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# Applied vs. fundamental research in heterogeneous photocatalysis: problems and perspectives. An introduction to “Physical Principles of Photocatalysis”

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## Introduction to special issue

The urgent need of reducing the use of fossil fuels to contrast global warming is one of the reasons of the exponential growth of the research activity in the area of photocatalysis. The birth of photocatalysis dates back to 1972 when a seminal paper by Fujishima and Honda, now cited in more than 27.000 articles, reported the first example of photoassisted water electrolysis [1].

A photocatalytic process aims at exploiting light to promote chemical transformations. The photocatalytic approach is therefore used for various purposes, including that originally accomplished by Fujishima seeking the production of solar fuels (the so-called artificial photosynthesis, APS) either by water photo-splitting or by CO<sub>2</sub> reduction. Other targets of photocatalytic research are pollutants remediation in water and in atmosphere (environmental photocatalysis), biocide processes and alternative routes in organic synthesis. In APS research, heterogeneous photocatalysis (based on irradiation of a finely divided solid dispersed in a fluid medium) coexists with a plurality of sophisticated approaches such as those relying on photoelectrochemical cells or on the coupling between photovoltaic devices and electrolyzers. At variance, in the case of environmental applications, heterogeneous photocatalysis remains the most viable approach. So far photocatalysis has made it only into some applications mostly related to environmental problems, leaving open the issue of the production of solar hydrogen and solar fuels. There are several reasons for this, including too low yields, insufficient stability, and problems related to the availability of the precious metals and rare earths that are required in many materials.

The design of better systems remains the main motivation for the exponential increase of studies and of related documents in the area of heterogeneous photocatalysis (searching for “photocatal\*” in the Web of Science in period 1970-2020 one can find 129.000 papers). This has generated some problems in the systematic analysis and critical evaluation of the results published in the literature. At first sight, there is a prevalence of papers focussing either on photocatalytic reactions applied to a specific process using a benchmark photocatalyst (e.g. the well-known P25 TiO<sub>2</sub> in the area of environmental photocatalysis) or on the performance of a newly prepared material in a benchmark process (e.g. the discoloration of a typical dye). This strong effort in the direction of pragmatic approaches to photocatalysis has not been accompanied by a sufficiently intense effort on fundamental studies. For this reason, after five decades of extensive studies in the field, we still lack accurate mechanistic insights into the fundamental photophysical processes occurring under well defined, and reproducible conditions.

The targets of photocatalytic research in the next future should become even more ambitious pointing (a) to a further progress towards the detailed knowledge of the individual steps, of the microscopic mechanisms, and, most important, of the physical mechanisms at the basis of photocatalytic phenomena, and (b) to the rational design of new and performant photocatalytic materials capable of extending the range of the radiation employed towards the visible frequencies. This, in particular, is the necessary condition to scale up the size of photocatalytic plants and to reach wider applications of these technologies.

To turn these purposes into concrete actions, a more extended use of advanced experimental physical techniques to the photocatalytic field is needed, possibly complemented by a systematic use

of computational approaches, often essential to design complex materials for which intuitive guesses may be difficult.

The special issue devoted to “Physical Principles in Photocatalysis” intends to contribute to the required collective effort here described, with particular emphasis on the physics of the process. The contributions are focusing on two main aspects of photocatalysis: (1) the search for new materials or their combinations that can help to avoid or at least to mitigate the physical problems that are at the basis of the low efficiency of most photocatalytic materials active under solar light, and (2) the development or implementation of advanced spectroscopic techniques to identify the key steps which contribute to generate photoexcited electrons and holes and their migration to the surface of photocatalyst where chemical reactions take place. In particular, the development of methods capable to identify and follow the kinetics of photogenerated charge carriers is of paramount importance in order to better understand the physical mechanisms of photocatalysis, hence to design new efficient photocatalytic materials. The papers in the special issue can thus be grouped according to these main lines.

### **Materials-related aspects**

The study by Nunes, Patrocinio, and Bahnemann [2], discusses the role of materials nanostructuring and in particular the use of lamellar nanostructures prepared by exfoliation of stacked niobates. The influence of the physico-chemical preparation conditions on the photocatalytic activity of Pt-hexaniobate nanocomposites has been analyzed in order to establish the main factors that control their photoreactivities. Morphological changes occur with thermal treatment at 500 °C and lead to a decrease of the specific surface area due to restacking of the individual layers. The paper discusses the correlations between the preparation conditions and the photocatalytic activity for different photoreactions, an essential aspect for the development of optimized materials for specific applications.

