PhD project: Patterning Light Traps in multi-metallic Oxides Photoanodes

Host institute: CINaM/Aix-Marseille Université (Marseille, France)
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Start: between September 1^{st} and October 31^{st} 2024.

Context: There are still several bottlenecks to obtain efficient solar water splitting which can produce hydrogen through a decarbonized approach. This PhD project focuses on enhancing the performance of photoanodes, where the oxidation evolution reaction (OER) takes place, typically known to be a limiting constituent in photoelectrochemical cells. By selecting a well-known ternary oxide catalyst, such as $BiVO_4$, with moderate light absorption and charge transport and favorable band structure for OER, this work aims at increasing the optical path while maintaining short charge carrier distances. This can be achieved by texturing the oxide film into ordered and disordered, resonant, dielectric structures using a low-cost, scalable technique: nanoimprint lithography of metal-oxides (MOx-NIL). The potential of such photonic metasurfaces remains mostly unexplored, especially in the field of energy harvesting and conversion. In addition, the favorable optical properties of $BiVO_4$ have not yet been harnessed, neither in its bulk nor its nanostructured form. Finally, this project follows a sustainable approach, prioritizing Earth-abundant components, as well as low-cost and energy-efficient fabrication techniques.

Description: The objective of this project is to improve the PEC performances of dielectric materials by shaping them into Mie resonant metasurfaces in order to trap light via a drastic increase in internal light scattering. Until now, scarce works have been attempting to overcome this challenge, with promising results with TiO2 and a-GaP, using RF sputtering method.[1-3] It has been determined that transferring these methods to dielectrics such as Fe_2O_3, $Cu_2V_2O_7$ and $BiVO_4$ is a priority,[1,4] although current fabrication methods are limited.

MOx-NIL is recognized as an ideal technique to pattern dielectric materials at the MRM scale we are interested in (100-500 nm), is inexpensive, simple and can easily be adapted to the industrial throughput requirements (Figure 1).[5,6] This technique is compatible with sol-gel chemical formulation and slurry of nanoparticles (NP), which can further enable the elaboration of Mie resonating metasurface (MRM) after well-designed thermal treatment (Figure 2). Here again, very few multi-metallic oxides (MMO) have been attempted outside of the traditional set {Si, Ti, Zn, Zr, Al, Nb}.[7] This is partly because oxides need to cross-link and condense from a sol-gel chemical formulation during the imprinting process, and most metal precursors cannot lead to homogeneous structure due to divergent reaction rates. One way to overcome differential reactivity rate in MMO is to employ

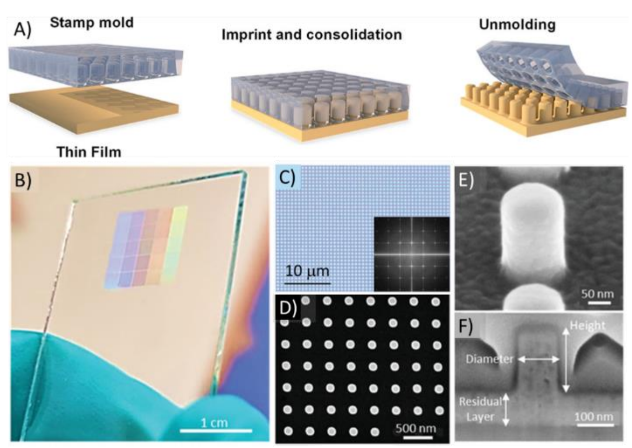

Figure 1. A) Illustration of the principle behind NIL.[5] B) Picture of a $ZrO_2:Eu^{3+}$ layer with 25 arrays covering a 1 cm^2 area, printed via soft-NIL.[6] C) Optical microscope dark-field image (100X) of an array with pitch 860 nm. The inset shows a Fourier transform of a larger microscope image.[6] D) Scanning electron micrographs (SEM) at normal incidence of an array with pitch 370 nm.[6] E) SEM with 52° tilt and F) cross-section SEM view of an individual pillar.[6]

the Pechini methods, where an alpha-hydroxycarboxylic acid (generally citric acid) can coordinate with ions from different metals and keep them from flocculating with their analogs. This results in a better dispersion and more homogeneous crystalline structure. However, when used in parallel with MOx-NIL, this excess of organic compound will ultimately be calcined during the final annealing process and lead to a significant volume loss, which generally reduce the pattern quality. Sintering of NP slurry is one possible way to circumvent such issues, since a negligible content of solvent and organic compound can be used to enable penetration within the mold. This ink can be aqueous or alcohol-based, using binders and capping agents such as polyvinylpyrrolidone (PVP), ethylene glycol (EG), α-terpineol, or other anionic surfactants. [8,9]

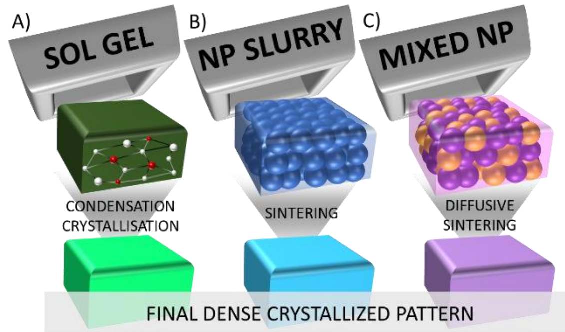

Figure 2. Illustration picturing different approaches to NIL-driven patterning of MMO-based MRM.

Besides developing the MRM fabrication process from nanopowders sintering, the student will carry standard materials characterization to correlate conditions with final crystal phases, along with advanced optical measurements to map light redirection after interacting with the resonators. Finally, the student will familiarize with photoelectrochemical measurements leading to evaluate the performance improvement associated to the MRM. Developing a simple electrochemical microscopy analysis will allow rapid screening on samples containing multiple patterns. Ultimately, larger size electrodes will be developed and tested in photoelectrochemicals reactor cells.

References:

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