Abstract of the Doctoral Dissertation
Doctoral Program in Physics (32th Cycle)

Physical properties of metal-oxide surfaces for CO_2 valorisation

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Abstract

The PhD work here presented is focused on the characterization of the physical surface properties of defective and doped metal oxides for CO_2 valorisation.

Titanium dioxide (TiO_2) and tin dioxide (SnO_2) have been selected for this study because they are cheap, easily scalable by following sustainable synthetic pathways, and environmental friendly.

The dissertation focuses in achieving four main goals:

- the study of the physical properties of both the surface and bulk of the selected semiconductor materials;
- the modification of the optical properties of these wide-band gap semiconductors through the introduction of surface defects (such as oxygen vacancies and surface hydroxyl groups);
- the valorisation of CO_2 through its reduction to added-value chemicals (such as CO, CH_4 and HCOOH), in agreement with the hosting research-centre scientific line (IIT-CSFT@PoliTO – Advanced Materials scientific line);
- the study and modelling of the semiconductor/electrolyte interface by using two approaches: 1) the reconstruction of the equivalent circuit model based on the analysis of the impedance measurements; 2) the representation of the band structure of the previously cited interface by following the Schottky junction model.

In line with the presented objectives, different techniques have been adopted to characterize these metal-oxide materials.

The morphology have been investigated by using electron microscopy techniques (FESEM and TEM), followed by X-ray diffraction measurements (XRD and EDX), in order to obtain a complete identikit of the analysed materials.

As previously mentioned, in agreement with the IIT scientific research line, the electrochemical tests have been carried on to evaluate the efficiency of the samples for CO_2 valorisation.

XPS, EPR and impedance spectroscopies have been employed to give a comprehensive interpretation of the CO_2 valorisation results. The evaluation of the flat band potential of the sample/electrolyte interface, together with an in deep analysis of the charge transfer kinetics (occurring in the bulk as well as on the surface) allowed to describe the physical surface properties affecting the catalytic properties of the investigated materials. This approach gave the fundamental knowledge to properly engineer semiconductor metal-oxides to achieve a target tuning of the surface properties.

With a major detail, the research-work on SnO_2 has been based on the analysis of the doping effect. Titanium and iron have been chosen as dopants, looking at density functional theory (DFT) results for CO_2 valorisation presented in literature. The Schottky junction model and the impedance measurements helped the results interpretation, demonstrating that through Fe (III) doping it is possible to enhance both the conductivity, as well as the charge transfer kinetics of SnO_2 for CO_2 valorisation.

Concerning titanium dioxide, the material was modified via hydrogen peroxide surface treatment. The synthesis of the semiconductor itself has been optimized and merged to the hydrogen peroxide treatment aiming to obtain a super-oxidized material (with a band gap reduction from 3.2 eV to 2.5 eV) through a one-step sustainable process. The effect of super-oxidized surface states has been studied with EPR and XPS spectroscopies – in collaboration with the Lawrence Berkeley National Lab –, and resulted in the modification of the valence band density of state, as observed in the HR-XPS of O 2p peak. As said before, the metal-oxide/electrolyte interface was investigated through impedentiometric measurements, using the equivalent circuit and Schottky junction models.