A very relevant aspect of photocatalysis is the possibility to generate efficient heterojunctions where different materials play complementary roles. This is subject of the paper by Piskorz et al. [3] where small titania aggregates deposited on graphene oxide are considered based on theoretical models which make use of density functional tight binding modeling. In particular, the authors discuss the role of the structural, electronic and optical properties of a reduced graphene oxide surface (r-GO) interfaced with hydrated TiO<sub>2</sub> small aggregates or nanocrystals of ~5 nm diameter. The electronic interactions at the r-GO(110)/TiO<sub>2</sub> interface give rise to a net charge flow from graphene oxide towards the TiO<sub>2</sub> supported particles. Furthermore, mid-gap C 2*p* states in the band gap show a direct role in the photocatalytic activity of the composites. The band alignment indicates the formation of the staggered type II scheme, with the electric field offset that is sensitive to the titania cluster size. When nano-reticular TiO<sub>2</sub> is considered, where only a fraction of the Ti atoms is involved in the Ti–O–C bonding, recombination of the photogenerated charges is inhibited, owing to favorable spatial separation effect. On the other hand, molecular TiO<sub>2</sub> clusters where all the Ti cations are anchored to the r-GO support lead to a fast cross-relaxation that quenches the beneficial interfacial charge separation effect. This shows the important role that details of the interface between two materials can have on the final photocatalytic performances.

In the field of heterojunctions, one that has attracted particular interest in recent times is that between two oxide semiconductors, WO<sub>3</sub> and BiVO<sub>4</sub>. This topic is addressed in two related studies, one experimental and one computational, where the role of the interface and of the materials dimensionality are discussed.

In the first of these two studies, Grigioni, Dozzi, and Selli [4] discuss the photocatalytic performances of a WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction where the BiVO<sub>4</sub> top layer has a fixed thickness while WO<sub>3</sub> layers of different thicknesses have been considered. The performance of the heterojunction has been compared with that of the same electrodes without a top BiVO<sub>4</sub> layer. The authors found that the performance increases with increasing the WO<sub>3</sub> thickness, and the presence of a BiVO<sub>4</sub> layer

leads to a decrease of incident photon to current efficiency in some regions of the spectrum due to charge carrier recombination effects occurring when both oxides get excited. This phenomenon is more relevant for thicker  $\text{WO}_3$  layers and shorter excitation wavelengths.

In the theoretical study of the same material, Di Liberto, Tosoni, and Pacchioni [5] have considered the problem of the alignment of the valence and conduction bands of the two materials. For the first time an explicit model of the  $\text{WO}_3/\text{BiVO}_4$  heterojunction has been proposed based on hybrid functionals density functional theory calculations. The good performance of  $\text{WO}_3/\text{BiVO}_4$  junctions in photocatalysis is attributed to the capability to reduce electron–hole recombination thanks to a favourable band alignment of the junction's components. This conclusion is often based on the analysis of the properties of the two isolated, non-interacting units. In this study, on the contrary, a real model of the interface is considered which includes the formation of an interface dipole. To this end, the (001) surface of  $\text{WO}_3$  and the (010) surface of  $\text{BiVO}_4$  have been put in contact at a particular angle to minimize the resulting strain. The results of the first principles calculations show that indeed the nature of the interface generates a flow of negative charge carriers towards  $\text{WO}_3$ ,

### Advanced experimental techniques

The study by Kuznetsov et al. [6] describes the opportunities offered by diffuse reflectance (DR) spectroscopy, and in particular temperature dependences of DR spectra at the fundamental absorption edge of semiconductors. The method is applied to the study of rutile  $\text{TiO}_2$ , a photochromic rutile  $\text{TiO}_2$ , and the halide double perovskite  $\text{Cs}_2\text{AgBiBr}_6$ . The data are analyzed in view of kinetics measurements of the separation of photogenerated charge carriers in various trap sites, their thermostimulated detrapping, and their recombination. In this way it has been possible to obtain physical evidence of the photo-formation of charge carriers under visible light irradiation of intrinsic defects in partly reduced rutile  $\text{TiO}_2$  (yellow color). The color centers in yellow  $\text{TiO}_2$  are assigned to  $\text{Ti}^{3+}$  centers as deep electron traps, but other types of  $\text{Ti}^{3+}$ -based color centers also exist, including  $\text{Ti}^{\delta+}$  centers ( $3 > \delta > 2$ ) where more charge is trapped. Photochromic phenomena observed in the Bi-doped perovskite  $\text{CsPbBr}_3$  under illumination are due to the photogeneration of charge carriers followed by their trapping, with formation of Bi-related electron color centers responsible for the photoinduced absorption. The observation of photochromism in perovskites is relevant for a better understanding of their photoactivity.

