SINCHEM PhD subject

"Visible-light driven catalysts for water oxidation: Towards solar fuel biorefineries"

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The development of solar fuels appears as one of the most suitable alternatives to develop a sustainable, high-efficient and clean technology for the future. In this context photocatalytic water splitting requires the design and optimization of photocatalytic materials durable and highly efficient. $BiVO_4$ has been found as one of the most active semiconductor materials for the water oxidation reaction, which would be suitable to work as a photoanode in a photocatalytic Z-scheme device. To present, the characteristics of $BiVO_4$ have been fairly studied; however, the properties connected to observe high O_2 evolution activity are still not clarified thoroughly, in particular the relation between morphology changes and activity of monoclinic $BiVO_4$.

On the other hand, in literature a series of O_2 evolution activities for $BiVO_4$ are reported utilizing a sacrificial reagent (usually $AgNO_3$). This electron scavenger has been reported to be highly efficient yet producing a deactivation of the photocatalytic material after short periods of irradiation. In order to circumvent this drawback, a recently developed mathematical model was applied here to determine a more accurate oxygen production rate, which in addition allows us to better understand the mechanisms taking place in the different samples synthesized.

The importance of this work relies on the development and optimization of highly active photocatalytic materials for water oxidation under visible light irradiation and thorough understanding of the physical parameters involved. More in details the research activity of the PhD student will be focused on the optimization of $BiVO_4$ photocatalyst to enhance O_2 evolution activity: although $BiVO_4$ has been regarded as one of the most active photocatalysts for visible-light water oxidation, bare $BiVO_4$ powders and photoanodes have usually proved relatively poor performance for photochemical and photoelectrochemical O_2 evolution due to slow O_2 evolution kinetics, slow electron transport in the conduction band; in addition of electron-hole recombination of bulk and surface. Morphology control and facet dependent properties will be addressed. Several attempts have been performed in order to obtain optimum crystal structures and morphologies that are capable of enhancing the O_2 evolution activity of $BiVO_4$ powders and photoanodes. Optical properties of $BiVO_4$ vary depending on the exposed facet.

Another aspect to consider is the doping. Doping, in the field of photocatalysis, is the deliberate introduction of impurity atoms into a semiconductor in order to control the optical and electrical properties of the bulk material. When introducing a transition-metal cation or an anion for metal-oxides doping, a donor or acceptor level is formed within the forbidden band, respectively; on the other hand, dopants might hinder photocatalytic activity by generating vacancies which act as recombination centers of electrons and holes due to the formation of a discrete energy level instead of an energy band. As a result of $BiVO_4$ doping, an increase in carrier density occurs. Firstly, it is considered that this effect raises the Fermi level of the n-type $BiVO_4$, which shifts the onset potential of the photoanode, producing a larger band bending due to a larger difference between the Fermi level of $BiVO_4$ and the redox potential of the electrolyte (or the applied bias). The resulting enhanced electric field in the space charge layer, positively, improves the electron-hole separation, although it will also decrease the width of the space charge layer. Secondly, an increase in electrical conductivity is expected due to the increase of charge carriers concentration; moreover, the mobility of the charge carriers should also be enhanced as a result of the curvature change at the VB and CB edges, which determine the effective masses of electrons and holes.

Finally, the activity of the PhD student will be focused on the preparation and testing of $BiVO_4$ electrodes. Although synthesis of $BiVO_4$ powders is useful for an in-depth analysis of crystal properties, they are actually unsuitable from the point of view of practical applications. Photoelectrodes are therefore addressed in the development of devices for solar water oxidation. Different approaches with diverse performance and efficiencies have been applied to date. In general, the formation of a thin film over a conductive substrate, typically Fluorine doped tin oxide (FTO) or the more expensive Indium Tin Oxide (ITO), is achieved via i) solution-based method, ii) electrochemical deposition, iii) direct crystal growth, or iv) powders synthesis (as described above) and later impregnation of these via drop casting, dip or spin coating. In the first approach, thin film electrodes are prepared by metal-organic decomposition (MOD). In this method, Bi and V precursor solutions (e.g. bismuth-2-ethyl-hexanote and vanadium (oxy)acetylacetonate are coated on a substrate by any liquid phase film growth technique (i.e. spraying, dip-, or spin-coating). The film is mildly heated to evaporate solvents and then at higher temperatures in order to pyrolyze the precursors, yielding an inorganic film. Annealing is applied in order to control crystallinity, oxygen stoichiometry and particle size. One of the advantages for MOD technique is the simple composition tuning which is achieved by adding the dopant ions to the precursor solution.

A second approach for photoelectrodes preparation is the electrochemical deposition, in which typically a working and a counter electrode are immersed into an appropriate plating solution. Desired ions and molecules will deposit after application of an electrochemical potential on the working electrode.

One more recurring approach for electrode fabrication is the synthesis of $BiVO_4$ powders with high crystallinity by means of e.g. HTS, as treated above, and its subsequent deposition on conducting substrates by e.g. spin coating.

One more interesting technique for $BiVO_4$ thin film fabrication is the in-situ growth of the $BiVO_4$ crystals on the FTO substrate via an aqueous seed-mediated process. In brief, the technique consists of an initial deposition of $BiVO_4$ layer via spin coating which serves as seed for further reaction in a suspension of $BiVO_4$ precursors and precipitating agents.