Such quasi-1D networks possess vertically aligned electronic conduction paths that favour electron transport rate and slow down charge recombinations, which is beneficial for the charge collection efficiency of the resulting PV cell. Internal and external walls of these nanotubes will be coated with p-type semiconducting substituted polythiophene thin layers using a photo-assisted electropolymerization process. In method B, titanium dioxide (TiO_2) based mesoporous layers will be produced using a self-assembling process of surfactant based micelles with oxide precursors according to a sol-gel type synthesis process. The TiO_2 phase will be initially annealed so as to adopt the anatase type cristallinity and therefore a n-type semi-conductor behaviour. Once freed thanks to a thermal treatment, the porosity of these layers will be filled with a substituted and undoped polythiophene polymer, a p-type semi-conductor belonging to the well-known family of electronically conducting polymers (ECPs), using a photo-assisted electropolymerization process already developed at LISE laboratory [2,3].

II / Elaboration of photovoltaic cells involving our 3D p-n junctions

In this project, hybrid solar cells will be assembled according to the following architecture: glass/FTO/TiO_2 anatase (dense layer)/3D p-n junction /poly(3-hexylthiophene) layer/Au.

In order to prevent any risk of short-circuit between the current collectors, the surface of the glass/ITO substrates will indeed be covered with a dense TiO_2 layer deposited using the dip-coating technique from a sol-gel solution and then annealed for two hours so as to obtain the anatase crystalline variety. The 3D p-n junction will then be produced using either one or the other of the two synthesis methods A and B described above. It is important to notice that method A will necessitate the deposition of a titanium layer on the dense and annealed TiO_2 layer using the sputtering technique.

A dense layer of poly(3-hexylthiophene) will be deposited using the dip-coating technique over the 3D p-n junction using a chemical polymerisation process. The back side contact will result from the deposition of a gold layer using the pulverisation technique. In our case, as the backside will be constituted by a p-type semiconducting P3HT layer prepared according to a chemical method, the resulting solar cell will be inverted by comparison with major organic PV cells.

III / Characterisation of photovoltaic conversion efficiency

The photovoltaic conversion efficiency of all the PV cells produced in this work will be characterised using the current-potential plots, the I(t) plots at a zero potential in obscurity or under constant or pulsed light, incident photon-to-electron conversion efficiency (IPCE) using a solar simulator (100 mW/cm^2, A.M. 1.5). The shape factor will be systematically calculated and the efficiency will be deduced from the IPCE curves. The PV cells showing the best performances will be more deeply investigated using the intensity modulated photocurrent spectroscopy (IMPS) technique in order to evaluate accurately the loss phenomena by charge recombination [4].

IV / Determination of correlations between nanostructure and performances

Porous oxide phases produced in the course of this project will be systematically characterised using the X-Ray Diffraction (XRD), Small-Angle X-rays Scattering (SAXS) and ellipsometry techniques in order to determine their cristallinity and their porosity. The resulting junctions obtained after the photo-assisted electropolymerisation step will be characterized with the help of Scanning Electron Microscopy (SEM-FEG) and Photo-Conducting Atomic Force Microscopy (pc-AFM) techniques in order to map respectively the morphology and the photocurrent of these junctions. On the basis of these characterisations carried out on the 3D p-n junctions only but also on the completed cells, correlations will be established and then exploited

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so as to optimize the synthesis conditions of our photo-active 3D p-n junctions. In synthesis method A, these correlations will be used to modified/optimize the mesostructuration as well as the cristallinity level of the oxide phase. In the synthesis method B, the parameters of the photo-assisted electropolymerisation step (identity (potential or light) and characteristics (duration or intensity) of the applied pulses, choice and concentration of the monomer and the electrolyte) will be selected so as to allow a optimised filling of the different porosities and as a consequence the production of a maximised surface contact area between the n and p components of the 3D p-n junction.

3) References

[1] Y. Bai, I. Mora-Sero, F. De Angelis, J. Bisquert, P. Wang, Titanium Dioxide Nanomaterials for Photovoltaic Applications, Chem. Rev., 114 (2014) 10095-10130.

[2] E. Ngaboyamahina, C. Debiemme-Chouvy, A. Pailleret, E.M.M. Sutter, Electrodeposition of polypyrrole in TiO_2 nanotube arrays by pulsed-light and pulsed-potential methods, J. Phys. Chem. C, (2014), 118, 26341-26350.

[3] E. Ngaboyamahina, H. Cachet, A. Pailleret, E.M.M. Sutter, Photo-assisted electro-deposition of an electrochemically active polypyrrole layer on anatase type titanium dioxide nanotube arrays, Electrochim. Acta, (2014), 129, 211-221.

[4] H. Cachet, E. Sutter, Kinetics of Water Oxidation at TiO_2 Nanotube Arrays at different pH Domains Investigated by Electrochemical and Light Modulated Impedance Spectroscopy, J. Phys. Chem. C, 119 (2015) 25548-25558.

4°) Profile of the Applicant (skills/diploma…)

The candidate will have to possess or will be ready to develop important skills in electrochemistry of semi-conductors and light-assisted electrodeposition methods, structural and chemical characterisation of oxide and polymer nanostructured thin films, and in characterisation methodologies of the opto-electronic properties of 3D hybrid p-n junctions and the performances of hybrid solar cells.

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