Electron magnetic resonance (EPR) is the topic of the paper by Chiesa et al. [7]. The role of EPR is essential in unravelling the nature and the features of extrinsic paramagnetic defects in semiconducting oxides. EPR has a key role in the identification of photoactive dopants such as nitrogen atoms in semiconducting oxides. However, EPR can also be used to monitor the processes that follow the photoinduced charge separation in photocatalysis. In particular, the generation, stabilisation, and migration of unpaired electrons and holes, and the induced reactivity can be followed accurately by EPR. Quite relevant is the fact that the use of EPR in photocatalysis is not restricted to solid state phenomena but it can be extended to the liquid phase thanks to the use of spin trapping techniques. In this way it is possible to monitor both the nature and the concentration of the reactive free radicals which are generated in the photocatalytic process.

The paper by Walenta, Tschurl, and Heiz [8] introduces the topic of surface science as a powerful tool to better understand phenomena in photocatalysis. The traditional interpretation of photocatalytic activity is based on the band-structure model, and on the notion of band-engineering. However, it is now well established that beside thermodynamic aspects, kinetics aspects are also very important in determining the final photocatalytic activity. In fact, the charge carrier dynamics is one of the key aspects determining the performance of a photocatalyst. In this respect, in the field of surface science various tools have been developed, mainly with the idea to better understand thermal catalysis. In this paper it is shown how these concepts and tools can be extended to the area of heterogeneous photocatalysis focusing on the photo-physics of well defined surfaces. As an example, the authors consider the role of titania single crystals in alcohol photo-reforming, where surface

science studies have been able to elucidate the reaction mechanism at molecular level, with identification of reaction intermediates and reactive sites. This is very important prerequisite for the design of new photocatalysts. In this respect, the paper provides a different view to approach the problem of photocatalytic efficiency, looking at it with the eyes of a surface scientist.

The role of the kinetics of photoinduced charge carriers is central also in the contribution of Paz that introduces the technique of Transient IR spectroscopy [9]. In particular, the paper deals with the kinetics of the charge carriers at short times (i.e. prior to their surface redox reactions). In this respect, while there is a significant amount of studies dealing with transient electronic spectra of photocatalysts, the corresponding transient vibrational spectra are rarely addressed. The paper by Paz provides an overview of the potential of transient IR spectroscopy (TRIR) as a tool for understanding the initial steps of photocatalytic processes. The paper discussing the pros and cons of the various techniques available to measure transient IR signals of photoexcited systems. Next, it reports a number of examples where various semiconductors are considered, from oxides ( $\text{TiO}_2$ ,  $\text{NaTaO}_3$ ,  $\text{BiOCl}$ ,  $\text{BiVO}_4$ ), to photosensitized oxides (dye-sensitized  $\text{TiO}_2$ ), organic polymers (graphitic carbon nitride) and organo-metallic complexes (rhenium bipyridyl). The interesting aspect is that these systems cover a wide range, from materials with no IR fingerprint signals ( $\text{TiO}_2$ ) to other where well-defined, narrow vibrational bands can be detected (carbon nitride). The paper also presents various pump & probe techniques that can be used to study transient IR spectroscopy.

The last technique discussed in the special issue is time-resolved spectroscopy, and this is done in the paper by Pöpcke, Friedrich, and Lochbrunner [10]. Time-resolved spectroscopy is a powerful tool to understand the individual steps of a photocatalytic process and to address specific problems of each component of a photocatalytic system. The article concentrates on homogeneous systems as these are easier to analyze and the focus is on the primary steps occurring after optical excitation: intramolecular relaxation and intersystem crossing in the photosensitizer, and electron transfer resulting from the interaction of the sensitizer with other parts of the system. Ultrafast pump-probe spectroscopy is helpful in particular to analyze new metal-based photosensitizers. One problem with these sensitizers is the short lifetime of the metal-to-ligand charge transfer states; these can be investigated at the pico- to microsecond timescale making use of a streak camera and by pump-probe spectroscopy. Thanks to the transient absorption spectroscopy the authors show that it is possible to observe the formation of charge transfer products and to determine their concentrations. This is essential in order to deduce the efficiency of the electron transfer and the relevance of quenching events.

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